Electronic phase diagram of disordered Co doped BaFe$_2$As$_2$–δ

F Kurth$^{1,2}$, K Iida$^1$, S Trommler$^{1,2}$, J Hänisch$^1$, K Nenkov$^1$, J Engelmann$^{1,2}$, S Oswald$^6$, J Werner$^4$, L Schultz$^{1,2}$, B Holzapfel$^{1,5}$ and S Haindl$^4$

$^1$ IFW Dresden, Institute for Metallic Materials, Helmholtzstrasse 20, D-01069 Dresden, Germany
$^2$ TU Dresden, D-01062 Dresden, Germany
$^3$ IFW Dresden, Institute for Complex Materials, Helmholtzstrasse 20, D-01069 Dresden, Germany
$^4$ IFW Dresden, Institute for Solid State Research, Helmholtzstrasse 20, D-01069 Dresden, Germany
$^5$ TU Bergakademie Freiberg, Akademiestrasse 6, D-09596 Freiberg, Germany

E-mail: Fritz.Kurth@ifw-dresden.de and S.Haindl@ifw-dresden.de

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Abstract

Superconducting and normal state transport properties in iron pnictides are sensitive to disorder and impurity scattering. By investigation of Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$–δ thin films with varying Co concentrations we demonstrate that in the dirty limit the superconducting dome in the electronic phase diagram of Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$–δ shifts towards lower doping concentrations, which differs significantly from observations in single crystals. We show that especially in the underdoped regime superconducting transition temperatures higher than 27 K are possible.

(Some figures may appear in colour only in the online journal)

1. Introduction

Almost simultaneously with the report of superconductivity by hole doping in BaFe$_2$As$_2$, [1] Sefat et al showed that electron doping in BaFe$_2$As$_2$ is also able to suppress the spin density wave (SDW) state and to stabilize superconductivity [2]. Since then, many studies have been devoted to an understanding of the competition between the SDW and the superconducting state in this intermetallic compound [3–8].

Investigations of the electronic phase diagram of Co doped BaFe$_2$As$_2$ revealed a structural transition from a high-temperature tetragonal to a low-temperature orthorhombic phase closely above the transition from the paramagnetic to the SDW state.

With increasing doping level $x$ in Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ the structural and magnetic transitions split further and are suppressed [3, 4]. In addition, a characteristic superconducting dome rises with a maximal critical temperature up to $T_c = 25$ K around the optimal doping of $x = 0.06 – 0.08$ until superconductivity vanishes beyond $x = 0.18 – 0.20$. In the underdoped region ($x ≤ 0.06$) superconductivity coexists with the SDW state microscopically. This extremely close vicinity of superconductivity to antiferromagnetism suggests the mediating role of spin fluctuations in the Cooper pairing.

The influence of increasing Co content in Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ on the electronic structure results in an increase of its three dimensionality, a gradual filling of the hole pockets near the $Γ$ point of the Brillouin zone, and therefore reduced nesting [9]. It has been argued that the loss of nesting (i.e. the weakening of interband transitions) and the suppressed spin fluctuations are responsible for the decrease in $T_c$ in overdoped samples, whereas in underdoped samples superconductivity has to compete with the SDW state for the carrier density [7, 8, 10, 11].

A more explicit difference between the effects of electron doping on the structural, magnetic and superconducting transitions was made by Canfield et al by comparing Co doping with Ni and Cu doping in BaFe$_2$As$_2$ [12]. They concluded that the occurrence of superconductivity depends primarily on the number of added electrons and the $c/a$ ratio, whereas the structural modifications, defects and magnetic phase transitions depend on the number of added impurity ions and the $c$-axis parameter. In this regard other...
perturbations in the FeAs tetrahedral sublattice (vacancies and interstitials included) should be considered in more detail.

All the investigations mentioned above have been performed on powder samples and on single crystals. Here, we will discuss the peculiarities in the growth of Co doped BaFe$_2$As$_2$ thin films with varying Co content and the influence on the electronic phase diagram. Since the first growth of Co doped BaFe$_2$As$_2$ thin films by pulsed laser deposition (PLD), [13–15] a detailed analysis of the chemical composition and homogeneity has been widely neglected. Therefore, part of our study is devoted to the investigation of thin film stoichiometry. Auger electron spectroscopy (AES) demonstrates that the chemical composition of the films is sensitive to the deposition conditions. One difference between thin films and single crystals of iron pnictide superconductors is their degree of disorder, easily demonstrated by RRR values. As observed in comparable films without a Fe buffer, typical RRR values for Co doped BaFe$_2$As$_2$ are in the range of 1 and 2.

2. Sample preparation

For the preparation of the target materials the starting elements (Ba, Fe, Co and As) are mixed and mechanically milled resulting in precursor powders of Fe$_2$As$_2$, Co$_2$As and BaAs. Precursor powders of $x = 0$, 0.02, 0.04, 0.06, 0.08, 0.10 and 0.15 were synthesized and pressed in pellets of Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ with different Co content. The oxygen impurities of the starting elements were taken into account during the weighing process. Impurities in As were negligible since As was cleaned by sublimation [16]. More details of the target preparation are given in appendix A.

Using the sintered Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ targets, thin films with different Co concentration were fabricated by PLD under ultrahigh vacuum (UHV) conditions (base pressure of $10^{-9}$ mbar) on MgO(100) substrates. A KrF exciplex laser ($\lambda = 248$ nm, pulse duration $= 25$ ns) was used for material ablation.

Before each film deposition the target surface was cleaned by approximately 1000 laser pulses. The substrates were cleaned in an ultrasonic bath using acetone and isopropanol and subsequently transferred into the UHV chamber. Heat treatment of the substrate at 1000°C for 30 min followed prior to the deposition process.

Thin film growth started with the deposition of a pure Fe buffer at room temperature. The Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ deposition followed at substrate temperatures between 650°C and 800°C depending on the nominal Co content (table 1). The deposition temperature was increased with increasing Co doping. The repetition rate was set to 5 Hz for Fe and to 10 Hz for Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$. Pulse numbers for the Fe buffer layer were set to 4000–5000 and for Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ to 8000. The estimated energy densities at the target surface of Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ are given in table 1.

3. Measurements and results

Table 1. Deposition conditions and structural data for Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$—Fe bilayers.

| $x_{nom}$ | $x_{AES}$ | Dep.-temp. (°C) | Energy density | $\varphi$-FWHM (°) | c-axis (Å) | $T_{c,90}$ (K) |
|----------|-----------|-----------------|----------------|--------------------|------------|--------------|
| 0        | 0         | 650             | Ba-122 (J cm$^{-2}$) | Fe (J cm$^{-2}$) | Ba-122(103) | Fe(110) |
| 0.02     | 0.015     | 700             | 2.45           | 2.85               | 1.82       | 1.23        | 12.9975    |
| 0.04     | 0.035     | 750             | 2.50           | 3.10               | 1.23       | 1.04        | 12.93307   |
| 0.06     | 0.049     | 750             | 2.65           | 3.30               | 0.78       | 0.75        | 12.79980   |
| 0.08     | 0.075     | 750             | 2.75           | 3.05               | 0.81       | 0.87        | 12.85912   |
| 0.10     | 0.107     | 750             | 2.75           | 3.15               | 0.81       | 0.80        | 12.84935   |
| 0.15     | 0.134     | 800             | 2.75           | 3.15               | 0.99       | 1.11        | 12.82454   |
| 0.15     | 0.132     | 750             | 2.50           | 2.50               | 1.14       | 0.81        | 12.74101   |
|          |           |                 |                |                    | 1.27       | 0.87        | 12.78704   |

The phase purity of the target material was analysed by powder x-ray diffraction (XRD) in Bragg–Brentano geometry (Co $K_α$ radiation with $\lambda = 1.7889$ Å). Powder XRD scans of the targets and a following Rietveld analysis [17, 18] show high phase purity of the target material (the $S$-values for the Rietveld analysis are less than 1.3). The obtained lattice parameters follow the trend of Vegard’s law and are similar to results from single crystal measurements (figure 1(a)).

The transition temperatures, $T_c$, of the processed targets were determined by superconducting quantum interference device (SQUID) and vibrating sample magnetometer (VSM) measurements. The resulting phase diagram shows a maximum $T_c$ of 23.7 K at a nominal composition of $x_{nom} = 0.08$ (figure 1(b)).

Epitaxial growth of the thin films was confirmed by x-ray $\theta$–$2\theta$ scans and texture measurements as shown, for example, in appendix B for the film grown from the Ba(Fe$_{0.92}$Co$_{0.08}$)$_2$As$_2$ target (figure B.1 and B.2). The epitaxial relation was confirmed to be $(010)[100]$Ba-122 || $(001)[110]Fe || (001)[100]MgO [20].

The thickness of the Fe buffer and the Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ layer was confirmed on a focused ion beam (FIB)-cut cross section in a scanning electron microscope equipped with a FIB stage [21]. For all films the Fe buffer thickness is between 15 and 20 nm, whereas the Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ layer thickness is about 100 nm. The $T_c$ of the samples was determined by the Van der Pauw method using a physical property measurement system (PPMS). A heating rate of 1 K min$^{-1}$ and a constant current of 100 μA were used in the electrical transport measurements. Due to the higher conductivity of the Fe buffer layer and the resulting shunting of the current [22], the SDW anomaly in the underdoped films cannot be detected through $R(T)$ measurements. In addition, the $T_c$ criterion (except
The target powders in dependence on the nominal doping level lattice parameters of the Ba

for $T_c(0)$ shifts towards lower resistivities and thus to lower temperatures because of the Fe buffer layer. In order to obtain the transition temperatures of the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$−δ layer, the $R(T)$ data were corrected using the method given by Trommler et al [22].

A key question in the PLD process addresses the stoichiometric transfer of the material from the target to the substrate. Thin film stoichiometry was determined by Auger electron spectroscopy (AES) where parts of the film were sputtered and the target material was used as a standard. The resulting depth profiles of the films not only reveal the stoichiometry but also inhomogeneities in the film compositions (figure 2(b)). The quantification of the film stoichiometry is based on calibrated AES measurement of target material, that was ground and sputter cleaned using the same conditions as in the depth profiles. Thus surface contamination is removed, preferential sputtering and some peak interferences (signals of Ba partly overlapped by Fe) are considered in the concentration quantification of the layers. The Ba-122 target material with a doping of $x_{\text{nom}} = 0.1$ assumed to be in nominal stoichiometry was used to create a set of sensitivity factors for calibration, confirmed also for the $x_{\text{nom}} = 0.02$ target material. The calibration thus works well in the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$−δ layer of the films, but cannot be used for quantification in the Fe buffer layer.

A remarkable observation is the As deficiency, especially in underdoped films compared to the target material. The maximum As deficiency is estimated from AES to be about $\delta = 0.15$ in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$−δ (figure 2(a)). We assume As diffusion into the Fe buffer during film growth. Additionally, diffusion of Co into the Fe buffer layer is noticeable, and its amount changes with varying Co content and deposition temperature. In the higher doped samples with a nominal Co content of $x_{\text{nom}} = 0.15$ a large Co gradient over the layer thickness was found for increased deposition temperatures. A diffusion of Co into the Fe buffer layer takes place, especially at elevated temperatures where the Co content in the Fe buffer increases. The Co content in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$−δ thin films deposited at higher temperatures ranges between $x = 0.20$ and $x = 0.09$. A steep Co concentration gradient along the film thickness as well as a strong Co diffusion into the Fe buffer can be observed. In contrast, the Co gradient of the thin film and the Co diffusion into the Fe buffer deposited at $750^\circ$C is significantly smaller (figure 2(b)). Despite local inhomogeneities, the measured Co concentration, $x_{\text{AES}}$, in the thin films follows the nominal Co content $x_{\text{nom}}$ quite well (figure 3).

The $c$-axis lattice parameter of the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$−δ phase decreases with increasing $x_{\text{AES}}$ (figure 4(a)). The $c$-axis of the thin films is always smaller than the $c$-axis of the bulk targets. The resulting electronic phase diagram determined from the thin films is shown in figure 4(b). The error bars in $x_{\text{AES}}$ indicate the difference between the highest and the lowest doping value determined by AES. The error bars in $T_c$ show the transition width of the corrected measurements from $T_c(90)$ to $T_c(10)$ ($T_c(90)$ and the $T_c(10)$ being taken at 90 % and 10 % of the normal state resistivity at 35 K).

4. Discussion

The measured Fe/Co ratio indicates a qualitative agreement between nominal and measured concentrations (figure 3). In
all thin films. As deficiency was observed up to approximately \( \delta = 0.15 \) (figure 2(a)). Quantitatively, the stoichiometric transfer from the target to the thin film cannot be exactly determined from our analysis yet.

Simultaneously, we have observed a Co concentration gradient along the film cross section for films with a high Co doping level. At elevated deposition temperatures, Co easily diffuses into the Fe buffer. The resulting gradient of the Co dopant in BaFe\(_2\)As\(_2\)–\(\delta\) is responsible for a sequence of differently doped regions along the thickness. Instead of a homogeneously overdoped film, there are also optimally Co doped layers which may be responsible for a higher \( T_c \) compared to bulk values in the electronic phase diagram.

The explanation for the enhanced \( T_c \) values in underdoped films is more subtle. The Co concentration gradient is less pronounced (figure 2(a)), hence it cannot be considered as a primary candidate for the high \( T_c \) values. Strain effects cannot be excluded completely; however, quantification is still missing. In addition, the role of the Fe buffer layer between substrate and iron pnictide thin film is as yet unclear. First, the buffer layer is supposed to act as a strain absorber. Second, it has to be further investigated how its ferromagnetism influences the SDW and/or the superconducting state of BaFe\(_2\)As\(_2\)–\(\delta\) due to proximity.

Instead of strain we propose disorder as a primary candidate to explain the observed \( T_c \) enhancement. Impurities in superconductors (one aspect of disorder) are generally classified according to their scattering potential as magnetic or non-magnetic and act as Cooper pair breakers leading to a \( T_c \) suppression described by the Abrikosov–Gor’kov formula in conventional superconductors [23]. The situation is more complex in multiband superconductors, where the effects of impurity scattering are dependent on the scattering strength and the anisotropy of the scattering potential, the coupling constant matrix, the symmetry of the superconducting gap \( (\pm, \pm, \text{d-wave}) \) and, finally the scattering channels commonly denoted as intraband and interband [24].

In the case of underdoped Ba(Fe\(_{1−x}\)Co\(_x\))\(_2\)As\(_2\)–\(\delta\), superconductivity coexists microscopically with a SDW state, i.e. SDW and superconductivity compete for the same electrons [10, 11]. Shifting the superconducting dome in the electronic phase diagram is thus a result of any mechanism suppressing the SDW but leaving the Cooper pairing intact.

A very recent theoretical work proposes that non-magnetic impurity scattering suppresses the SDW transition more strongly than the superconducting transition. Thus it is responsible for an enhancement of \( T_c \) in underdoped Ba(Fe\(_{1−x}\)Co\(_x\))\(_2\)As\(_2\) [25]. This was experimentally demonstrated by additional Cu doping of Ba(Fe\(_{1−x}\)Co\(_x\))\(_2\)As\(_2\) [26]. Under the assumption of \( s^\pm \) pairing [27, 28] and dominant intraband impurity scattering, the superconducting state survives but at the same time the SDW state is weakened [25].

The same argument, however, holds for any additional (non-magnetic or magnetic) intraband scattering in the hole pocket [24, 29, 30] that acts detrimentally on the SDW formation without strong influence on \( (s^{++} \text{ or } s^\pm) \) superconductivity. This might be the case for the thin films investigated here, where we suggest As vacancies act as active impurities. Although As vacancies may be primarily regarded as non-magnetic defects, they are also able to form localized magnetic moments [31, 32]. Similarly, Se vacancies have been reported to act as magnetic defects in FeSe\(_{1−\delta}\) [33]. Investigations of As deficient oxypnictides found a ferromagnetically ordered Fe cluster around As vacancies [34–37] which does not suppress \( T_c \). A contribution to magnetic impurity scattering due to As vacancies would favour \( s^\pm \) pairing in the Ba(Fe\(_{1−x}\)Co\(_x\))\(_2\)As\(_2\)–\(\delta\) thin films. However, in the dirty limit a crossover from \( s^\pm \) to \( s^{++} \) is also possible.

![Figure 3.](image1.png)  
**Figure 3.** The doping \( x_{\text{AES}} \) measured by AES in the thin films compared to the nominal Co content \( x_{\text{nom}} \).

![Figure 4.](image2.png)  
**Figure 4.** (a) The \( c \)-axis values for thin films with different Co content, \( x \). (b) The phase diagram of the Co doped BaFe\(_2\)As\(_2\)–\(\delta\) thin films (red). The error in \( T_c \) is given by the values for \( T_{c,00} \) and \( T_{c,10} \) and hence the transition width. The error bars for the Co doping represent the Co gradient measured by AES. The blue dots represent the data points of the bulk material, used for PLD.
In addition, Cveticovic and Tesanovic [38] have argued that the itinerant character of the FeAs tetrahedral sublattice is reduced with increased flattening. The c-axis lattice constants of Ba(Fe1−xCo)x2As2−δ thin films are drastically smaller than in the bulk samples. This structural modification might be responsible for a further stabilization of Cooper pairing in the underdoped regime; however, more systematic results are required in order to qualify and quantify strain effects.

5. Conclusions

To summarize, we have studied the superconducting transition in the electronic phase diagram of Co doped BaFe2As2−δ thin films prepared by PLD. The thin films allow us to study the effect of disorder and superconductivity in the dirty limit. We have reported a significant effect on the electronic phase diagram: the measured Tc values are higher compared to single crystal data, and the superconducting dome shifts towards lower Co content. The highest Tc,90 of 27.9 K was achieved at δAES = 0.035 (±0.013). Generally, this change in the electronic phase diagram for Co doped BaFe2As2−δ thin films can be qualitatively understood by taking into account disorder effects and impurity scattering. Additional (non-magnetic or magnetic) intraband scattering weakens the SDW but has less effect on the superconducting state. The thin films in this work are As deficient compared to single crystals. We thus propose As vacancies as a possible candidate for additional intraband scattering centres in Co doped BaFe2As2−δ, being responsible for a suppression of the SDW in favour of Cooper pairing. A more detailed analysis of the role of As vacancies as impurity scatterers in Co doped BaFe2As2−δ is currently under investigation. Strain and the influence of the ferromagnetic Fe buffer layer may have similar effects on SDW and superconductivity. Their contribution is unclear and cannot yet be separated or quantified completely. Finally, due to the high complexity of disorder effects and impurity scattering in multiband superconductivity as well as the coexistence of superconductivity with a SDW state, the term dirty limit in the iron pnictides may describe qualitatively quite different scenarios and its meaning for superconducting properties has to be specified carefully.

Note added: The critical temperatures of a doping series of Ba(Fe1−xCo)x2As2−δ thin films published in Katase et al [39] do not show an enhancement but follow the known results obtained on bulk specimens or target materials [3]. However, there are various differences between the films prepared in [39] and the films of our study: The films presented here are thinner and are grown on a Fe buffer layer. In addition, Katase et al claim to have stoichiometric films (without As deficiency). In contrast, we observe As deficiency in the underdoped thin films presented here which offers an explanation for the observed increase in critical temperatures.

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Appendix A. Target preparation

For the preparation of the BaAs precursor a two-zone quartz ampoule was used to guarantee a safe solid state reaction under an Ar shielding gas atmosphere. Prior to this, the ampoule was baked out under a vacuum for 10 h at 500°C to remove contamination. The heat treatment for the reaction

\[ \text{Ba} + \text{As} \rightarrow \text{BaAs} \]  

(A.1)

is shown in figure A.1(a) and consists of a heating ramp (120°C h⁻¹) and a holding step at 500°C for 24 h. Afterwards the heating continued at a rate of 60°C h⁻¹ up to 700°C above the sublimation point of As. BaAs was held at this temperature for 48 h before cooling down to room temperature at a fast rate of 600°C h⁻¹.

For the production of Fe2As and Co2As, mechanically milled elements with a homogenous grain size of 100 μm were used. Fe and As as well as Co and As were mixed under consideration of oxygen impurities in the ratio of 2:1, respectively.

All milled powders were pressed into cylindrically shaped pellets with a diameter of 10 mm by the use of...
a hydraulic press (Perkin Elmer) with a pressure of 12 · 10^6 N m^{-2}. The pellets were placed in a quartz ampoule, and the heat treatment took place under Ar shielding gas. After a heating to 500 °C at a rate of 300 °C h^{-1} the temperature was held for 2 h. A further ramp to 800 °C at a rate of 120 °C and a holding time of 10 h followed. The pellets were cooled down to room temperature (figure A.1(b)).

Finally, after milling, mixing via the reaction

\[ \text{BaAs} + (1 - x) \cdot \text{Fe}_2\text{As} + x \cdot \text{Co}_2\text{As} \to \text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2 \]  

(A.2)

and pressing the powder material to pellets with a diameter of 10 mm, Ba(Fe_{1-x}Co_x)_2As_2 was synthesized according to the heat treatment given in figure A.1(c).

Appendix B. XRD data for thin films

Examples of the XRD thin film data and the texture data are given in figure B.1 and B.2. The full width at half maximum (FWHM) of the ϕ-scans of the Ba(Fe_{1-x}Co_x)_2As_2-reflection is between 0.78° and 1.82° (table 1). These values are not corrected for device broadening. Applying the Nelson–Riley extrapolation for θ–2θ-scans, the c-axes of the thin films were determined. Within the doping series, the c-axis lattice parameters follow Vegard’s law (figure 4).

The pole figure of the Ba(Fe_{0.92}Co_{0.08})_2As_{2−δ} reflection and the ϕ-scans of the Ba(Fe_{0.92}Co_{0.08})_2As_{2−δ}, the Fe(110) and the MgO(220) reflection are presented in figures B.2(a) and (b) and demonstrate the epitaxial relation between film and substrate.

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