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# Combined external pressure and Cu-substitution studies on BaFe<sub>2</sub>As<sub>2</sub> single crystals

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## Abstract

We report a combined study of external pressure and Cu-substitution on BaFe<sub>2</sub>As<sub>2</sub> single crystals grown by the in-flux technique. At ambient pressure, the Cu-substitution is known to suppress the spin density wave (SDW) phase in pure BaFe<sub>2</sub>As<sub>2</sub> ( $T_{\text{SDW}} \approx 140$  K) and to induce a superconducting (SC) dome with a maximum transition temperature  $T_{\text{c}}^{\text{max}} \simeq 4.2$  K. This  $T_{\text{c}}^{\text{max}}$  is much lower than the  $T_{\text{c}} \sim 15$ –28 K achieved in the case of Ru, Ni and Co substitutions. Such a lower  $T_{\text{c}}$  is attributed to a Cu<sup>2+</sup> magnetic pair-breaking effect. The latter is strongly suppressed by applied pressure, as shown herein,  $T_{\text{c}}$  can be significantly enhanced by applying high pressures. In this work, we investigated the pressure effects on Cu<sup>2+</sup> magnetic pair-breaking in the BaFe<sub>2-x</sub>Cu<sub>x</sub>As<sub>2</sub> series. Around the optimal concentration ( $x_{\text{opt}} = 0.11$ ), all samples showed a substantial increase of  $T_{\text{c}}$  as a function of pressure. Yet for those samples with a slightly higher doping level (over-doped regime),  $T_{\text{c}}$  presented a dome-like shape with maximum  $T_{\text{c}} \simeq 8$  K. Remarkably interesting, the under-doped samples, e.g.  $x = 0.02$  display a maximum pressure induced  $T_{\text{c}} \simeq 30$  K which is comparable to the maximum  $T_{\text{c}}$ 's found for the pure compound under external pressures. Furthermore, the magnetoresistance effect as a function of pressure in the normal state of the  $x = 0.02$  sample also presented an evolution consistent with the screening of the Cu<sup>2+</sup> local moments. These findings demonstrate that the Cu<sup>2+</sup> magnetic pair-breaking effect is completely suppressed by applying pressure in the low concentration regime of Cu<sup>2+</sup> substituted BaFe<sub>2</sub>As<sub>2</sub>.

Keywords: superconductivity, pressure effects, magnetic pair-breaking

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

## 1. Introduction

The Fe-based superconductors  $R\text{FeAsO}$  ( $R = \text{La} - \text{Gd}$ ) and  $A\text{Fe}_2\text{As}_2$  ( $A = \text{Ba}, \text{Sr}, \text{Ca}, \text{Eu}$ ), with superconducting transition temperatures ( $T_{\text{c}}$ ) as high as 56 K, have become focus of intense scientific investigation since their discovery. Particularly, these families of compounds excel as a remarkable playground to explore the interplay between a high temperature spin-density wave (SDW) phase and a low temperature superconducting (SC) one that can be tuned by either chemical substitution or applied pressure [1–13].

Among the distinct families of Fe-based superconductors, the semi-metallic BaFe<sub>2</sub>As<sub>2</sub> member displays a SDW phase transition closely connected to a tetragonal-to-orthorhombic structural transition at about  $T \simeq 140$  K and conveniently yields high quality single crystals [14] for which superconductivity can be induced by both applied hydrostatic pressure and chemical substitution (out-of-plane: Ba by K or in-plane: Fe by Co, Ni, Cu, or Ru). In the latter case, the emergent SC state must be robust against the impurity pair-breaking mechanisms associated with strain/stress caused by the chemical substitution [15–19]. In this regard, some

substitutions, have revealed a strong pair-breaking mechanism. In fact, superconductivity does not emerge in Mn and Cr substituted  $\text{BaFe}_2\text{As}_2$  despite their effectiveness in suppressing the SDW order [17, 18]. Moreover, the inexpressive maximum  $T_c \sim 5$  K observed in  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  within a narrow range of  $\text{Cu}^{2+}$  concentrations contrasts with  $T_c \sim 26$  K observed for Co-substituted samples [14, 20]. Nonetheless, as we will present in the following, the case of Cu-substitution is remarkably interesting because  $T_c$  can be dramatically enhanced by applying pressure as a result of a pressure-induced screening of the  $\text{Cu}^{2+}$  local moments and the suppression of their magnetic pair-breaking effects [15–19].

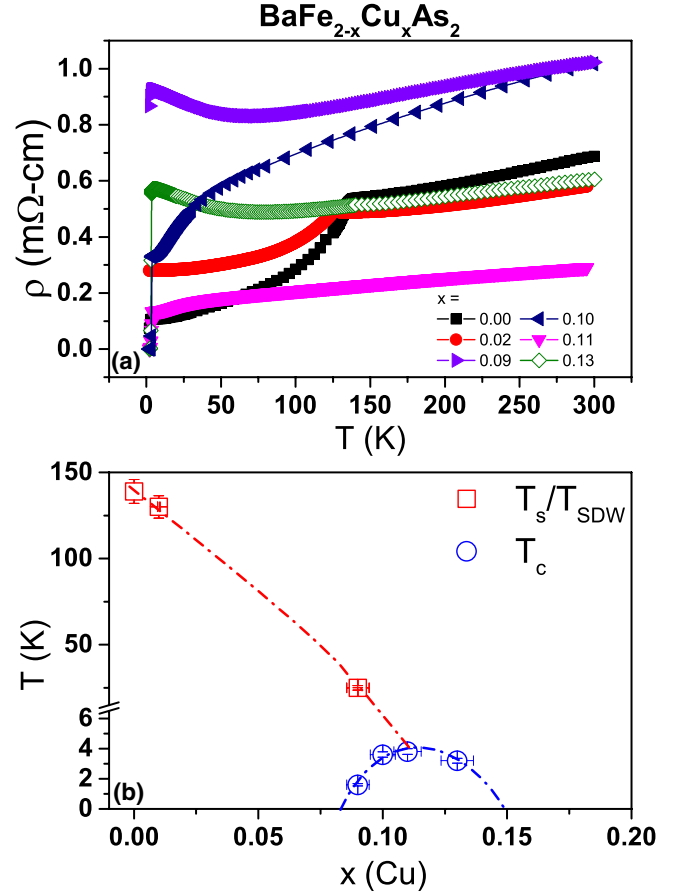
In this work, we shed new light on this fascinating property of Cu-substituted  $\text{BaFe}_2\text{As}_2$  single crystals by performing electrical resistivity experiments under external pressure ( $P \lesssim 10$  GPa). We find that, around the optimally doped (OPD) ( $x_{\text{opd}} = 0.11$ ) region, all samples show a substantial increase of  $T_c$  as a function of pressure. As the samples become slightly over-doped,  $T_c(P)$  presents a dome-like shape reaching its maximum value around 8 K. Interestingly, for lower Cu-concentration  $x = 0.02$  the sample displays a maximum pressure-induced  $T_c$  of 30 K which is comparable to the maximum  $T_c$  found for the pure compound under pressure. These results indicate that the  $\text{Cu}^{2+}$  magnetic pair-breaking effect can be completely suppressed by applying pressure in the low concentration regime. The magnetoresistance effect in the normal state for the  $x = 0.02$  sample also presents an evolution consistent with the screening of the  $\text{Cu}^{2+}$  local moments as a function of pressure.

## 2. Experimental details

The Cu-substituted  $\text{BaFe}_2\text{As}_2$  single crystals were grown using the in-flux technique as described elsewhere [14]. All crystals were checked by x-ray powder diffraction and submitted to elemental analysis using a commercial energy dispersive spectroscopy (EDS) micro-probe. The in-plane electrical resistivity,  $\rho_{ab}(T)$ , was measured using a standard four-probe method. Pressures up to 2.8 and 10 GPa were generated in a self-contained double-layer piston-cylinder-type Cu-Be pressure cell, with an inner-cylinder of hardened NiCrAl and in a miniaturized Bridgman-type pressure cell, respectively. In the former pressure cell, a silicon fluid was used as pressure transmitting medium, while in the latter steatite was chosen. In both pressure cells, lead served as a manometer. Different cryostats equipped with SC magnets capable of generating magnetic fields up to 9 T have been used to reach temperatures down to 1.5 K. In case of the piston-cylinder-type pressure cell the field was applied in the  $ab$ -plane while it was parallel to the  $c$ -direction in the Bridgman-type cell. In both cases, the current was flowing perpendicular to the magnetic field direction.

## 3. Results and discussion

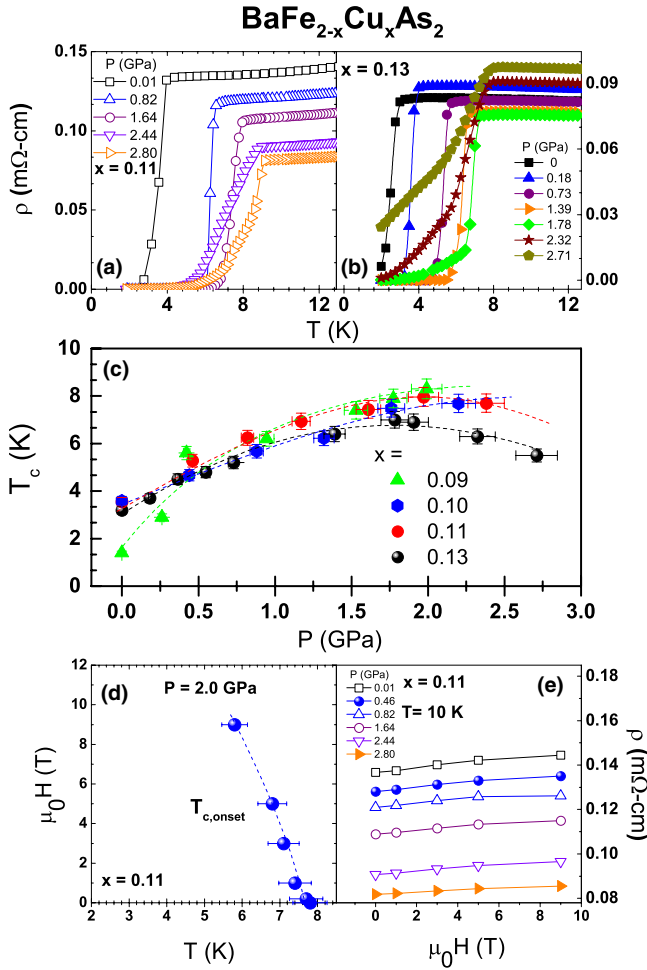
Figure 1(a) displays the  $\rho_{ab}(T)$  at ambient pressure for the  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  single crystals with  $x = 0, 0.02, 0.09, 0.10, 0.11$  and  $0.13$ . At high- $T$ , a linear metallic behavior is found for all samples. A clear kink occurs at  $T_{\text{SDW}}$  for  $x = 0$



**Figure 1.** (a)  $\rho_{ab}(T)$  at ambient pressure for the  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  single crystals for  $x = 0, 0.02, 0.09, 0.10, 0.11$  and  $0.13$ ; (b) Temperature-composition phase diagram for  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  at ambient pressure. The dashed-dotted lines are guides to the eye.

and 0.02. For  $x \geq 0.09$ , some of the samples show a slight upturn in  $\rho_{ab}(T)$  upon further decreasing temperature, as typically found for substituted  $\text{BaFe}_2\text{As}_2$  samples [4–13, 15, 16, 21]. This behavior happens at temperatures around 60–90 K and, in some cases, it might be associated with a vestige of the structural/SDW transitions. However, we are convinced that this is the case only for the  $x = 0.09$  for which a corresponding anomaly was also found in specific heat and magnetic susceptibility measurements (not shown). The samples with  $x = 0.10$  and  $0.11$  show metallic-like behavior in the whole temperature range. The SC samples present the onset of  $T_c$  varying from 2.5 to 4.2 K. So, based on the relevant transition temperatures obtained from the data displayed in figure 1(a), we constructed the phase diagram presented in figure 1(b).

The in-plane electrical resistivity  $\rho_{ab}(T)$  for the studied single crystals around the OPD limit ( $x_{\text{opd}} = 0.11$ ) at several selected pressures is shown in figures 2(a) and (b). The phase diagram displayed in figure 2(c) summarizes the results from figures 2(a) and (b). Additional data from previous reports completed the concentrations around the SC dome [16, 22]. At a first glance, one can observe a clear increase of  $T_c$  as a function of pressure for all samples. This effect strongly indicates that a pair-breaking mechanism is being suppressed by pressure. Interestingly, for samples with  $x > 0.10$ , the

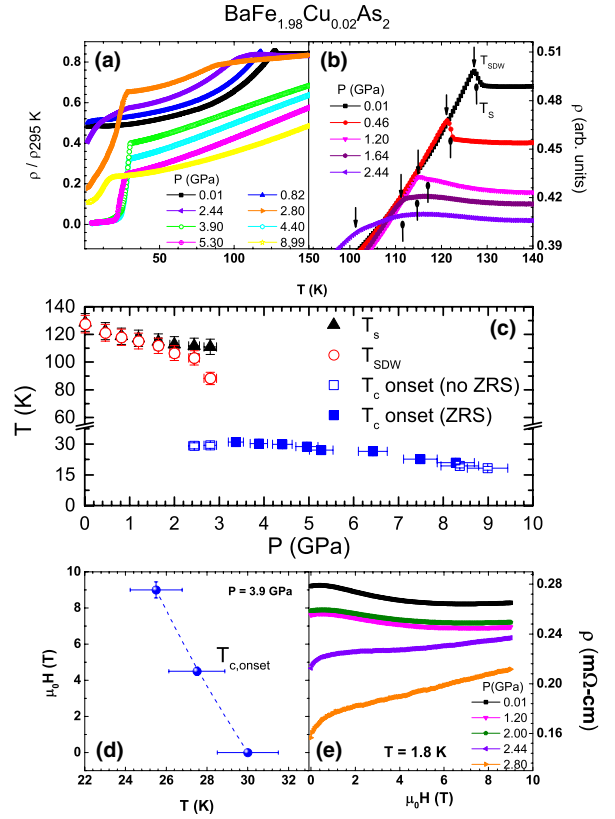


**Figure 2.** (a) and (b)  $\rho_{ab}(T)$  at several pressures for the  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  single crystals in the vicinity of the OPD regime ( $x = 0.11$  and  $0.13$ , respectively); (c) temperature-pressure phase diagram for our  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  single crystals around the OPD region. The dashed lines are guides to the eyes. (d) Dependence of the onset of  $T_c$  with magnetic field  $B \parallel ab$  at  $P = 2.0$  GPa for  $x = 0.11$ ; (e) magnetic-field dependence of the  $\rho_{ab}(P, T)$  data for  $x = 0.11$ .

relative increase of  $P$  diminishes for higher Cu-concentrations and a tendency to saturation is observed. Upon further increasing pressure,  $T_c$  starts to decrease. This is an expected behavior since the magnetic fluctuations, considered to be the pairing glue in the Fe-based SC [33], only decrease after the maximum of the SC dome has been reached. As such, one would expect a decreasing of  $T_c$  as a function of pressure in the absence of any suppression of the pair-breaking mechanism only for concentrations equal or larger than the OPD limit.

The magnetic field dependence of  $\rho_{ab}(P, T)$  for all studied single crystals around the OPD region is exemplified by the  $x = 0.11$  sample in figure 2(d). The small suppression of the SC transition as a function of field up to 9 T is consistent with the high critical fields observed in these compounds [4–13, 32]. Interestingly, the resistivity in the normal state of  $\text{BaFe}_{1.89}\text{Cu}_{0.11}\text{As}_2$  shows a small positive magnetoresistance (MR) for all applied pressures (see figure 2(e)).

Figure 3(a) displays  $\rho_{ab}(T)$  at several pressures for the low Cu-concentration sample,  $x = 0.02$ . This small



**Figure 3.** (a)  $\rho_{ab}(T)$  at several pressures for the low Cu-concentration sample,  $x = 0.02$ ; (b) details of the resistivity anomalies around the structural/SDW transitions; (c) temperature-pressure phase diagram for  $\text{BaFe}_{1.98}\text{Cu}_{0.02}\text{As}_2$ ; (d) magnetic field dependence ( $B \parallel c$ ) of  $T_{c,onset}$  at  $P = 3.9$  GPa. The dashed line is a guide to the eyes and, (e) magnetic field dependence of the  $\rho_{ab}(P, T)$  at  $1.8$  K ( $B \parallel c$ ).

Cu-concentration is enough to shift the SDW/tetragonal-to-orthorhombic phase transition down to roughly 130 K. A closer inspection of the resistivity data around these transitions, presented in figure 3(b)), allows us to verify the expected splitting between the structural transition at  $T_s \approx 129$  K and SDW transition at  $T_{SDW} \approx 127$  K at ambient pressure [23, 24]. The values of  $T_s$  and  $T_{SDW}$  are in good agreement with the reported ones for  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  samples with the same Cu-concentration, measured by nuclear magnetic resonance and heat-capacity experiments [23]. Upon increasing pressure,  $T_s$  and  $T_{SDW}$  are both suppressed but with different rates leading to an increase of the split between the transitions, as displayed in the  $T$ - $P$  phase diagram shown in figure 3(c). A drop in the resistivity around 29 K (open symbols in figure 3(c)) starts to develop for  $P \geq 2.8$  GPa and evolves to a complete zero resistance state (ZRS) (solid symbols in figure 3(c)) at  $P = 3.4$  GPa. By increasing the pressure, the onset of  $T_c \approx 29$  K remains nearly constant while the width of the SC transition becomes sharper. At  $P_{op} \approx 4.0$  GPa a sharp SC transition is established with a  $T_c \approx 31$  K. This value of  $T_c$  is close to the maximum  $T_c$  achieved in the pure  $\text{BaFe}_2\text{As}_2$  under pressure [4–13] indicating that for this range of Cu-concentration and pressure, the  $\text{Cu}^{2+}$  magnetic pair-breaking effect is completely suppressed by pressure. In fact, pressure

is well known to lead to a screening of the local moments by enhancing their hybridization with the conduction electrons in many compounds [15, 16, 25–29]. For pressures higher than  $P_{op} \approx 4.0$  GPa, the onset of  $T_c$  slowly decreases as a function of pressure and the ZRS disappears for  $P \geq 8.4$  GPa.

The small suppression of the SC transition temperature as a function of field up to 9 T, shown in figure 3(d), is again in agreement with the high critical fields of this family of compounds [4–13, 32]. The magnetic field dependence of  $\rho_{ab}(P, T)$  at 1.8 K for several pressures for  $x = 0.02$  is presented in figure 3(d). Interestingly, the normal state resistivity for this compound shows a negative MR that evolves into a positive one for  $P > 2.4$  GPa. A positive MR with a  $H^2$ -dependence is usually expected in the Fermi-liquid regime of normal metals. The negative MR in metals usually indicates the presence of a spin-dependent scattering mechanism that can be suppressed by magnetic field. The results presented in figures 2(e) and 3(e) suggest the presence a spin-dependent scattering mechanism that tends to be reduced by increasing the Cu-concentration or pressure. As the SDW magnetic character of the Fe 3d electrons is nearly unaffected by the magnetic field (not shown), we attribute this spin-dependent scattering mechanism to the  $\text{Cu}^{2+}$  ( $s = 1/2$ ) local moments shown by recent ESR experiments, which directly probe the Cu oxidation state [16]. The ESR data are in contrast to previous reports based on ARPES, XAS and NMR measurements, which suggest that the Cu atoms are in the  $\text{Cu}^{1+}$  oxidation state [31, 34–36]. However, the data reported here is consistent with a  $\text{Cu}^{2+}$  spin-dependent scattering mechanism. Such mechanism is responsible for the impurity magnetic pair-breaking effect [15, 16] which can be strongly suppressed by the application of pressure, leading to the significant enhancement of  $T_c$ , as seen in figure 2. As such, it is expected that the suppression of the  $\text{Cu}^{2+}$  spin dependent scattering mechanism by pressure would also lead to a negative MR in the normal state, as observed at low temperatures for the  $x = 0.02$  sample in figure 3(e). Furthermore, the local moment character of  $\text{Cu}^{2+}$  is supposed to decrease as a function of the Cu-concentration given that  $\text{BaCu}_2\text{As}_2$  is a Pauli paramagnet [30]. This assumption is consistent with the fact that OPD samples show a positive MR in the normal state indicating a tendency to a more Fermi-liquid-like behavior. In fact, it has been recently suggested that the electronic character of the Cu and the strength of the As–As inter-layer bonds both strongly change between weakly Cu-substituted  $\text{BaFe}_2\text{As}_2$  and pure  $\text{BaCu}_2\text{As}_2$ , perhaps via a first-order lattice instability such as a miscibility gap in the  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  system [31].

#### 4. Conclusions

In summary, we report a combined study of external pressure ( $P \leq 10$  GPa) and Cu substitution on  $\text{BaFe}_2\text{As}_2$  single crystals grown by in-flux technique. This study aimed to investigate the pressure effects on  $\text{Cu}^{2+}$  magnetic pair-breaking in the  $\text{BaFe}_{2-x}\text{Cu}_x\text{As}_2$  series for different Cu-concentrations. Around the optimal concentration  $x_{opd} = 0.11$ , all samples showed a substantial increase of  $T_c$  as a function of pressure, although, for the samples with concentrations slightly above

the OPD limit,  $T_c$  presented a dome-like shape with a maximum value around 8 K. Remarkably, the low concentration sample  $x = 0.02$  showed a maximum pressure induced  $T_c$  of about 30 K, which is comparable to the maximum  $T_c$ 's found in the pure compound under external pressure. This result indicates that the  $\text{Cu}^{2+}$  magnetic pair-breaking effect can be completely suppressed by applying pressure in the low concentration regime. Finally, we also found a magnetic field dependent scattering mechanism which leads to a negative MR at low temperatures and low pressures ( $P < 2.0$  GPa) for  $x = 0.02$ . This negative MR evolves to a more Fermi-liquid-like positive MR as a function of pressure and/or increasing Cu-concentration as the Cu 3d electrons are supposedly loosing their local-moment character.

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