Robust $s(+/−)$ pairing in CaK(Fe$_1$-xNi$_x$)$_4$As-4 ($x=0$ and 0.05) from the response to electron irradiation

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Abstract
Controlled pointlike disorder introduced by 2.5-MeV electron irradiation was used to probe the superconducting state of single crystals of CaK(Fe1-x Ni-x)(4)As-4 superconductor at x = 0 and 0.05 doping levels. Both compositions show an increase of the residual resistivity and a decrease of the superconducting transition temperature, T-c, at the rate of dT(c)/d ρ(T-c)≈0.19 K/(μΩ cm) for x = 0 and 0.38 K/(μΩ cm) for x = 0.05, respectively. In the Ni-doped compound (x = 0.05), the coexisting spin-vortex crystal (SVC) magnetic phase is suppressed at the rate of dT(N)/d ρ(T-N)≈0.16 K/(μΩ cm). The low-temperature variation of London penetration depth is well approximated by the power-law function, Δλ(T) = AT(n), with n≈2.5 for x = 0 and n≈1.9 for x = 0.05 in the pristine state. Detailed analysis of λ(T) and T-c evolution with disorder is consistent with two effective nodeless energy gaps in the density of states due to robust s(+/−) pairing. Overall the behavior of CaK(Fe1-xNix)(4)As-4 at x = 0 is similar to a slightly overdoped Ba1-y K-y Fe2As2 at y approximate to 0.5, and at x = 0.05 to an underdoped composition at y approximate to 0.2.

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Robust $s_\pm$ pairing in CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ ($x = 0$ and 0.05) from the response to electron irradiation


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Controlled pointlike disorder introduced by 2.5-MeV electron irradiation was used to probe the superconducting state of single crystals of CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ superconductor at $x = 0$ and 0.05 doping levels. Both compositions show an increase of the residual resistivity and a decrease of the superconducting transition temperature, $T_c$, at the rate of $dT_c/d\rho(T_c) \approx 0.19 \, \text{K/(}\mu\Omega \text{ cm})$ for $x = 0$ and $0.38 \, \text{K/(}\mu\Omega \text{ cm})$ for $x = 0.05$, respectively. In the Ni-doped compound ($x = 0.05$), the coexisting spin-vortex crystal (SVC) magnetic phase is suppressed at the rate of $dT_N/d\rho(T_N) \approx 0.16 \, \text{K/(}\mu\Omega \text{ cm})$. The low-temperature variation of London penetration depth is well approximated by the power-law function, $\Delta \lambda(T) = AT^n$, with $n \approx 2.5$ for $x = 0$ and $n \approx 1.9$ for $x = 0.05$ in the pristine state. Detailed analysis of $\lambda(T)$ and $T_c$ evolution with disorder is consistent with two effective nodeless energy gaps in the density of states due to robust $s_\pm$ pairing. Overall the behavior of CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ at $x = 0$ is similar to a slightly overdoped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ at $y \approx 0.5$, and at $x = 0.05$ to an underdoped composition at $y \approx 0.2$.

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I. INTRODUCTION

The hole-doped iron-based superconductor, Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (BaK122), has a complex temperature-doping phase diagram [1]. In the parent compound, BaFe$_2$As$_2$, stripe-type magnetic order sets in at the Néel temperature, $T_N$, simultaneously with the tetragonal to orthorhombic structural transition at $T_s$ [2]. Upon K-doping, the magnetic order is suppressed and superconductivity appears at about $y \approx 0.18$. The coexistence of stripe magnetic order and superconductivity in the underdoped regime ($y \lesssim 0.24$) [3] leads to substantial anisotropy of the superconducting gap [4], rapidly increasing in the underdoped compositions. These observations suggest that the interplay of superconductivity and magnetism may be of importance for the superconducting pairing, in line with theoretical suggestions [5–7].

The discovery of stoichiometric CaFe$_4$As$_4$ (CaK1144) [8–10] provided a unique opportunity to effectively study a hole-doped system without additional scattering from chemically substituted ions. In terms of electron count, CaFe$_4$As$_4$ corresponds to Ba$_{1-x}$K$_x$Fe$_2$As$_2$ at $y = 0.5$, and, indeed, their properties are very similar [9,11], but with a notably lower residual resistivity in CaK1144 due to the absence of substitution-induced disorders. London penetration depth [11,12] and scanning tunneling microscopy [11,13] studies of the CaFe$_4$As$_4$ are consistent with the two effective gaps $\Delta_0$ and $\Delta_2$ in the ranges of $6–10$ meV and $0.4–4$ meV, respectively, which is close to the behavior found near the $y = 0.5$ composition of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [14]. Electron doping of CaFe$_4$As$_4$ with Ni and Co leads to a magnetic order, similar to the underdoped composition with $y \lesssim 0.25$ of Ba$_{1-x}$K$_x$Fe$_2$As$_2$, albeit of a different type, which is the spin-vortex crystal (SVC) magnetic order [15]. In view of the clear effect of magnetism on superconducting gap anisotropy in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [4,16] it is of interest if a change from stripe spin density wave to SVC magnetic structure would affect superconductivity.

In this work, we study the superconducting gap structure of CaFe$_4$As$_4$ in both stoichiometric and Ni-doped samples with different amounts of pointlike disorder. This controlled disorder is characterized by measuring normal state resistivity as described elsewhere [17]. The effect on the superconducting state is revealed by measuring the changes in $T_c$ and low-temperature variation of the London penetration depth $\Delta\lambda(T)$. We find nodeless superconducting gaps, along with a rapid suppression of $T_c$ with disorder, a strong indication for $s_\pm$ pairing [18]. We do not find any obvious effect of the SVC type of magnetic ordering on superconductivity in the Ni-doped compound.

II. EXPERIMENT

Single crystals of CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ ($x = 0$ and 0.05) were grown from a high-temperature solution rich in Fe and As [9,10]. The composition of Ni-doped crystals was determined by electron probe microanalysis with wavelength dispersion spectroscopy. Detailed descriptions of crystal synthesis and characterization using x-ray diffraction, magnetization, heat capacity, and resistivity are reported elsewhere [9,15]. Since microscopic inclusions of superconducting impurity phases below x-ray diffraction resolution are frequently observed in CaFe$_4$As$_4$ crystals [9,10], samples for penetration depth and resistivity measurements were screened using a custom-made...
sensitive radio-frequency susceptometer [19]. Only samples with sharp transitions and no additional features on temperature scans were selected. In the end, a pair of samples selected for high-resolution penetration depth measurement had typical dimensions of $0.5 \times 0.5 \times 0.02$ mm$^3$. Samples for resistivity measurements were shaped into bars with dimensions about $0.7 \times 0.2 \times 0.02$ mm$^3$. Electrical contacts to the samples were made by soldering silver wires using tin [20,21]. The contacts were sufficiently mechanically stable to survive irradiation, so that the same samples were measured before and after irradiation, thus enabling quantitative comparison without invoking uncertainty of geometric factor determination. Four-probe electrical resistivity was measured in a Quantum Design PPMS.

A self-oscillating tunnel-diode resonator technique was used for in-plane London penetration depth measurements. The samples were placed into a 40-turns inductor coil, which is a part of an LC tank circuit. The sample and the coil were thermally decoupled, and the temperature of the circuit and coil was actively stabilized around 5 K with submillikelvin accuracy. The change in the resonant frequency shift due to temperature-dependent screening of a small, $\sim 20$ mOe, excitation ac magnetic field into the sample was calibrated by determining the sample geometry and measuring frequency change when the sample is physically removed from the coil at the base temperature ($\sim 450$ mK). Detailed descriptions of the technique and calibration can be found elsewhere [22–24]. Dedicated crystals for penetration depth study were also measured before and after irradiation, which are separate from the set of crystals for resistivity.

Electron irradiation was performed at SIRIUS Pelletron linear accelerator in Laboratoire des Solides Irradiés at École Polytechnique in Palaiseau, France. The irradiation was conducted using 2.5-MeV electrons in a liquid hydrogen environment at $\sim 22$ K to provide efficient heat dissipation and prevent immediate recombination of the vacancy-interstitial defects (Frenkel pairs). Upon warming to room temperature after irradiation, about 20%–30% of defects are annealed as indicated by the decrease of the residual resistivity measured in situ [17]. After this initial annealing, the defects remain relatively stable as long as the samples are kept at room temperature. We re-measured several Ba$_{1-y}$K$_y$Fe$_2$As$_2$ samples near optimal doping after months of passive storage in a desiccator at room temperature and did not detect significant changes [14]. We plan to perform similar measurements on the CaKNi1144 samples used in this study. On the other hand, some fraction of the remaining defects can be annealed by deliberately warming samples above the room temperature. When a sample was warmed up to 400 K, $T_x$ was increased [Fig. 2(a)]. The defect concentration produced by electron irradiation in the MeV range is homogeneous throughout the sample due to the large penetration depth, $\sim 2$ mm for 2.5 MeV electrons [25]. This can be seen directly from the fact that the transitions remain sharp after irradiation. The acquired irradiation dose presented in this Rapid Communication is in the units of coulomb per square centimeter, where $1$ C/cm$^2 = 6.24 \times 10^{19}$ electrons/cm$^2$. The total charge of electrons penetrated through the sample was measured by the Faraday cage behind the sample stage.

### III. RESULTS AND DISCUSSION

Figure 1 shows the in-plane resistivity of the parent CaKFe$_4$As$_4$ (top panel) and Ni-doped CaK(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$ (bottom panel) before (solid lines) and after (dashed lines) electron irradiation with 2.08 C/cm$^2$ and 2.38 C/cm$^2$, respectively. The in-plane resistivity of the $x=0$ sample in pristine state shows a crossover feature at about 200 K, typical for all hole-doped compositions. Approaching $T_c$, on cooling, $\rho(T)$ shows a small upward curvature, similar to Ba$_{1-y}$K$_y$Fe$_2$As$_2$ where it can be fitted with $\sim T^{3/2}$ dependence in a limited temperature range from 40 to 60 K [26]. A similar power law fits the data well in CaKFe$_4$As$_4$ as shown in the top panel of Fig. 1 (cyan line). The resistivity just above the onset of resistive transition is about 12 times lower than $\rho(300$ K). The actual residual resistivity is impossible to extrapolate

![Figure 1. In-plane resistivity of the stoichiometric CaKFe$_4$As$_4$ sample ($x=0$, top panel (a)) and Ni-substituted sample ($x=0.05$, bottom panel (b)). Solid and dashed lines show resistivity of the samples before and after irradiation, with doses 2.08 C/cm$^2$ ($x=0$) and 2.38 C/cm$^2$ ($x=0.05$). Red lines show the difference of resistivity between irradiated and pristine states. The cyan line in the top panel is the fit of the curve in the pristine $x=0$ sample to $\rho(0)+\rho(T) T^{3/2}$. The right insets zoom on the superconducting transition range. The left inset in the bottom panel shows the temperature-dependent resistivity derivative zooming on the features at $T_x$, suppressed upon irradiation from 50.6 to 47.5 K.](140508-2)
convincingly, since $T^{3/2}$ fit gives a small negative value of $\rho(0)$ and $T_c$ is large. The resistive transition to the superconducting state at $T_c$ (onset) = 35.2 K is very sharp (see the lower inset in the top panel of Fig. 1) with a width of $\Delta T_c < 0.5$ K, reflecting good sample quality. Electron irradiation of 2.08 C/cm$^2$ leads to a vertical shift of the $\rho(T)$ curve, with the red line in the top panel of Fig. 1 showing the difference between $\rho(T)$ curves before and after irradiation. The shift is not constant, but its value just above $T_c$ is about two times higher than at room temperature, suggesting violation of the Matthiessen rule. The superconducting transition remains sharp after the irradiation supporting homogeneous defect distribution. The suppression of $T_c$ with an increase of residual resistivity $\rho(T_c)$ happens at a rate $dT_c/d\rho(T_c) = -0.19$ K/(\Omega cm)$^{-1}$, which is remarkably close to that of slightly overdoped Ba$_{1-y}$K$_y$Fe$_2$As$_2$ [see Fig. 3(a) below for a direct comparison].

The electrical resistivity $\rho(T)$ of the Ni-doped sample, $x = 0.05$, in the pristine condition is shown by a solid curve in the bottom panel of Fig. 1. It has a similar broad crossover feature at 200 K, although it is much less pronounced due to a significant increase of residual resistivity compared to the pure $x = 0$ compound [$\approx 100 \ \Omega \text{cm}$; lower inset in Fig. 1(b)]. An additional feature in the $\rho(T)$ curves of the $x = 0.05$ sample can be distinguished in the temperature-dependent resistivity derivative at $\sim 50$ K [top inset in Fig. 1(b)], most likely due to the spin-vortex crystal (SVC or so-called “hedgehog”) magnetic ordering [15]. Electron irradiation with a total dose of 2.38 C/cm$^2$ with subsequent annealing at room temperature [dashed curve in Fig. 1(b)] leads to an upward shift of the $\rho(T)$ curve. Similar to the pristine sample, the shift is temperature dependent and is significantly bigger for $T < T_N \sim 47$ K suggesting partial loss of the carrier density. The magnetic transition temperature is suppressed from 50.6 to 47.5 K, while the superconducting transition temperature is suppressed from 10.5 to 4 K [lower inset in Fig. 1(b)]. The rate of $T_c$ suppression with increase of residual resistivity is substantially higher than in the sample with $x = 0$ [see Fig. 3(a)]. Rapid suppression of both superconducting and magnetic transition temperatures with irradiation is very similar to underdoped BaK122 [27] where superconductivity also coexists with magnetism, albeit with a different antiferromagnetic structure (stripe type).

To probe the superconducting state, London penetration depth measurement on a pair of samples was done before and after irradiation. While only a single irradiation dose of 2.36 C/cm$^2$ was applied to a Ni-doped ($x = 0.05$) sample, multiple irradiations with intermediate annealing to 400 K were performed on the pure ($x = 0$) sample. The top panel of Fig. 2 shows total variation $\Delta \lambda(T)$ over the whole superconducting range from the base temperature of 0.4 K to above superconducting $T_c$ for both samples. For the $x = 0$ sample, the superconducting transition temperature, $T_c$, was suppressed by 3.2 K from $T_c^{\text{pristine}}$ (onset) = 36.1 K at the first dose of 2.08 C/cm$^2$, partially recovered by 1.3 K after 400 K annealing, and then further decreased by 9.7 K after the second 5.46 C/cm$^2$ and third 4.38 C/cm$^2$ irradiations, so in the end $T_c^{\text{final}} = 24.5$ K. The sample in the pristine state (red curve) has the lowest residual resistivity in resulting a small value of skin depth, so the total rf field penetration above $T_c$ is determined by the skin depth. However, the skin depth gets larger than the sample size for doped and irradiated samples due to the increase of residual resistivity, so the total rf field penetration depth above $T_c$ is determined by the sample size. The change in total penetration depth above $T_c$ is shown in Fig. 2(a).

The bottom panels of Fig. 2 zoom on the low-temperature part of the $\Delta \lambda(T/T_c)$. The range $T/T_c < 0.3$ is considered “low temperatures,” where the superconducting gap can be considered as practically temperature independent and thermally excited quasiparticles reflect the gap topology in the reciprocal space. Panel (b) shows the data for the $x = 0$ sample after multiple irradiations. Panels (c) and (d) show the data for sample $x = 0.05$ plotted as a function of $T/T_c$ [panel (c)] and of $(T/T_c)^n$ [panel (d)].

FIG. 2. (a) Full temperature range $\Delta \lambda(T)$. For the stoichiometric ($x = 0$) sample the data were taken in a sequence of irradiation/annealing treatments as indicated in the legend. (b) Low-temperature part of $\Delta \lambda(T/T_c)$ in the $x = 0$ sample. The exponent $n$ monotonically decreases with irradiation/annealing treatments in a sequence specified in the top panel. The two right bottom panels show $\Delta \lambda$ in the Ni-doped sample $x = 0.05$ plotted as a function of $T/T_c$ [panel (c)] and of $(T/T_c)^n$ [panel (d)].
An alternative explanation could invoke the $c$-axis point node [24] suggested for electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ from anisotropic thermal conductivity [31,32] and $c$-axis penetration depth [33] measurements. However, this scenario does not have any current theoretical or $k$-resolved spectroscopic support, and therefore is unlikely.

At this point, it is clear that the behavior of CaK(Fe$_{1-y}$Ni$_y$)$_4$As$_4$ with $x = 0$ ($x = 0.05$) projects nicely on the Ba$_{1-y}$K$_y$Fe$_2$As$_2$ system at $y \approx 0.5$ ($y \approx 0.2$). Indeed, it is possible to fit CaK(Fe$_{1-y}$Ni$_y$)$_4$As$_4$ into the Ba$_{1-y}$K$_y$Fe$_2$As$_2$ phase diagram, which is best illustrated in Figs. 3(b) and 3(c), where the comparison to Ba$_{1-y}$K$_y$Fe$_2$As$_2$ compounds is presented by plotting $T_c$, and its sensitivity to disorder, as a function of potassium doping. In Fig. 3(b), following the Ba$_{1-y}$K$_y$Fe$_2$As$_2$ “dome,” stoichiometric CaKFe$_4$As$_4$ can be placed in the vicinity of the optimal and slightly overdoped region ($y = 0.48$), whereas electron-doped CaK(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$ can be positioned on the underdoped side ($y = 0.18$) where superconductivity and magnetism coexist. Figure 3(c) shows suppression of $T_c$ normalized by the irradiation dose and $T_{co}$ which serves as an experimental measure of the sensitivity to scattering and allows a comparison between different materials. Compared to BaK122, pure CaKFe$_4$As$_4$ seems to be somewhat more sensitive to disorder but CaK(Fe$_{0.95}$Ni$_{0.05}$)$_4$As$_4$ actually matches very nicely. These observations are naturally explained by the fact that pristine CaK1144 ($x = 0$) is cleaner than BaK122 ($y \approx 0.5$), so the effect of additional disorder is more pronounced. In the doped system, on the other hand, substitution disorder is similar between the two systems. It is rather remarkable that such good mapping is possible in similar, but still different and complex materials. Considered together, the presented results make a very strong case for robust and ubiquitous $s_\pm$ pairing in iron-based superconductors.

**IV. CONCLUSIONS**

Electron irradiation with 2.5-MeV electrons results in a rapid suppression of the superconducting transition temperature, $T_c$, in both stoichiometric CaKFe$_4$As$_4$ and SVC antiferromagnetic Ni-doped CaKFe$_4$As$_4$, $x = 0.05$, suggesting a sign changing superconducting energy gap. In both cases the low-temperature variation of London penetration depth is consistent with the nodeless superconducting state. The two observations provide the strongest support for $s_\pm$ pairing in these multiband superconductors. A detailed analysis shows a remarkable similarity between CaK(Fe$_{1-x}$Ni$_x$)$_4$As$_4$ ($x = 0$ yields $n = 1.9$, which slightly increased to 2.2 after irradiation of 2.36 C/cm$^2$. By plotting $\Delta \lambda(T)$ vs $T^n$, we verify the quality of the fit. It is easy to notice the notable increase of the prefactor $A$ after irradiation, reflecting increased quasiparticle density [28]. The slight increase of the exponent to above $n = 2$ suggests that in the pristine state, the $x = 0.05$ sample is not yet in the regime where impurity scattering dominates (dirty limit) in which case the exponent should saturate at $n = 2$ with increasing disorder [29]. Rather, in light of previous study in underdoped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ in which long-range magnetism gives rise to gap anisotropy [4,30], the increase of the exponent is consistent with the averaging of the gap structure causing the gap to become more isotropic and minima to be elevated.
and 0.05) and Ba$_{1-x}$K$_x$Fe$_2$As$_y$ (y = 0.5 and 0.2), respectively, despite the difference in the spin structure in the magnetically ordered state.

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