First and second order magnetic and structural transitions in BaFe$_{2(1-x)}$Co$_{2x}$As$_2$

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We present here high resolution magnetization measurements on high-quality BaFe$_{2(1-x)}$Co$_{2x}$As$_2$, 0$\leq x \leq$0.046 as-grown single crystals. The results confirm the existence of a magnetic tricritical point in the $(x,T)$ plane at $x^*_m \approx 0.022$ and reveal the emergence of the heat capacity anomaly associated with the onset of the structural transition at $x^* \approx 0.0064$. We show that the samples with doping near $x^*_m$ do not show superconductivity, but rather superconductivity emerges at a slightly higher cobalt doping, $x \approx 0.0315$.

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The 122 series (AFe$_2$As$_2$, A = Ba, Sr, Ca, Eu) is one of the most studied among the newly discovered iron arsenide high temperature superconductors. One intriguing fact is that in this series superconductivity can be induced by doping in any of the three atomic sites; the cobalt doped system BaFe$_{2-2x}$Co$_{2x}$As$_2$ is, for instance, one of the most studied systems. The antiferromagnetic (spin-density wave) and structural (tetragonal to orthorhombic) transitions that are near-coincident in the parent compounds are concomitantly and gradually suppressed upon doping. A large number of papers have been written on the thermodynamic nature of the transitions in 122s arguing for either 1$^{\text{st}}$ order or 2$^{\text{nd}}$ order phase changes. If we solely consider the BaFe$_2$As$_2$ system, reports range from both 2$^{\text{nd}}$ order structural and magnetic phase transitions, to both transitions 2$^{\text{nd}}$ order but with the possibility of magnetic 1$^{\text{st}}$ order transition within 0.5 K of $T_N$, to 1$^{\text{st}}$ of a order magnetic transition, to indiscernibility between the two scenarios for the magnetic phase transition (did not see either the abrupt change at $T_N$ of the magnetic order parameter that is expected for a first-order transition, or the divergence of the correlation length at $T_N$ that would suggest a second-order transition).

More recent combined high resolution X-ray diffraction and heat capacity measurements on exceptionally high quality BaFe$_2$As$_2$ crystals revealed a 1$^{\text{st}}$ order magnetic transition preceded by a structural transition that starts as a 2$^{\text{nd}}$ order transition at a slightly higher temperature but with a first order jump in the orthorhombic distortion coincident with the first order magnetic transition. Since data on some doped Ba122 samples show clear 2$^{\text{nd}}$ order magnetic and structural transitions, it has been theoretically suggested that the magneto-structural transition in the parent is close to a tricritical point that is tunable through doping. The only exception appears to be the case of the hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ for which both the magnetic and structural transitions seem to be 1$^{\text{st}}$ order over the entire phase diagram. Further, ARPES measurements on cobalt doped Ba122 evidenced a Lifshitz transition at the onset of superconductivity, while high-resolution x-ray diffraction and x-ray resonant magnetic scattering (XRMS) pointed to a magnetic tricritical point at $x \approx 0.022$, but with a structural transition whose onset is 2$^{\text{nd}}$ order across the whole cobalt doping range.

![FIG. 1: $d(\chi)/dT$ versus $T$ of the BaFe$_{2(1-x)}$Co$_{2x}$As$_2$, 0$\leq x \leq$0.0211 crystals.](image)

Magnetic and structural order parameters are normally obtained through scattering measurements. At the same time, measurements of thermodynamic quantities such as the heat capacity give direct information about the fluctuations associated with the order parameters and they can often be performed with quite high precision. For instance, fittings of high resolution heat capacity data in the critical region of a second order transition can give information about the values of the critical expo-
change of the transition. The theoretical result had been successfully tested initially on MnO and MnFe$_2$. Although this theoretical result was initially meant for antiferromagnetic transitions, it seems that $\partial(\chi(T))/\partial T$ mimics $C$ for both the magnetic and structural transitions of Co-doped Ba122 itself, other 122s and 1111s as well. While establishing a precise equivalence between $C(T)$ and $\partial(\chi(T))/\partial T(T)$ is beyond the present study, we will exploit here the direct proportionality between the two physical measures at the transitions, i.e. $C(T=T_1)\propto\partial(\chi(T))/\partial T(T=T_1)$, where $T_1=T_N$, $T_s$.

The measurements were made on as-grown single crystals of BaFe$_{2(1-x)}$Co$_{2x}$As$_2$ that were grown by the self-flux method. Inductively coupled plasma (ICP) and electron microprobe wavelength-dispersive X-ray spectroscopic (WDS) analysis were used to determine the actual stoichiometry of the samples, particular attention being given to the cobalt content. The samples (as determined by WDS) under study were: $x=0$, 0.0035±0.0006, 0.0064±0.0005, 0.0157±0.0007, 0.0211±0.0005, 0.0220±0.0005, 0.0282±0.0010, 0.0315±0.0011, 0.0366±0.0015, 0.0391±0.0011 and 0.046±0.0015. The ± represents the standard deviation from the average $x$ value of readings on ten randomly chosen points on each sample. The magnetic susceptibility measurements on the samples were made using a Quantum Design Magnetic Property Measurement System (MPMS) with a magnetic field of 5 T parallel with the $(a,b)$ crystallographic plane, unless otherwise noted. The machine was "finely tuned" before the measurements to exploit the limits of its sensitivity, and also special care was taken to avoid oxygen contamination.

In brief, we describe high resolution magnetic susceptibility measurements on BaFe$_{2(1-x)}$Co$_{2x}$As$_2$, 0≤$x$≤0.04 that confirm the prediction of a magnetic tricritical point at the doping $x\approx0.022$ and reveal in addition the emergence of the heat capacity anomaly associated with the onset of the second order structural transition at a lower doping, $x=0.0064$. Our data further show that the superconductivity emerges at a higher cobalt doping than the doping that corresponds to the magnetic tricritical point: at $x\approx0.0315$.

Figures 1 and 2 show $d(\chi(T))/dT$ versus $T$ of the as-grown crystals BaFe$_{2(1-x)}$Co$_{2x}$As$_2$ for 0≤$x$≤0.0211 and 0.0211≤$x$≤0.046, respectively. For the undoped sample ($x=0$) the corresponding $d(\chi(T))/dT$ signature for both

![FIG. 2: $d(\chi(T))/dT$ versus $T$ of the as-grown crystals BaFe$_{2(1-x)}$Co$_{2x}$As$_2$, 0.0211≤$x$≤0.046.](image1)

![FIG. 3: Magnetic susceptibility $\chi$ versus $T$ of BaFe$_{2(1-x)}$Co$_{2x}$As$_2$ for cobalt doping $x=0.0282$, 0.0315, 0.0366, 0.091, and 0.046 measured in 20 Oe. The inset shows in magnified scale only the data of samples $x=0.0282$ and 0.0315.](image2)
the antiferromagnetic (AFM) and structural transitions in this sample cannot be further apart than 0.25 K. This is consistent with previous results from our group. Given the $T_N$ and $T_s$ dependence on the annealing (therefore synthesis) conditions, it is not surprising that a $(T_c-T_N)$ as large as 0.75 K has been reported. Samples with $x=0$ and $x=0.0038$ (data not shown) show a single sharp peak which can be unambiguously identified with the combined magnetic and structural first order transition observed by Rotundu et al. and Kim et al. However, the anticipated heat capacity anomaly associated with the initial second order tetragonal-orthorhombic structural transition is not resolvable from the tail of the first order transition. However, as is evident in Fig. 1, for $x=0.0064$ cobalt doping, the heat capacity signature associated with the second order structural peak first emerges as a subtle but clear shoulder on the high temperature side of the first order jump (lower panel of Fig. 1).

Figure 3 shows magnetic susceptibility $\chi$ versus $T$ of $\text{BaFe}_2(1-x)\text{Co}_2\text{As}_2$ for cobalt doping $x=0.0282$, 0.0315, 0.0366, and 0.0391 measured in 20 Oe. Samples $x=0.022$ and 0.0282 show a positive low temperature magnetization and therefore no signs of superconductivity. For sample $x=0.0315$, although $\chi$ shows a clear diamagnetic behavior, the superconducting volume fraction is lower than 1% (inset). The full superconducting volume fraction is reached with a $\approx 0.5\%$ increase of $x$, i.e. at $x\approx 0.0366$, attesting once more to the high quality of the crystals. The value of doping for which superconductivity is stabilized is in good agreement with values from the literature.

![Figure 4](image1.png)

**FIG. 4:** The $d(\chi/T)/dT$ magnitudes at $T_N$ (■) and $T_s$ (▲) of $\text{BaFe}_2(1-x)\text{Co}_2\text{As}_2$ versus $x$, for $0.0064 \leq x \leq 0.046$.

Figure 4 shows the magnitudes of $d(\chi/T)/dT$ at $T=T_N$ (■) and at $T=T_s$ (▲) of $\text{BaFe}_2(1-x)\text{Co}_2\text{As}_2$ versus $x$ for $0.0064 \leq x \leq 0.0391$. The $x=0$ point is not included in the graph since the peak associated with the onset second order structural transition could not be separated from the large first order jump. For $d(\chi/T)/dT(T=T_N)$ the crossover points $x_{tr}$ marks the separation between a globally abrupt and non-monotonic doping evolution (characteristic of 1st order transitions region) and a monotonic variation (region characteristic of 2nd order transitions). The magnetic crossover at $x_{tr}^m=0.022$, appears to be a tricritical point; this confirms, albeit with much more precision, the suggestion of Kim et al. Any possible structural crossover is more difficult to discuss given that at $x=0$ the transition is characterized by a second order onset followed by a large first order jump presumably driven by the first order magnetic transition. At $x^m=0.0064$ the heat capacity of the second order structural transition becomes clearly visible. Figure 5 summarize the above results in a phase diagram ($T$ vs. $x$). For $T_s$ and $T_N$ the discontinuous line indicates first order transition and the continuous line second order transition. The phase diagram here is similar to the one for the 122s predicted by Cano et al. Their Ginzburg-Landau model contains a magnetoelastic coupling term as a key ingredient. Using a slight variation of the afore mentioned model, Kim et al. predicted that the magnetic tricritical point is $x=0.022$. It should be noted that Wilson et al. have shown that in $\text{BaFe}_2\text{As}_2$ below the first order transition the magnetic and structural order parameters exhibit identical temperature dependencies. This requires that there is a dominant biquadratic coupling between the magnetic and structural order parameters. The biquadratic term is not included in the above-mentioned theories.

![Figure 5](image2.png)

**FIG. 5:** The phase diagram for the doping range near the tricritical points. For $T_s$ and $T_N$ the discontinuous line indicates first order transition and the continuous line second order transition.
In summary we have systematically studied the magnetic susceptibility of high quality BaFe$_{2(1-x)}$Co$_2$xAs$_2$, $0 \leq x \leq 0.046$ as grown single crystals. Our measurements confirm the existence of a magnetic tricritical point at the cobalt doping $x \approx 0.022$. They also demonstrate that the anomaly associated with the putative second order structural transition emerges clearly separated from the first order combined magnetic and structural transition at a doping of about 0.0064. We show further that the superconductivity emerges at higher cobalt doping than that at the magnetic tricritical point: namely $x \approx 0.0315$.

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