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Pressure effects on magnetic pair-breaking in Mn- and Eu-substituted BaFe$_2$As$_2$

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We report a combined study of hydrostatic pressure ($P \leq 25$ kbar) and chemical substitution on the magnetic pair-breaking effect in Eu- and Mn-substituted BaFe$_2$As$_2$ single crystals. At ambient pressure, both substitutions suppress the superconducting (SC) transition temperature (T_c) of BaFe$_{2-x}$Co$_x$As$_2$ samples slightly under the optimally doped region, indicating the presence of a pair-breaking effect. At low pressures, an increase of T_c is observed for all studied compounds followed by an expected decrease at higher pressures. However, in the Eu dilute system, T_c further increases at higher pressure along with a narrowing of the SC transition, suggesting that a pair-breaking mechanism reminiscent of the Eu Kondo single impurity regime is being suppressed by pressure. Furthermore, Electron Spin Resonance (ESR) measurements indicate the presence of Mn^{2+} and Eu^{2+} local moments and the microscopic parameters extracted from the ESR analysis reveal that the Abrikosov–Gor'kov expression for magnetic pair-breaking in a conventional sign-preserving superconducting state cannot describe the observed reduction of T_c. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4861577]

Since the report of superconductivity (SC) in the Fe-based superconductors RFeAsO (R = La – Gd) and AFe$_2$As$_2$ (A = Ba, Sr, Ca, Eu), with T_c as high as 56 K, great efforts have been made to reach a definitive answer about the symmetry of the SC state.[1–4] The connection between the spin density-wave (SDW) phase and SC is also a topic of intense investigation, since SC is usually found when the SDW phase has been sufficiently suppressed. The semi-metal member BaFe$_2$As$_2$ (BFA) provides the possibility of growing high quality single crystals[5] with a $T_{SDW} = 139$ K which can be suppressed toward SC by both chemical substitution and/or applied pressure. In this regard, it is controversial whether these substitutions act as chemical pressure or as effective carrier donors.[6–8] It has been suggested that apart of their charges, the chemical substitutions, similarly to applied pressure, introduce local variations in two key structural parameters: The iron–pnictogen distance (d_{FeAs}) and the tetrahedron shape.[8–11] Although SC can be induced by several types of chemical substitution (e.g., K, Co, Ni, Cu, and Ru), some substitutions have revealed to introduce significant pair-breaking effects. For instance, despite their effectiveness in suppressing the SDW, SC does not emerge in BFA with Mn and Cr substitutions.[12,13] Also, SC in BaFe$_{2-x}$Cu$_x$As$_2$ has a maximum reported T_c of only ~ 5 K in a narrow range of concentration, whereas the Co-substitution has a maximum T_c of 26 K.[5,14]

In this report, we shed new light on this fascinating problem of impurity effects on the SC state of these compounds by exploring the interplay between chemical substitution (both in and out of the FeAs plane) and applied hydrostatic pressure ($P \lesssim 25$ kbar) using in-plane electrical resistivity measurements, ρ_{ab} (T). Furthermore, the results of impurity effects on T_c are confronted to the analysis of the Electron Spin Resonance (ESR) experiments. Single crystals of Ba$_{0.8}$Eu$_{0.2}$Fe$_{1.9}$Co$_{0.1}$As$_2$ (Eu$_{0.2}$), Ba$_{0.99}$Eu$_{0.01}$Fe$_{1.9}$Co$_{0.1}$As$_2$ (Eu$_{0.01}$), and BaFe$_{1.895}$Co$_{0.1}$Mn$_{0.005}$As$_2$ (Mn$_{0.005}$) were grown using In-flux as described elsewhere.[5] The crystals were checked by x-ray powder diffraction and submitted to elemental analysis using a commercial Energy Dispersive Spectroscopy (EDS) microprobe. ρ_{ab} (T) was measured using a standard four-probe method and a self-contained piston-cylinder type Be-Cu pressure cell, with a Pb manometer. The ESR spectra were taken in a commercial Bruker X-band ($\nu = 9.5$ GHz) spectrometer equipped with a continuous He gas-flow cryostat.

Figs. 1(a)–1(c) displays ρ_{ab} (T) as a function of pressure for single crystals with concentrations below the optimally doped (OPD) region. At ambient pressure, a linear metallic behavior is observed at high T, and the T_{SDW} of the BFA is suppressed for all compounds. As T is further decreased, there is a slight upturn although no anomaly is observed by specific heat or magnetic susceptibility measurements. It occurs at 89 K, 68 K, and 75 K and indicates that the samples are slightly below the OPD region. The midpoint of T_c occurs at 21 K, 22.4 K, and 15.7 K for the Eu$_{0.2}$, Eu$_{0.01}$, and Mn$_{0.005}$ substitutions, respectively.[17]

Fig. 1(d) shows the pressure dependence of T_c constructed from the data of Figs. 1(a)–1(c). At first, one can observe that, after a small increase of ~ 1 K, a clear decrease
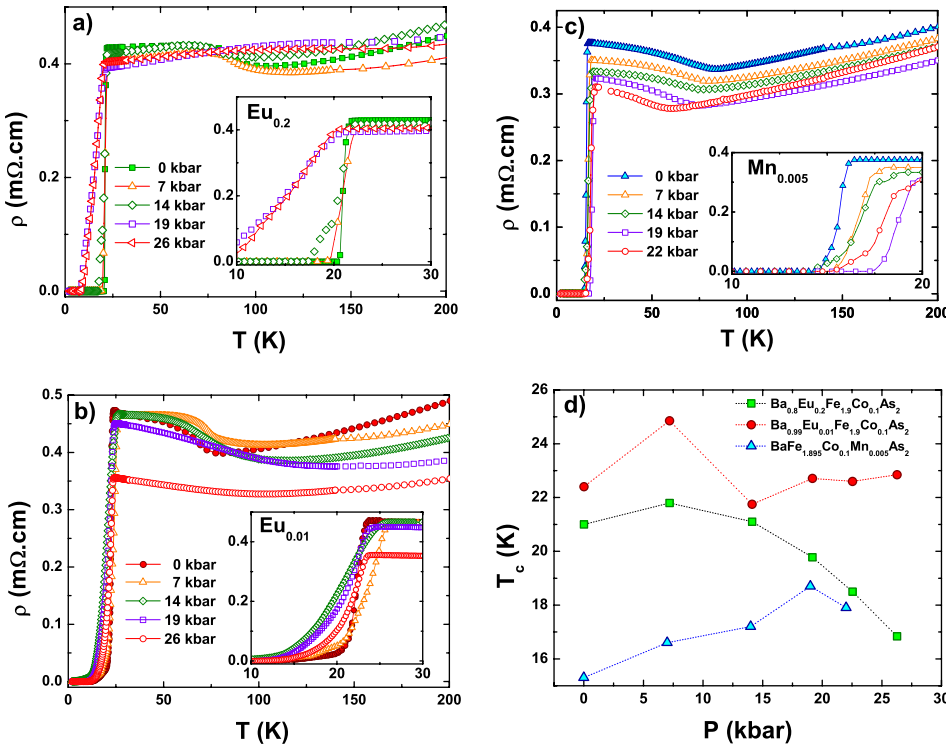
FIG. 1. ρ_{ab} (*T*) for (a) $Ba_{0.8}Eu_{0.2}Fe_{1.9}$ $Co_{0.1}As_2$ (Eu$_{0.2}$), (b) $Ba_{0.99}Eu_{0.01}Fe_{1.9}$ $Co_{0.1}As_2$ (Eu$_{0.01}$), and (c) $BaFe_{1.895}Co_{0.1}$ $Mn_{0.005}As_2$ (Mn$_{0.005}$) single crystals as a function of pressure. The insets show the superconducting transitions.

of T_c occurs with pressure for the Eu$_{0.2}$, as expected for nearly OPD samples. On the other hand, the Eu$_{0.01}$ sample displays an unexpected further increase of T_c along with a narrowing of the SC transition at higher pressures. These effects strongly indicate that a pair-breaking mechanism is being suppressed by pressure since the magnetic fluctuation strength is expected to only decrease in the overdoped region. In this manner, one would expect that T_c would also only decrease with pressure after it reaches its maximum value. It has been suggested that Eu ions act as Kondo ions in these compounds.[15,16] Thus, it is reasonable to speculate that the observed behavior with pressure is reminiscent of a Kondo single impurity regime and that the Eu local moments become screened by the conduction electrons as one apply pressure. Finally, Figs. 1(c) and 1(d) display an almost linear increase of T_c for the Mn$_{0.005}$ sample up to 18.7 K at 20 kbar, also suggesting that a pair-breaking effect is being suppressed by pressure together with the decreasing in the strength of the pairing interaction. In this case, a plausible explanation is that the hybridization between the Mn 3d bands and the conduction electron bands increases as a function of pressure and, consequently, they become more itinerant, progressively losing their local moment character.

To support our claim about the magnetic pair breaking effect of Eu and Mn ions, we sought for stronger evidence by performing ESR—a powerful spin probe technique sensitive to the presence of local moments and their coupling to the conduction electrons.[18] Our ESR data reveals an intense resonance line for all studied compounds. Fig. 2 shows the X-Band ESR lines at $T = 200$ K for the selected samples. The ESR line for the Eu$_{0.2}$ single crystal has an asymmetric Dysonian character due to the fact that the skin depth is smaller than the sample size.[18] However, to increase signal to noise ratio in the dilute samples, we have measured a fine powder of gently crushed single crystals for the Eu$_{0.01}$ and

Mn$_{0.005}$ compounds, and, consequently, the lineshapes have become more symmetric (Lorentzian-like). The Dysonian fit of the spectra reveals a linewidth of $\Delta H = 1070(100)$ G and a *g*-value of $g = 2.03(4)$ for the Eu$_{0.2}$ sample. On the other hand, the Lorentzian fits for the dilute samples show a narrower linewidth of $\Delta H = 750(75)$ G for Eu$_{0.01}$ sample and $\Delta H = 850(85)$ G for Mn$_{0.005}$ sample, indicating weaker Eu–Eu and Mn–Mn interactions, as expected for the dilute regime. In this case, we are able to extract more accurate g-values of 2.05(2) and 2.06(2) for the Eu$_{0.01}$ and Mn$_{0.005}$ samples, respectively.

By using ESR, one can also study the spin dynamics in these compounds, which provides microscopic information about impurity pair-breaking mechanisms as long as the impurity is ESR active. A crucial microscopic parameter of the magnetic pair-breaking impurity is the **q**-dependent averaged

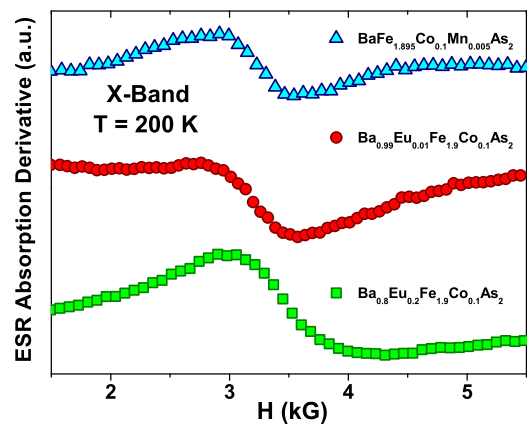FIG. 2. X-Band ESR lines at $T = 200$ K for powdered crystals of Eu$_{0.01}$ and Mn$_{0.005}$ and a single crystal of Eu$_{0.2}$ for $H||ab$-plane. The solid lines are Lorentzian and Dysonian fits to the spectra. We note that, in order to obtain the ESR signal, the sample surface must be completely clean and free of flux.

TABLE I. Experimental and calculated parameters for FeAs-based SC (this work and Ref. 23) and conventional SC (Refs. 22 and 24).

Sample	c(%)	g_{ESR}	$|\Delta T_c^{exp}|$ (K)	$T_{c,0}$ (K)	$\langle J^2(\mathbf{q})\rangle^{1/2}_{ESR}$ (meV)	$\langle J^2(\mathbf{q})\rangle^{1/2}_{AG}$ (meV)
$BaFe_{1.9}Cu_{0.1}As_2$[23]	5	2.08(3)	22	26	1.2(5)	103(10)
$BaFe_{1.88}Mn_{0.12}As_2$[23]	6	2.05(2)	≥ 26	26	0.7(5)	$\geq 31(9)$
$BaFe_{1.895}Co_{0.100}Mn_{0.005}As_2$	0.25	2.06(2)	10	26	0.8(5)	92(9)
$Ba_{0.8}Eu_{0.2}Fe_{1.9}Co_{0.1}As_2$	20	2.04(2)	4	0.319	1.4(8)	4.9(5)
$Ba_{0.99}Eu_{0.01}Fe_{1.9}Co_{0.1}As_2$	1	2.04(2)	2	0.02	0.5(4)	11(1)
$Lu_{1-x}Gd_xNi_2B_2C$	0.5	2.035(7) (Ref. 22)	≈ 0.3	15.9	10(4)	11(1)
$Y_{1-x}Gd_xNi_2B_2C$	2.1	2.03(3) (Ref. 22)	≈ 0.9	14.6	9(3)	10(1)
$La_{1-x}Gd_xSn_3$	0.4	2.010(10) (Ref. 24)	≈ 0.5	6.4	20(2)	$\approx 20(2)$

squared exchange coupling $\langle J^2(\mathbf{q})\rangle^{1/2}$ between the impurity spin and the conduction electrons of the host. Within the Abrikosov–Gor'kov (AG) formalism, $\langle J^2(\mathbf{q})\rangle$ plays the role of a magnetic impurity potential responsible for the pair-breaking effects that reduce T_c.[19,20] In the ESR experiments, $\langle J^2(\mathbf{q})\rangle^{1/2}$ is the microscopic parameter responsible for the linear increase of ESR linewidth of local moments diluted in metallic hosts (Korringa behavior)[16,21,22,24,25] (see Table I).

To estimate whether the extracted value of $\langle J^2(\mathbf{q})\rangle_{ESR}$ for the studied samples can account for the observed suppression of T_c, we consider the conventional AG pair-breaking formalism[19,20] for the case where the gap function has the same amplitude and sign across the entire Brillouin zone

$$\left|\frac{\Delta T_c}{\Delta c}\right| = \frac{\pi^2}{8}\eta(E_F)\langle J^2(\mathbf{q})\rangle S(S+1), \qquad (1)$$

where $\Delta T_c = T_c - T_{c,0}$. We take $T_{c,0} = 26\,K$, the transition temperature of OPD $BaFe_{1-x}Co_xAs_2$, since Co substitution provides no ESR signal, indicating that Co is a non-magnetic impurity. From the ESR data, we extract $\langle J^2(\mathbf{q})\rangle^{1/2}$ and the g value, and from the EDS data, we have the impurity concentration, Δc (in %). From the linear coefficient of the low-temperature specific heat, γ, we obtain roughly the same density of states $\eta(E_F) = 3.34$ states/eV·spin·f.u. calculated for one mole for all compounds.[2,21] Therefore, by using the experimental ΔT_c^{exp}, we thus estimate the magnetic pair-breaking impurity potential $\langle J^2(\mathbf{q})\rangle^{1/2}$ from the AG equation that would be necessary to cause the observed suppression of T_c and compare it with the experimental value from the ESR data.

The results are shown in Table I, and one can clearly see that the $\langle J_{fs}^2(\mathbf{q})\rangle^{1/2}$ values calculated by the AG equation are in gross disagreement with the ESR values when the impurity substitution is in the FeAs plane. On the other hand, Eu-substituted compounds exhibit a less dramatic disagreement between the two obtained values. This is probably because the spin-dependent unconventional pair-breaking mechanism revealed here is clearly more pronounced for impurities in the FeAs-planes. In contrast, for conventional superconductors, such as $Lu_{1-x}Gd_xNi_2B_2C$ and $Y_{1-x}Gd_xNi_2B_2C$, as well as to $La_{1-x}Gd_xSn_3$, the calculated $\langle J^2(\mathbf{q})\rangle_{AG}$ and the measured $\langle J^2(\mathbf{q})\rangle_{ESR}$ are in very good agreement.[22,24]

Finally, enlightened by the ESR analysis, we further discuss the data in the phase diagram T_c *vs.* P of Fig. 2. For the

$Eu_{0.2}$ sample, the rate d T_c/dP $\sim 0.1\,K/kbar$ reflects the expected behavior for OPD samples. However, this rate is two times larger for the Mn-substituted sample, indicating that another mechanism for the decrease of T_c is being suppressed by pressure. Moreover, for the dilute $Eu_{0.01}$, there is an unexpected further upturn of T_c at higher pressure indicating that the Kondo single-ion regime is being suppressed by pressure. It remains to be confirmed whether applying higher pressures with Diamond Anvil Pressure cells would further enhance or even suppress T_c in this case.

In conclusion, we show irrefutable evidence that the FeAs compounds do not behave as conventional superconductors, and that a non-conventional magnetic impurity pair-breaking is present and must be associated with the local Eu^{2+} and Mn^{2+} spins. The enhancement of T_c with pressure for the $Mn_{0.005}$ and $Eu_{0.01}$ samples and the existence of Mn^{2+} and Eu^{2+} ESR lines provide strong evidence of a spin-dependent pair-breaking mechanism suppressed by pressure.

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