Decoupling of the superconducting and magnetic (structural) phase transitions in electron-doped BaFe$_2$As$_2$

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(Dated: April 20, 2009)

Abstract

Study and comparison of over 30 examples of electron doped BaFe$_2$As$_2$ for transition metal (TM) = Co, Ni, Cu, and (Co/Cu mixtures) have lead to an understanding that the suppression of the structural/antiferromagnetic phase transition to low enough temperature in these compounds is a necessary condition for superconductivity, but not a sufficient one. Whereas the structural/antiferromagnetic transitions are suppressed by the number of TM dopant ions (or changes in the c-axis) the superconducting dome exists over a limited range of values of the number of electrons added by doping (or values of the a/c ratio). By choosing which combination of dopants are used we can change the relative positions of the upper phase lines and the superconducting dome, even to the extreme limit of suppressing the upper structural and magnetic phase transitions without the stabilization of low temperature superconducting dome.

PACS numbers: 74.10.+v; 74.62.Dh; 74.70.Dd; 75.30.Kz
The discovery of superconductivity in the LaFeAsO [1] and BaFe$_2$As$_2$ [2] systems has lead to a renaissance in interest in transition metal based superconductivity. Both of these systems manifest substantial $T_c$ values when the structural/antiferromagnetic phase transitions are sufficiently suppressed by substitution on the alkali-earth, transition metal and/or oxygen site. Although the systematic studies of F- and K-doping have been difficult due to problems in controlling and assessing stoichiometry, transition metal doping, especially of the BaFe$_2$As$_2$ system has been tractable and quantifiable.

In the case of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ a comprehensive, and highly reproducible, $T(x)$ phase diagram has been determined [3] and confirmed/reproduced by several groups [4-6]. The structural phase transition is suppressed by roughly 15 K per atomic percent Co and increasingly separates from the lower, magnetic phase transition as more Co is added [3,4,7,8]. For intermediate doping levels, superconductivity has been observed to strongly interact with the magnetic order and fluctuations in the antiferromagnetically ordered, orthorhombic state [7]. For higher Co doping levels both the structural and antiferromagnetic phase transitions are suppressed and superconductivity occurs in the tetragonal phase. These data are all consistent with the idea that superconductivity is stabilized when the tetragonal phase is brought to ”low enough” temperatures by perturbing the parent compound. This may be associated with reducing the size of the orthorhombic distortion and ordered moment ”enough” or bringing the magnetic fluctuations associated with the tetragonal phase to ”low enough” temperatures. Superconductivity does not require the complete suppression of the orthorhombic/antiferromagnetic phase, just its suppression to an adequately low temperature [3-6].

There is a clear correlation between the upper (structural and magnetic) phase transitions and the lower temperature, superconducting phase, but, to date, it is a qualitative one at best. In this Letter we have studied over 30 samples of electron doped BaFe$_2$As$_2$ where the electron doping is coming from 3$d$ transition metal substitutions on the Fe site. We have grown and examined single crystalline samples of the Ba(Fe$_{1-x}$TM$_x$)$_2$As$_2$ system for TM = Co, Ni, Cu, and (Co/Cu mixtures) and find that whereas the suppression of the upper structural phase transitions is a necessary condition for low temperature superconductivity, it is not a sufficient one. This distinction can be understood by our observation that whereas the upper transitions appears to be suppressed by the number of impurity atoms substituted for Fe (or the change in the crystallographic $c$-axis) the location and extent of the super-
conducting dome scales with the number of additional electrons, one for each Co, two for each Ni and three for each Cu atom (or the change in the ratio or the crystallographic $a$-axis to $c$-axis). By choosing which combination of dopants are used, we can change the relative positions of the upper phase lines and the superconducting dome, even to the extreme limit of suppressing the upper structural and magnetic phase transitions without the stabilization of low temperature superconducting dome.

Single crystals of $\text{Ba(Fe}_{1-x}\text{TM}_x\text{)}_2\text{As}_2$ system for $\text{TM} = \text{Ni}, \text{Cu},$ and (Co/Cu mixtures) were grown in a similar manner as the $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$ compounds [3]. Actual doping levels (rather than nominal) were determined via WDS analysis using an electron probe microanalyzer of a JEOL JXA-8200 electron microprobe and are denoted as $x_{\text{WDS}}$. Powder X-ray diffraction spectra with Si standard were measured using a Rigaku MiniFlex and unit cell parameters were extracted using "UNITCELL" analysis package. Although we attempted to synthesize similar doping levels of the various Co, Ni, Cu and Co/Cu series by using identical nominal values, experimentally determined doping levels revealed slightly different actual values of incorporation of these different TM dopants. Electrical resistivity measurements were made using a standard 4-probe configuration and Quantum Design PPMS (Physical Property Measurement System) and MPMS (Magnetic Property Measurement System) units to provide the temperature/field environment. Although single crystals can be shaped into well defined geometries, the AEF$_2$As$_2$ materials are prone to exfoliation along the $c$-axis that can lead to spurious resistivity values due to poorly defined current path lengths and cross-sections [3, 9, 10]. For this reason normalized resistivity values are plotted. Although only resistivity data is presented in this Letter, detailed magnetization and specific heat data have also been collected; as in the case of $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$ [3], these thermodynamic data further support the $T(x)$ phase diagrams we infer from transport data.

Figures 1a and 1b present the temperature dependent, normalized resistivity for $\text{Ba(Fe}_{1-x}\text{TM}_x\text{)}_2\text{As}_2$ system for $\text{TM} = \text{Co}$ and Ni respectively. For each TM dopant there is a clear suppression (and separation) of the upper transitions with increasing $x$ and superconductivity is clearly stabilized once the structural/magnetic phase transitions are sufficiently suppressed and exists in both the orthorhombic/antiferromagnetic phase as well as in the tetragonal one at high dopings [3, 7, 11]. Although $\text{BaCu}_2\text{As}_2$ itself appears to be a relatively innocuous compound [12, 13], the $\text{Ba(Fe}_{1-x}\text{Cu}_x\text{)}_2\text{As}_2$ series (Fig. 1c) reveals a key difference: although the signature of the structural/antiferromagnetic phase transition is suppressed in
a manner similar to that seen for TM = Co and Ni, there is no superconductivity found for any \( x \) value tried (up to values six times greater than the \( x = 0.061 \) shown). This means that the signatures of the orthorhombic/antiferromagnetic transitions are not truncated by superconductivity and can be observed to fade as \( x \) is increased.

In order to clarify the effect of Cu as a dopant (i.e. Is it particularly pernicious to superconductivity or is it essentially part of a continuum that contains Co and Ni dopants as well?) we studied a Ba(Fe\(_{1-x-y}\)Co\(_x\)Cu\(_y\))\(_2\)As\(_2\) series (\( x \sim 0.022 \) and \( 0 \leq y < 0.05 \)). Fig. 1d presents selected normalized resistivity plots for this series. As can be seen in Fig. 1a, a Co-doping of \( x = 0.024 \) is insufficient to induce superconductivity, but additional doping by Cu (Fig. 1d) can indeed induce superconductivity. These data clearly show that Cu is not inherently antithetical to the superconducting state and that there may well be a deeper and more profound realization to be made based on these data.

The data presented in Fig. 1 can be summarized in a \( T - x \) phase diagram. The transition temperature values for the upper structural and magnetic phase transitions were inferred from these data in manner similar to that used in reference 3 and subsequently supported by microscopic measurements [7, 8]. For the higher Cu concentrations (\( x = 0.05 \) and 0.061) the resistive features become so broad that the error bars associated with the determination of the upper (only detectable) transition are defined by the temperature of the resistance minima on the high side and the temperature of the inflection point on the low side. Fig. 2a displays the \( T - x \) phase diagram for each of the Ba(Fe\(_{1-x}\)TM\(_x\))\(_2\)As\(_2\) (TM = Co, Ni, Cu, and Co/Cu) series. Whereas the suppression of the upper phase transitions for each of these different series appear to depend on \( x \) in a similar manner, the occurrence of superconductivity is not well described by this parameterization. Superconductivity is found for an wide range of Co doping values, a narrower range of Ni doping values and a even narrower range of Cu doping values (in the Ba(Fe\(_{1-x-y}\)Co\(_x\)Cu\(_y\))\(_2\)As\(_2\) series).

There is, of course, a second way of plotting these data: transition temperature as a function of extra conduction electrons added by the dopant, i.e. grossly assuming the validity of a rigid band approximation for these dopants. For TM = Co, the number of impurity atoms, \( x \), per TM site is the same as the number of extra electrons, \( e \), per TM site. When TM = Ni or Cu, this is not the case. A second parameterization of the data inferred from Fig. 1 is show in Fig. 1b: a \( T - e \) phase diagram, where \( e \) is the number of extra electron
added per Fe/TM site (for the case of Co $e = x$, for the case of Ni $e = 2x$, for the case of Cu $e = 3x$). This parameterization does a much better job of unifying the superconducting domes of these compounds, but clearly does a much poorer job of capturing the physics of the suppression of the upper structural/antiferromagnetic phase transitions.

Although $x$ and $e$ are intuitive (and relatively easy to determine) parameters, they are certainly not unique ones. Figs. 3a-d demonstrate that whereas the $c$-lattice parameter variation is similar to $x$, the variations in the $a$-lattice parameter, the volume, and the $a/c$ ratio do not show universal behavior when plotted as a function of $x$. This means that the statement that the upper structural and antiferromagnetic phase transitions scale with $x$ is equivalent (experimentally) with the statement that they scale with the variation in the $c$-lattice parameter.

Further examination of Figs. 3a-d reveals that whereas a change of parameter from $x$ to $e$ will not lead to a collapse of the data for $a/a_0$, $c/c_0$ or $V/V_0$ onto a universal curve, the variation of the $a/c$ data appears promising, showing variations with $x$ that differ by factors of two and three. Fig. 3e plots the variation of $a/c$ as a function of $e$. As clearly shown, $a/c$ and $e$ are experimentally equivalent variables (for 3$d$ TM electron doping) as well.

One obvious parameter that has not been examined in this study is the As-Fe-As bonding angle. Unfortunately this was not extracted from our diffraction data, and given that the location of the As site is free to vary, it is hard to model. Future measurements will have to determine whether this angle is related to either $x$ or $e$.

The phase diagrams in Fig. 2 provide graphic evidence that the structural/antiferromagnetic phase transitions and the occurrence of superconductivity depend on different parameters for electron doping via TM substitution: number of impurities (change in $c$-axis parameter) and number of additional electrons ($a/c$ ratio) respectively. This difference allows for the decoupling of these transitions and the ability to realize that the suppression of the structural/antiferromagnetic phase transition to low enough temperature is a necessary condition for superconductivity, but not a sufficient one. The data from the Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ series clearly demonstrate that if too many electrons are added in the process of suppressing the structural/antiferromagnetic phase transition the superconducting dome can be overshot, i.e. by the time the structural/antiferromagnetic transition is suppressed enough, too many conduction electrons have been added and window for superconductivity has been missed. A closer examination of Fig. 2b brings this point
even further into focus: although the superconducting dome for the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, Ba(Fe$_{1-x}$Ni$_x$)$_2$As$_2$, and Ba(Fe$_{1-x-y}$Co$_x$Cu$_y$)$_2$As$_2$ series are essentially indistinguishable on the higher doping side, they differ, somewhat, on the lower doping side. This difference would be consistent with needing to bring the upper transition to low enough temperature to allow the superconductivity to turn on: Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with its more rapidly decreasing upper transitions manifest superconductivity at slightly earlier $e$-values than the Ni-doped or Cu/Co doped series.

The observation that the upper transitions depend on either the number of TM dopant atoms added, $x$, or, equivalently, the change in the $c$-axis dimension, leads to two differing scenarios for what physical parameter controls this suppression. If $x$ is the salient parameter, then the upper transitions are controlled by local physics such as vacancies on the Fe sublattice or the disruption of very short range fluctuations. On the other hand if the size of the $c$-axis parameter is the salient variable, then details of band structure (nesting or not) or degree of As-As bonding across the Fe-plane would be more likely to control/affect the value of the upper transition temperatures.

The observation that the superconducting dome is delineated by a minimum and maximum number of extra conduction electrons (or possibly $a/c$ ratio) provides a clear theoretical constraint/test for current theories of superconductivity in these fascinating, complex and potentially useful [14] compounds.

In conclusion, the study and comparison of over 30 examples of electron doped Ba(Fe$_{1-x}$TM$_x$)$_2$As$_2$ have lead to an understanding that the suppression of the structural/antiferromagnetic phase transition to low enough temperature in these compounds is a necessary condition for superconductivity, but not a sufficient one. Whereas the structural/antiferromagnetic transitions are suppressed by the number of TM dopant ions (or changes in the $c$-axis) the superconducting dome exists over a limited range of values of $e$, the number of electrons added by doping (or values of the $a/c$ ratio). As clearly shown by the Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ series, if too many electrons are added per TM dopant, then the window for superconductivity can be completely missed. Further work, including the quantitative and comparative analysis of K-doping and TM-based hole doping, as well as 4$d$ and even 5$d$ TM-based electron doping will have to be carried out to see how general this decoupling of the structural and superconducting transitions is and perhaps help resolve which parameterization it the physically most relevant.
Acknowledgements: We would like to thank N.H.Sung for help in the samples growth. Work at the Ames Laboratory was supported by the Department of Energy, Basic Energy Sciences under Contract No. DE-AC02-07CH11358.

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FIG. 1: The temperature dependent resistivity, normalized by room temperature value, for electron doped Ba(Fe$_{1-x}$TM$_x$)$_2$As$_2$ (TM = Co, Ni, Cu, and Co/Cu) series: (a) Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [3]. Inset: low temperature data for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (b) Ba(Fe$_{1-x}$Ni$_x$)$_2$As$_2$. Inset: low temperature data for Ba(Fe$_{1-x}$Ni$_x$)$_2$As$_2$ (c) Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ (d) Ba(Fe$_{1-x-y}$Co$_x$Cu$_y$)$_2$As$_2$. Inset: low temperature data for Ba(Fe$_{1-x-y}$Co$_x$Cu$_y$)$_2$As$_2$
FIG. 2: (a) Transition temperature as a function of the number of substitutional transition metal ions per Fe site; (b) Transition temperature as a function of extra electrons contributed by TM substitution per Fe site. For both plots the transition temperatures were determined in a manner similar to that described in [3] and the text.
FIG. 3: Normalized structural parameters measured at $\sim 300$K. (a) $a/a_0$, (b) $c/c_0$, (c) $V/V_0$ and (d) $(a/c)/(a_0/c_0)$ as a function of transition metal doping, $x$, and (e) $(a/c)/(a_0/c_0)$ as a function of extra conduction electrons, $e$. ($a_0=3.9621\text{Å}$, $c_0=13.0178\text{Å}$)