A neutron scattering study of the under-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$, $x=0.09$ and $0.17$
self-flux grown single crystals and the universality of the tricritical point

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We present a combination of elastic neutron scattering measurements in zero and 14.5 T and magnetization measurements in zero and 14 T on under-doped superconducting Ba$_{1-x}$K$_x$Fe$_2$As$_2$
$x=0.17$, and the same measurements in zero field on a non-superconducting crystal with $x=0.09$.

The data suggest that the under-doped materials may not be electronic phase separated but rather
have slightly inhomogeneous potassium doping. The temperature dependence of the magnetic order parameter (OP) below the transition of the sample with $x=0.09$ is more gradual than that for the
case of the un-doped BaFe$_2$As$_2$, suggesting that this doping may be in the vicinity of a tricritical point.

We advance therefore the hypothesis that the tricritical point is a common feature of all superconducting 122s. For the $x=0.17$ sample, while $T_c$ is suppressed from $\approx 17$ K to $\approx 8$ K by a magnetic field of 14 T, the intensity of the magnetic Bragg peaks (1 0 3) at 1.2K is enhanced by 10%
showing competition of superconductivity (SC) and antiferromagnetism (AFM). The intensity of the
magnetic Bragg peaks (1 0 3) in the $(T_c, T_x)$ temperature interval remain practically unchanged in
14.5 T within a 10% statistical error. The present results are discussed in the context of the existing
literature.

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I. INTRODUCTION

High temperature superconductivity (HTSc) in the iron pnictides, with a $T_c$ as high as 55 K for the case of
SmFeAsO$_{1−δ}$ and SmFeAsF$_x$O$_{1−δ}$, is one of the most perplexing discoveries of the decade in the field of
condensed matter physics. The 122 series (AFe$_2$As$_2$, A = Ba, Sr, Ca, Eu) is of great interest since it is an oxygen-free HTSc. Superconductivity in the 122s can be induced by doping in any of the three atomic sites. The hole-doping achievable through chemical substitution with either K, Na or Cs in the atomic site A can give a $T_c$ as high as 39 K in the case of Ba$_{0.5}K_{0.5}$Fe$_2$As$_2$. The antiferromagnetic (spin-density wave) and structural (tetragonal to orthorhombic) transitions that are near-coincident in the parent compounds are comitantly and gradually suppressed upon doping. Although in the electron-doped BaFe$_2$As$_2$ the two transitions separate with doping, it seems that there are examples pointing otherwise, as in the case of the isovalent ruthenium doped BaFe$_2$As$_2$ and the case of electron-doped SrFe$_{2(1−x)}$Co$_2$As$_2$. The last is surprising if we consider the result on Sn-flux grown Ca(Fe$_{1−x}$Co$_x$)$_2$As$_2$ which for the two transitions are clearly separated. In the case of potassium (hole) doped BaFe$_2$As$_2$ the question of concomitant or separated transitions remains controversial. While powder neutron diffraction data argue for concomitant magnetic and structural transitions across the whole series, heat capacity on Sn-flux grown Ba$_{0.84}$K$_{0.16}$Fe$_2$As$_2$ single crystals shows two distinctive peaks attributed by the authors to the magnetic and structural phase transitions, respectively. In most cases the source of contradictory results appears to be connected to issues of sample quality. It has been pointed out that the proper flux to grow the 122s is FeAs$_{23,25}$, as other fluxes contaminate the sample with flux element inclusions, with a consequent impact on the physical properties. Neutron diffraction on powder BaFe$_2$As$_{14}$ determined a first-order structural and magnetic transition. Complementary high resolution X-ray diffraction and heat capacity measurements on high quality BaFe$_2$As$_2$ crystals revealed a $1^{st}$ order magnetic transition preceded by a structural transition that starts as a $2^{nd}$ order transition at a slightly higher temperature but with a first order jump in the orthorhombic distortion coincident with the first order magnetic transition. For the electron-doped BaFe$_{2(1−x)}$Co$_2$As$_2$ it has been shown recently that the magnetic transition order changes upon doping from $1^{st}$ to $2^{nd}$ through a tricritical point, which is believed to be relevant to the superconductivity phenomenon itself. For this series the structural transition is $2^{nd}$ order. This seems to be different for the case of polycrystalline hole-doped Ba$_{1−x}$K$_x$Fe$_2$As$_2$ of C. Avci et al., for which both the magnetic and structural transitions are $1^{st}$ order over the entire doping range. An early report on Sn-flux grown K-doped BaFe$_2$As$_2$ revealed an electronic phase separated material. A more recent atom probe tomography study on self-flux grown underdoped Ba$_{0.72}$K$_{0.28}$Fe$_2$As$_2$ provides evidence for a mixed scenario of phase coexistence and phase sep-
II. EXPERIMENTAL PROCEDURE

Single crystals of Ba$_{2-x}$K$_x$Fe$_2$As$_2$ with potassium dopings $x$ of 0.09, 0.17, 0.41, and 0.45 were synthesized by a self-flux method with details given in an earlier report. Samples with $x$=0.41 and 0.45 show no sign of AFM ordering, and are fully superconducting with $T_c$=38 K and 39 K, $\Delta T_c$=2 K, respectively. The potassium doping has been extrapolated by comparing the $c$ lattice determined from room temperature neutron data with $c$ vs. $x$ (K doping) data on crystals of H. Lou et al. (Fig. 1). This data agree with $c$ vs. $x$ (polycrystalline samples). Crystals of SrFe$_{2-x}$Ni$_x$As$_2$, $x$=0.155 were grown by self-flux method as well and the precise Ni doping value was determined by inductively coupled plasma analysis.

Magnetization measurements on the K-doped samples were carried out using a Magnetic Property Measurement System (MPMS) and a Physical Property Measurement System (PPMS) from Quantum Design. Resistivity measurements on the Ni-doped SrFe$_2$As$_2$ were performed in the PPMS. Zero field neutron diffraction measurements were performed at Oak Ridge National Laboratory (ORNL) with the High Flux Isotope Reactor’s HB-1A triple axis spectrometer, using a horizontal collimation 40'–40'–68' and fixed energy $E_f=14.6$ meV. The samples studied had K concentrations of $x$=0.09, 0.17, and 0.41 with masses of 19.5 mg, 45 mg, and 71.5 mg, respectively. In order to assess further sample quality, rocking curves of the (008) Bragg peak were recorded. For the $x$=0.09 sample the rocking curve showed two peaks that were separated by approximately 0.7°. Fitting these peaks to a Lorentzian squared profile gave FWHMs of 0.60° and 0.70°.

For the $x$=0.17 sample, the rocking curve of the same peak gave one main peak with a FWHM of 0.77°.

Neutron diffraction measurements of the $x$=0.17 sample of 50 mg in zero field and 14.5 T were performed at the Helmholtz-Zentrum Berlin (HZB) with a configuration of 60°–20° - sample – 20° and fixed $E_f$=5.0 meV. The rocking curve of the (002) Bragg peak showed two peaks that were separated by 0.86°, both peaks had a FWHM of 0.47°.

For both ORNL and HZB neutron scattering experiments, the samples were mounted in a closed-cycle refrigerator and studied in the vicinity of the magnetic Bragg position $Q_{AFM}=(1 0 3)$. For all magnetization and neutron scattering measurements, the magnetic field was parallel with the (a b) crystallographic plane.

III. RESULTS AND DISCUSSION

The thermal evolution of the integrated intensity of the (1 0 3) magnetic Bragg peak in the non-SC $x$=0.09 sample is shown in Fig. 2, upper panel. In addition, the scattering from the same magnetic Bragg peak of the undoped parent compound BaFe$_2$As$_2$ is also shown (data is taken from Ref. 38). The peak intensity scales like the magnetic OP squared. For the sample $x$=0.09 the Néel temperature is 136 K. The figure shows that the magnetic OP squared in the $x$=0.09 sample evolves in a much more gradual manner than Wilson et al.’s data on $x$=0.45. Even so, there is a clear and sharp jump (within 1 K) of magnetic OP squared directly below the Néel temperature. This clearly shows that magnetic phase transition in this sample is still first order, albeit one that is weaker than the parent compound’s. In critical phenom-
FIG. 2: The upper panel shows the integrated intensity of the (1 0 3) magnetic Bragg peak versus reduced temperature of the non-SC K-doped sample $x=0.09$ (□) plotted against the same data for the un-doped $x=0$ (○) (from Ref. 38). The inset shows the magnitude of the $dp/dT$ peaks vs. $x$ potassium doping of the series extracted from Ref. 39. Similar $dp/dT$ vs. $x$ data is plotted for the isovalent phosphorus-doped BaFe$_2$As$_2$ in the lower left panel, and for the electron cobalt-doped in the lower right panel. The thick vertical lines indicate the doping corresponding to emergence of superconductivity in the series.

FIG. 3: Integrated intensity of the magnetic OP versus temperature for the sample $x=0.17$. The downturn of the OP below $T_c$ shows coexistence of AFM and SC. In the inset it is the sum of counts versus temperature near $T_c$. The vertical interrupted line is a guide to the eye for $T_c$. The rounded transition at $T_N$ is due to the slight K-doping inhomogeneity.
also show that a field of 14.5 T leaves the magnetic scattering practically unchanged within the errors for the \((T_c, \; T_N)\) temperature range. This result certainly contrasts with the clear decrease of the magnetic intensity by \(\approx 10\%\) in 13.5 T reported on Sn-flux grown higher potassium doped BaFe2As2 (with \(T_c=32 \pm 1\) K) of J. T. Park et al\(^{30}\). Therefore our 14.5 T data on the hole K-doped BaFe2As2 is similar to the 10 T high resolution neutron data on the electron underdoped BaFe1.92Ni0.08As2 (\(T_c=17\) K)\(^{44}\). Here, below \(T_c\), the intensity of the magnetic \((1\;1\;3)\) peak is enhanced with \(\approx 10\%\), while above \(T_c\) the intensity remains almost unchanged. One experiment to test the interplay between AFM and SC would be to determine whether or not a high magnetic field induces AFM in an optimally doped sample (without any trace of static AFM in zero field). This is very difficult to apply to the case of the optimally K-doped BaFe2As2, as the critical field is over 75 T. Since for the case of the electron-doped 122s the critical field is much lower, we performed zero and in-field (14 T) resistivity measurements of optimally doped Ni-doped SrFe2As2.

Figure 6 shows resistivity vs. temperature of the SrFe2-xNi_xAs2, x=0.155 normalized at its value at 320 K, in zero field and in 14 T//c. Before the measurement, the sample was annealed in low argon pressure for 24 hours at 700° C.

Figure 5 shows elastic neutron-scattering scans of the \((1\;0\;3)\) magnetic Bragg peak at different temperatures: \(T=1.2,\; 8,\; 71,\;\) and 92 K of the sample \(x=0.17\). For each temperature the zero field data are indicated with filled squares and data in 14.5 T with filled circles, and the curves are Lorentzian fittings.

have a lower critical field \(H_{c2}\) than those that are optimally doped, where the critical field was estimated to be above 75 T\(^{22}\).

Figure 5 shows elastic neutron-scattering scans of the \((1\;0\;3)\) magnetic Bragg peak at different temperatures: \(T=1.2,\; 8,\; 71,\;\) and 92 K of the \(x=0.17\) sample, in zero and 14.5 T. While for the 1.2 K the 14.5 T magnetic intensity is \(\approx 10\%\) higher than for the zero field, our data

FIG. 6: Resistivity vs. temperature of the SrFe2-xNi_xAs2, x=0.155 normalized at its value at 320 K, in zero field and in 14 T//c. Before the measurement, the sample was annealed in low argon pressure for 24 hours at 700° C.

...showing the onset of the diamagnetism at \(\approx 17\) K (right axis). In 14 T (left axis) \(T_c\) decreases to \(\approx 8\) K.
agreement therefore with neutron measurements in a 13.5 T//c field on optimally electron-doped BaFe$_{1-x}$Ni$_x$As$_2$ that showed that the field did not induce static AFM order\cite{13}. Therefore, part of the results of the hole- and electron-doped 122s seems to be consistent with a competing static AFM order and SC, similar to that for cuprate HTSc. The high field results reported here on the hole-doped Ba$_{0.85}$K$_{0.17}$Fe$_2$As$_2$ are similar to the case of cuprates for which the AFM order is strengthened with application of a magnetic field\cite{14,15}. Despite the resemblance of the shape of the phase diagrams\cite{14} for both iron pnictide and cuprate HTSc, the superconductivity in these materials appears to be of a different nature. We believe that these results will stimulate further exploration.

IV. SUMMARY

In summary, in the present article we report complementary elastic neutron scattering in zero and 14.5 T and magnetization measurements in zero and 14 T on under-doped SC x=0.17, and zero field on non-SC x=0.09. While for the non-SC x=0.09 sample the AFM transition is sharp consistent with a weakly 1$^\text{st}$ order transition, for higher doping x=0.17 the transition presents a broad distribution on T$_{\text{c}}$ due to a slight variation of the K dopant. For sample x=0.09 the temperature dependence of the magnetic OP is more gradual than for the case of parent BaFe$_2$As$_2$, indicative of proximity to a tricritical point. This tricritical point seems to be an universal feature among all superconducting 122s. The slight variation on the K dopant in the x=0.17 SC sample contributes to the fractional SC volume. Although the SC under-doped x=0.17 sample has a SC volume fraction of $\approx$40%, we were able to observe a downturn in the AFM order parameter below T$_{\text{c}}$, a clear sign of competition between AFM and SC, and similar to the one observed in the electron-doped 122s. As for the case of electron-doped 122s, a 14.5 T magnetic field enhances the AFM below T$_{\text{c}}$ with $\approx$10%. This points, for the case at least of the 122s, toward a s$^\pm$ SC pairing symmetry\cite{16,17} in the hole-doped material, similar to that in the electron-doped 122s. Finally we mention that while writing the current paper, we became aware of related work by E. Wiesemayer et al\cite{18}. Their combined X-ray and muon spin rotation on powder samples of the potassium under-doped materials show microscopical coexistence of AFM and SC.

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