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Ba(Fe$_{1-x}$Rh$_x$)$_2$As$_2$ Single Crystals
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Disorder-driven transition from $s^{\pm}$ to $s^{++}$ superconducting order parameter in proton irradiated Ba(Fe$_{1-x}$Rh$_x$)$_2$As$_2$ single crystals

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Microwave measurements of London penetration depth and critical temperature, $T_c$, were used to show evidence of disordered-driven transition from $s^{\pm}$ to $s^{++}$ order parameter symmetry in optimally doped Ba(Fe$_{1-x}$Rh$_x$)$_2$As$_2$ single crystals, where disorder was induced by means of 3.5-MeV proton irradiation. Signatures of such transition, as theoretically predicted [V. D. Efremov et al., Phys. Rev. B 84, 180512(R) (2011)], are found as a drop in the low-temperature values of the London penetration depth and a virtually disorder-independent superconducting $T_c$. We show how these experimental observations can be described by multi-band Eliashberg calculations in which the effect of disorder is accounted for in a suitable way. To this aim, an effective two-band approach is adopted, allowing to treat disorder in a range between the Born approximation and the unitary limit.

Introduction — Iron based superconductors (IBS) are nowadays among the most studied superconducting materials. They arose interest both due to their potential technological impact and their intriguing fundamental multi-band and pairing properties. The leading candidate pairing state of most IBS, and in particular of the compounds based on doped BaFe$_2$As$_2$ (122-family), is the fully gapped $s^{\pm}$ phase [1, 2]. This consists of an extended s-wave pairing with a sign reversal of the order parameter between different Fermi surface sheets and with interband coupling between hole and electron bands provided by antiferromagnetic spin fluctuations. Although this model is widely accepted, direct experimental confirmations are rare.

A promising approach to identify this phase makes use of disorder to induce a transition between the $s^{\pm}$ and $s^{++}$ symmetries, therefore assigning the $s^{\pm}$ state to the pristine material [3, 4]. This transition should occur because the gaps tend to converge with increasing disorder [4]: if the pristine state is characterized by the $s^{\pm}$ symmetry and the gaps converge to a finite value, it inevitably implies the closing and reopening of the smallest gap(s) and the realization of the $s^{++}$ symmetry. It was suggested that this transition could leave specific hallmarks in the low temperature quasiparticle conductivity and London penetration depth, but they were observed experimentally only in the former [5]. The $s^{++}$ state is characterized by the absence of sign reversal between different bands and has different properties from the $s^{\pm}$ state. In particular, the critical temperature of an $s^{++}$ superconductor is expected to show a weaker disorder dependence.

In this Letter, we aim to observe and identify the hallmark of the $s^{\pm}$ to $s^{++}$ transition driven by proton-irradiation-induced disorder in the London penetration depth, $\lambda_L$, of Ba(Fe$_{1-x}$Rh$_x$)$_2$As$_2$ single crystals, by employing a microwave resonator technique. Ion irradiation is an efficient tool to introduce disorder into materials without contributing to charge doping or huge structural distortions. The choice of light projectiles at moderate energies such as 3.5-MeV protons ensures that only isotropically-distributed point-like defects and small cascades are produced in the system, provided that the thickness of the sample is smaller than the implantation depth of the ions. Then, we show how the $\lambda_L(T)$ experimental behavior and the $s^{\pm}$ to $s^{++}$ transition can be described in a quantitative way by Eliashberg calculations where disorder is suitably accounted for. Thus the Letter is organized as follows: after a background about the electronic structure of the compound and the $s^{\pm}$ to $s^{++}$ transition, the experimental and the theoretical techniques are presented. Then, the results are discussed in light of the possible transition and finally conclusions are drawn.

The $s^{\pm}$ to $s^{++}$ transition — The electronic structure of Ba-122 compounds can be approximately described by a three-band model. The nature of such bands depends on doping: two hole bands and one equivalent electron band for hole-doped compounds, as Ba$_{1-x}$K$_x$Fe$_2$As$_2$, one hole band and two electron bands for electron-doped materials, as Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$. With this regard, there is a lack of literature about Ba(Fe$_{1-x}$Rh$_x$)$_2$As$_2$, but since Rh and Co are isoelectronic species and very similar experimental behaviors were observed [6, 7], it is reasonable to assume for both Rh- and Co-doped Ba-122 the same electronic structure.

Within the $s^{\pm}$ wave model, due to the antiferromagnetic spin fluctuation coupling, the gap of the elec-
tron band has opposite sign with respect to the gaps of the hole bands [2]. Recently, sign-reversal s± symmetry of the order parameter has been proved for Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ by phase-sensitive measurements [8], and it was even possible to induce it by disorder in the case of BaFe$_2$(As$_{1-x}$P$_x$)$_2$, which shows accidental gap nodes when in the pristine state [9]. This demonstrates that the topology of the superconducting gap can be controlled by disorder: a unique feature of the iron pnictides. Moreover, even much more complex situation can occur in the presence of an external field or superconducting currents, when coexistence of s++ and s± superconducting states in dirty multiband superconductors can be detected [10], but these peculiar conditions are not considered here.

Thus, a three-band s± model is the most appropriate to correctly describe the physical properties of these compounds. Recently, we have used such approach to successfully explain the measured temperature dependence of the London penetration depth of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ crystals [11]. In another work, we have investigated the effects of irradiation-induced disorder on the properties of the same crystals [12]. Due to the fact that disorder was moderate, we could use the same three-band approach, treating disorder within the Born approximation: we were able to reproduce both the experimental $T_c$ reduction and the $\lambda_L(T)$ behavior of the irradiated crystals, with the remarkable result of a change of sign of the smaller gap for the most disordered sample, but preserving the s± symmetry [12].

In this Letter, aiming at investigating the s± to s++ transition, we want to analyze the case of Ba(Fe$_{1-x}$Rh$_x$)$_2$As$_2$ with a much higher degree of disorder, when the Born approximation is expected to lose its validity. The problem emerges that in such a framework the three-band calculations become tricky and the parameter space enlarges too much to allow drawing reasonable conclusions. For these reasons, we implemented a $T-$matrix approach within an effective two-band model, allowing us to treat disorder in a range from the Born approximation to the unitary limit. Accordingly, we consider both inter-band and intra-band scattering, but it is intended that intra-band terms have no direct physical meaning, representing a combination of inter-band terms of a more realistic three-band model. In fact, it can be said that in these systems the inter-band coupling is predominant [13].

On this premise, we look for the experimental signatures of a disordered-induced s± to s++ transition, i.e. a transition to a state where the sign of the two (or more) gaps is preserved. The signature we are focusing on is a drop in the low-temperature value of $\lambda_L$, as qualitatively predicted, but not yet observed [4, 5]. Then, we show how this experimental behavior can be described by a two-band Eliashberg model.

Experimental techniques – Optimately doped single crystals of Ba(Fe$_{1-x}$Rh$_x$)$_2$As$_2$, with $x=0.068$ and critical temperature $T_{c0}=23.5$ K, were grown out of self flux using conventional high-temperature solution growth techniques [14–16]. The investigated samples were cleaved to have thickness, along the c-axis, smaller than the implantation depth of 3.5-MeV protons in the material. The characterization of their superconducting properties was carried out by means of a microwave resonator technique that has already been applied to other IBS crystals [11, 12, 17]. It allows obtaining the absolute value of the London penetration depth and the surface impedance as a function of temperature by measuring the modifications induced to the resonance of an YBa$_2$Cu$_3$O$_{7-x}$ coplanar waveguide resonator by coupling the sample to it [18]. Since the technique is non-destructive, it is suitable for measurements on the pristine crystals and after each irradiation session, in order to observe the evolution of the superconducting properties with increasing disorder, avoiding sample to sample variability.
Proton irradiation was performed at the CN facility of the LNL laboratories of the Italian National Institute for Nuclear Physics (INFN). The samples were irradiated with 3.5 MeV protons in multiple sessions, up to a total fluence of \(2.08 \times 10^{17} \text{ cm}^{-2}\). Further details are reported in [18]. The irradiation process was addressed by Monte Carlo simulations performed with the PHITS [29] and SRIM [30] codes in order to replicate the experimental conditions and estimate the irradiation effects on the samples. To this aim, the displacement per atom (dpa) profile as a function of depth inside the material was estimated within the Kinchin-Pease approach [18]. This allows to obtain the position of the implantation peak in the material, that would be at about 67 \(\mu\)m, and in turn to keep the thickness of the samples well below this value to avoid ion implantation. Moreover, the amount of introduced disorder in a particular crystal is estimated as the dpa averaged over its thickness.

Figure 1 shows the critical temperature, \(T_c\), of an irradiated crystal normalized to its pristine value and the width of the superconducting transition, as a function of disorder expressed by the irradiation-induced displacement per atom. In the lower panel of Fig.1, experimental low-temperature values of the London penetration depth are reported. \(T_c\) and \(\lambda_L(0)\) show a clear change of behavior at a given value of disorder, highlighted in the figure by a change in the background color, while the unaltered increase of the transition width testifies that disorder continuously increases. In particular, as stated in the Introduction, the clear drop of \(\lambda_L(0)\) can be considered to be a sign of the transition from the \(s\pm\) to the \(s++\) state. Basing this hypothesis on the experimental results, we propose in the following a model that could validate it within realistic assumptions. For the sake of completeness, we should say that Schilling et. al. [5], tracing the \(s\pm\) to \(s++\) transition in the related material Ba(Fe\(_{1-x}\)Co\(_x\))\(_2\)As\(_2\) by observing the behavior of the optical conductivity, did not discern the discontinuity of \(\lambda_L(0)\). This is not in contrast with our results since the experimental conditions were very different as for the compound, the morphology (thin film in [5]) and the particle (200-keV protons in [5]).

Figure 1 also shows that \(T_c\) starts to slightly recover, at the higher disorder values. This behavior can be explained by two opposite scenarios. A \(T_c\) enhancement can be attributed to the competition between superconductivity and a secondary order (spin density wave) that is suppressed more rapidly by disorder than superconductivity itself [31]. Conversely, the induction of a local magnetic phase could stabilize the superconductivity, even leading to a slight enhancement of the superconducting order parameter [32] (indeed, we observed a magnetic phase in proton-irradiated crystals [16]). In both cases, it results that this feeble effect can only emerge in the \(s++\) state, where the pair-breaking effect of disorder is much weaker than in the \(s\pm\) state.

The model – To calculate the critical temperature and the penetration depth within the \(s\pm\) wave by the two-band Eliashberg equations [33], one has to solve four coupled equations for the gaps \(\Delta_i(i\omega_n)\) and renormalization functions \(Z_i(i\omega_n)\), where \(i\) is a band index and \(\omega_n\) are the Matsubara frequencies. The imaginary-axis
The values of the plasma frequencies, \( \omega_n \), are unknown, but since the weights in (3) are normalized to unity, \( \left( \frac{\omega_{s+}}{\omega_p} \right)^2 + \left( \frac{\omega_{s-}}{\omega_p} \right)^2 = 1 \), a single free parameter can be considered for fitting the experimental data, \( w_1 = \left( \frac{\omega_{s+}}{\omega_p} \right)^2 \).

We reproduced the experimental \( T_c \) and \( \rho_s(T) \) in the non-disordered case (unirradiated crystal) with \( \lambda_{11} = 1.0, \lambda_{22} = 2.65 \) and \( \lambda_{12} = -0.17 \), for a total coupling \( \lambda_{tot} = \frac{N_1(0)(\lambda_{11} + \lambda_{12}) + N_2(0)(\lambda_{21} + \lambda_{22})}{N_1(0) + N_2(0)} = 1.74 \), and with \( w_1 = 0.98 \). In this case, the Eliashberg equations at \( T = 0.5 \) K gave the low-temperature values of the gaps, \( \Delta_1 = -2.64 \text{ meV} \) and \( \Delta_2 = 5.71 \text{ meV} \), which are actually obtained by the analytical continuation to the real axis of the imaginary-axis solutions of (1) and (2), by using the technique of the Padé approximants.

To describe the effects of disorder we can operate on \( \Gamma_i \), which include the three free parameters \( \Gamma_1, \sigma \) and \( \eta \), proportional to structural disorder in an \textit{a priori} unknown way.

\textbf{Discussion} – The model described above is now used to reproduce the experimental results, i.e. \( T_c \) and \( \rho_s(T) \) of disordered samples, assuming reasonable values for the parameters: we keep \( \eta = 1 \), as in [5], \( \Gamma_1 \) linearly increasing with the irradiation dose (from 0 to 2.35 meV for the most irradiated samples). Right: low-temperature values of the gaps from the real-axis solutions of the Eliashberg equations, obtained by the Padé approximants, as a function of disorder, expressed here in terms of irradiation-induced displacement per atom (dpa). The transition from the \( s \pm \) to the \( s^{++} \) state is highlighted by the change in the background colors.
tual results are reported in the inset of Fig.2(c) and, as a table, in [18]. In Fig.2(a)-(b) the experimental values of $\lambda_{L}^{-2}(T)$ as a function of temperature and disorder are compared to calculations based on (3), showing a remarkable matching. The $s\pm$ to $s++$ transition is identified at a dpa value of about 0.0046. The superfluid density is reported as a function of the reduced temperature in Fig.2(c), where the experimental data (symbols) are compared to calculations (lines). The shape clearly changes after first irradiation doses and again after the $s\pm$ to $s++$ transition. The calculated curves correctly describe the general behavior, but fail to reproduce the experimental data exactly, mainly because of the approximation of considering two effective gaps instead of at least three (more realistic model), imposed by the need to suitably describe the effects of disorder. This choice, together with the assumptions we made to limit the parameter space, impose severe constraints to the results of the calculations. Finally, Fig.3 shows the calculated gaps, resulting from such parameters. On the left, the energy gaps obtained by the solution of the imaginary-axis Eliashberg equations, for the same crystal before and after each irradiation, are given. On the right, the low-temperature values of the gaps from the real-axis solutions of the Eliashberg equations, obtained by the Padé approximants, are reported as a function of disorder. The transition from a sign-reversal to a sign-preserving symmetry of the order parameter is shown at the same disorder level as in Figs.1-2. In the $s++$ state, the difference between $\Delta_{1}$ and $\Delta_{2}$ does not continue to decrease, which is consistent with the $T_{c}$ behavior discussed above.

Conclusions — We have shown, by means of a microwave technique, the experimental evidence of a disordered-induced $s\pm$ to $s++$ transition in Ba(Fe1−xRhx)2As2 single crystals, in the form of a clear drop in the low-temperature values of the London penetration depth, as already predicted in literature but not yet observed. Disorder was induced by 3.5-MeV proton irradiation, up to $6.63\times10^{-3}$ displacements per atom. The transition was validated through a two-band Eliashberg model, where disorder is considered in a variable range between the Born approximation and the unitary limit. Self-consistent calculations with realistic parameter values reproduced the experimental critical temperature and superfluid density, with the $s\pm$ to $s++$ transition at the expected disorder level. The agreement is only semi-quantitative, since at least three bands should be considered to correctly describe the physics of the compound, but this was made impractical by the need to correctly account for a high level of disorder.

In summary, our approach is an effective and general way to determine whether a material is characterized by the $s\pm$ symmetry, through its evolution with disorder. Hopefully, these findings will stimulate the development of further experiments aimed to shed more light onto the underlying coupling mechanisms.

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[18] See Supplemental Material at http://............. for further
details on the experimental techniques, on the irradiation process and on the model calculations, which also includes Refs. [19-28].