Suppression of the Critical Temperature of Superconducting NdFeAs(OF) Single Crystals by Kondo-Like Defect Sites Induced by α-Particle Irradiation

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We report the effect of α-particle irradiation on the reduction of the critical temperature T_c of a NdFeAs(OF) single crystal. Our data indicate that irradiation defects cause both nonmagnetic and magnetic scattering, resulting in the Kondo-like excess resistance $\Delta\rho(T) \propto \ln T$ over 2 decades in temperatures above T_c. The critical density of magnetic irradiation defects which suppresses T_c is found to be much higher than those for cuprates and multiband BCS superconductors. We suggest that such anomalously weak pair breaking by irradiation defects indicates that magnetic scattering in pnictides is coupled with pairing interactions mediated by spin fluctuations.

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Superconductivity in ferropnictides has attracted much interest because of high critical temperatures T_c and the interplay of multiband superconductivity and antiferromagnetism (AF) mediated by the magnetic Fe ions in semimetallic AF parent compounds [1]. In rare-earth pnictides *RE*OFeAs (*RE* = Ce, Pr, Nd, Sm), magnetism can also manifest itself in the rare-earth $4f$ states causing competition between superconductivity, paramagnetism, AF, and the Kondo effect [2]. It has been suggested that superconductivity in pnictides results from a superexchange repulsion mediated by magnetic excitations, which couple electron and hole pockets of the Fermi surface [3,4]. Such pairing interactions favor either isotropic s-wave order parameters with opposite signs on different sheets of the Fermi surface ($s^{\pm}$ model) or anisotropic s-wave or d-wave order parameters with nodes [3,4]. Experimental confirmations of these scenarios remain inconclusive. Measurements of the London penetration depth $\lambda(T)$ have shown both exponential temperature dependencies consistent with a fully gapped Fermi surface [5] and power law behaviors indicative of nodal quasiparticles [6] or impurity-induced bound states at the Fermi level [7]. The response of the superconducting state to magnetic and nonmagnetic impurities is thus one of the key manifestations of pairing symmetries in pnictides.

The effect of impurity scattering could be revealed by measuring T_c as the concentration of impurities is varied. Recently, it was shown that Co, Ni, and Zn substitutions on Fe sites only weakly suppress T_c [8]. However, such experiments are often complicated by uncertainties in the substitutional chemistry, inhomogeneous distribution of impurities or precipitation of second phases. Impurities can also result in doping, shifting the chemical potential, all of which can mask the effect of disorder on T_c. By contrast, irradiation is a more straightforward way of introducing disorder without doping effects. However, because pnictides are built of magnetic ions, their displacements by irradiating particles can produce point defects, which cause both nonmagnetic and spin-flip scattering. The magnetic component may come from disruption of nearest neighbor Fe and As orbitals and a partial restoration of the magnetic moment of the Fe ion [9] or displacements of magnetic *RE* ions. Thus, irradiation of pnictides enables us to probe the effect of both nonmagnetic and magnetic scattering on T_c. So far only one group by Karkin *et al.* has shown the suppression of T_c by neutron irradiation of a polycrystalline LaFeAs(OF) [10]. In this Letter we report resistivity measurements of a NdFeAs(OF) single crystal in which irradiation-induced point defects have been used to progressively suppress T_c. We find that $\rho(T)$ develops a low temperature upturn consistent with the Kondo-type spin-flip scattering by irradiation defects, which, however, cause an unexpectedly weak T_c suppression even for strong magnetic and nonmagnetic disorder.

Our experiment was performed on a 1 μm thick $NdFeAsO_{0.7}F_{0.3}$ (Nd-1111) single crystal with T_c = 46.4 K grown by a multistep flux process [11]. Pt contacts for resistivity and Hall measurements were made by a Focused Ion-Beam. The α-particle irradiation was carried out at 300 K using a 2 MeV $^4He^{2+}$ ion beam from a Tandem accelerator. A total dose of $5.25 \times 10^{16}/cm^2$ was achieved after 14 steps of irradiation. Simulations using the Stopping and Range of Ions in Matter-2008 software [12] gives the mean free path ≈ 4.2 μm for $^4He^{2+}$ ions in Nd-1111, which ensures uniform radiation damage throughout the sample, the collisions occurring mainly on the Nd, Fe, and As sites.

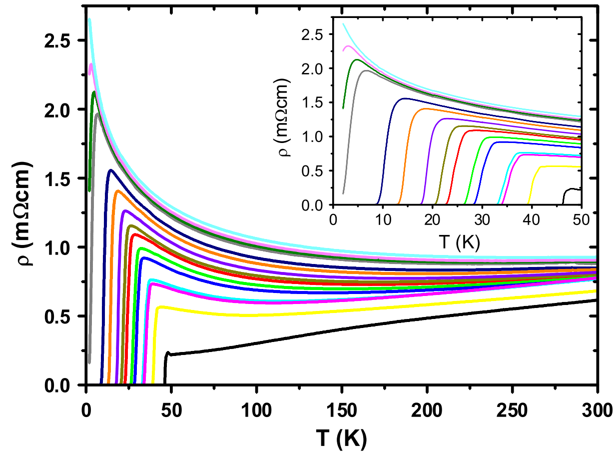

FIG. 1 (color online). $\rho(T)$ for the pristine sample (black curve) and measured after each step of irradiation. Inset shows magnified temperature region near T_c.

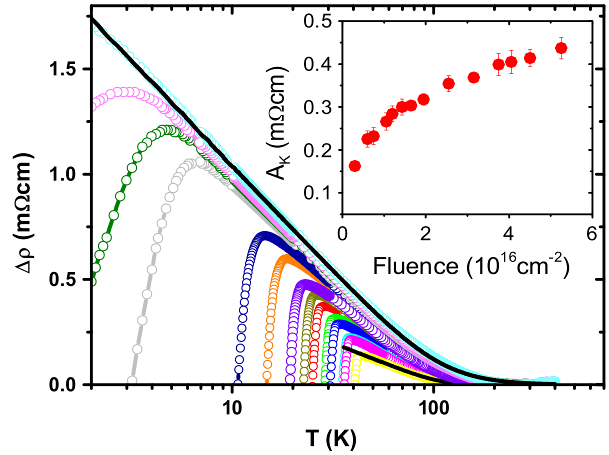

FIG. 2 (color online). $\Delta\rho(T)$ versus T after each irradiation step. The best fits to $\Delta\rho = (A_K/n)\ln[1 + (T_0/T)^n]$ for the highest and lowest doses are shown by continuous black lines. Inset shows A_K as a function of fluence.

Figure 1 shows that T_c decreases monotonically after each irradiation step without significant broadening of the transition. Resistivity $\rho(T)$ progressively increased after each irradiation with a significant upturn developing at low T. Such evolution of $\rho(T)$ is different from what has been observed on other superconductors: in MgB_2 the residual resistivity ρ_0 increases without any upturn at low temperatures [13,14] while in cuprates a logarithmic upturn develops only after much higher doses [15,16]. The observed excess resistivity $\Delta\rho \propto \ln T$ caused by Zn substitutions, irradiation or strong magnetic fields in cuprates [17] has been attributed to a metal insulator transition or scattering on magnetic defects but the detailed microscopic mechanisms remain unclear.

To reveal the low-T resistivity upturn, we first evaluated the high-T part of $\rho(T)$ at $200 < T < 400$ K where it can be fitted well by the quadratic polynomial $\rho_2(T) = \rho_0 + a_1T + a_2T^2$ for all doses, the parameters ρ_0, a_1 and a_2 depending on fluence. Next, we define the excess resistivity $\Delta\rho(T) = \rho(T) - \rho_2(T)$ for each dose. As shown in Fig. 2, $\Delta\rho(T)$ at $T_c < T <$ 70–80 K exhibits the logarithmic temperature dependence which can be fitted by $\Delta\rho(T) = A_K \ln(T_0/T)$. Here A_K plotted in the inset of Fig. 2, increases monotonically with fluence and nearly triples from the first to the last irradiation while T_0 does not vary significantly, remaining between 106 K and 119 K. At higher temperatures $\Delta\rho(T)$ is no longer logarithmic but it can be fitted well by $\Delta\rho(T) = (A_K/n)\ln[1 + (T_0/T)^n]$ in the entire temperature range where A_K and T_0 are evaluated at low T, and n decreases from 5 to 3 with increasing fluence. The ratio $\Delta\rho(T)/\rho_0$ for different doses collapses onto a universal curve, as shown in Fig. 3.

The logarithmic dependence of $\Delta\rho(T)$, the increase of A_K with fluence and the independence of T_0 of irradiation can be understood by assuming that Kondo-like scattering occurs on the magnetic moments of irradiation defects [18]. The significant increase of the residual resistivity ρ_0 indicates that irradiation produces nonmagnetic scatters as well. Moreover, the fact that $\Delta\rho(T)/\rho_0$ for all doses collapses onto a single curve implies that both magnetic and nonmagnetic scattering rates have the same dependence on the irradiation defect density. A logarithmic dependence of $\Delta\rho(T)$ was observed on electron-irradiated $YBa_2Cu_3O_{7-x}$ [15]. However, A_K for Nd-1111 is more than twice that for $YBa_2Cu_3O_{7-x}$, consistent with the idea that displacements of Nd and Fe ions produce uncompensated magnetic moments. The Kondo excess resistivity $\Delta\rho(T) \propto \ln T$ usually saturates at low T and is suppressed by magnetic fields [18], but at our lowest temperature of 2 K, we only observed a slight flattening of $\Delta\rho(T)$, and a negative magnetoresistivity $[\rho(9T) - \rho(0T)]/\rho(0T) \approx -0.05$ consistent with the low-T upturn $\Delta\rho(T)$ caused by the spin-flip scattering. This indicates that the Kondo temperature T_K at which the moment of the

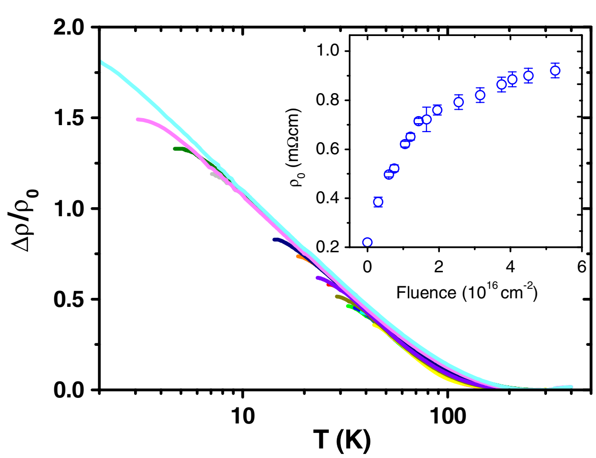

FIG. 3 (color online). The ratio $\Delta\rho(T)/\rho_0$ for all irradiation doses. Inset shows ρ_0 as functions of fluence.

defect is screened by the conduction electrons [18] is lower than 2 K.

As shown in Figs. 2 and 3, neither A_K nor ρ_0 increases linearly with fluence. This may be due to the partial annihilation of defects generated during previous doses or to a shift of the chemical potential. We use the quantity $\Delta\rho_0 = \rho_0^{(i)} - \rho_0^{\mathrm{unirr}}$ where $\rho_0^{(i)}$ is the residual resistivity after i-th irradiation as a measure of irradiation defect density. Figure 4 shows that $T_c(\Delta\rho_0)$ first drops linearly with $\Delta\rho_0$ and then decreases steeper. Since irradiation can shift the chemical potential, we also measured the Hall resistivity $R_H(T)$ from which we found that the effective carrier density $n_H = 1/eR_H$ increases linearly with irradiation (less than by a factor 2 for the maximum dose). In multiband pnictides, R_H may not be a good measure of the carrier density, yet replotting T_c as a function of $\Delta\rho_H = \Delta\rho_0 R_H/R_H{}^{(i)}$ in which only the mean free path is affected by irradiation, makes $T_c(\Delta\rho_H)$ nearly linear and doubles the value of $\Delta\rho_H$ at which $T_c(\Delta\rho_H)$ goes to zero.

The nonmagnetic scattering rate Γ of irradiation defects can be estimated from the relation $\Gamma = \Delta\rho_0/\mu_0\lambda_0^2$ assuming that intraband and interband scattering rates are of the same order of magnitude and taking $\lambda_0 = 195$ nm as the London penetration depth for Nd-1111 at $T = 0$ [19]. Furthermore, the fact that $\Delta\rho(T_c) \sim \rho_0$ (see Figs. 1 and 2) indicates that nonmagnetic and spin-flip scattering rates are also of the same order of magnitude. The dimensionless interband scattering rate $g = \Gamma\hbar/4\pi k_B T_{c0} \cong \hbar\Delta\rho_0/4\pi k_B T_{c0}\mu_0\lambda_0{}^2$ which defines the pair breaking effect in multiband models [7] is shown on the upper axis in Fig. 4. The parameter g varies from 0 to 1.7 and its maximum value nearly doubles if the increase of the n_H with disorder is taken into account. These g values are much larger than the critical g_c at which the $s^{\pm}$ superconductivity is destroyed if impurity scattering is taken into account in the Born approximation. For equal gaps Δ of opposite signs on different sheets of the Fermi surface, the theory [7] gives the equation $\ln(T_{c0}/T_c) = \psi(1/2 + g) - \psi(1/2)$ in which T_c vanishes if $g > g_c \approx 0.15$. Here $\psi(x)$ is the di-gamma function, T_{c0} is the critical temperature before irradiation, $g = (\Gamma_s^{\mathrm{intra}} + \Gamma_n^{\mathrm{inter}})\hbar/4\pi k_B T_{c0}$ where $\Gamma_s^{\mathrm{intra}}$ and $\Gamma_n^{\mathrm{inter}}$ are the spin-flip intraband and the nonmagnetic interband scattering rates, respectively. This estimate of g_c is more than 10 times smaller than the experimental value of $g_c \approx 1.5$ (or 20 times smaller if the change in n_H is taken into account). The large values of g result from a high density of irradiation defects: the estimate of the mean free path $l = v_F/\Gamma$ with the Fermi velocity $v_F = 1.3 \times 10^5$ m/s [20] gives $l \approx 2.4$ nm (or $\sim$1 nm if the increase of n_H is taken into account). It is remarkable that multiband superconductivity in Nd-1111 turns out to be so resilient to such strong magnetic and nonmagnetic disorder. In this respect Nd-1111 appears to behave more like the s-wave MgB_2 and V_3Si rather than the d-wave $YBa_2Cu_3O_7$, as shown in the inset of Fig. 4.

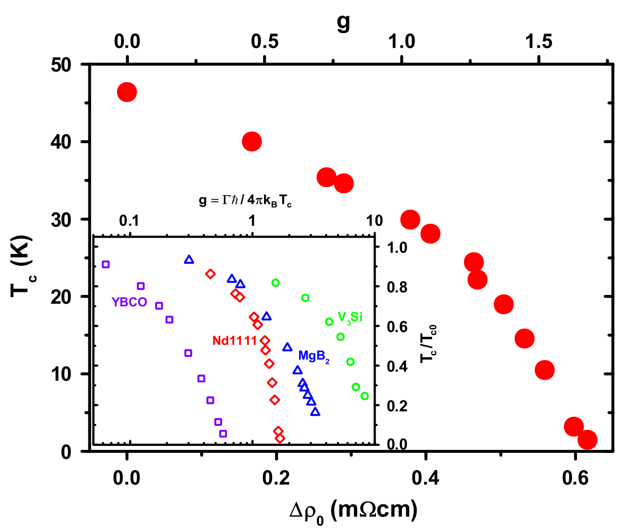

FIG. 4 (color online). T_c versus $\Delta\rho_0$ and $g = \Gamma\hbar/4\pi k_B T_{c0}$. Inset shows comparison of T_c suppression by irradiation for Nd-1111 (this work), YBCO [15], MgB_2 and V_3Si [24].

The results presented here show that the suppression of T_c by irradiation disorder in Nd-1111 is much weaker than what would follow from multiband models with uncorrelated scattering by dilute impurities [7]. The weaker effect of interband nonmagnetic scattering could be understood by suppressed pair breaking in the unitary limit [7], although for high densities of irradiation defects with l of the order of a few unit cells, spatial correlations of impurity scattering [21] may become important. Most striking is the anomalously weak pair breaking by magnetic irradiation defects which results in $\Delta\rho(T) \propto \ln T$ with no apparent saturation at low T due to interaction of magnetic moments [22]. Unlike interband nonmagnetic scattering, the suppression of T_c by intraband magnetic scattering is not reduced in the strong scattering limit if the Kondo temperature T_K is much lower than T_{c0} as is indeed characteristic of our sample, for which $T_K < 2$ K and $T_{c0} = 46$ K. For $T_K \ll T_{c0}$, the theories of the Kondo effect in BCS superconductors [23] predict that spin-flip intraband scattering causes a multivalued dependence of T_c on defect density and even stronger suppression of T_c than what follows from the above Born estimates. Thus, the weak suppression of T_c observed in our irradiated Nd-1111 appears incompatible with Kondo intraband scattering in a BCS superconductor irrespective of particular interband pairing symmetries. However, this conclusion implies traditional BCS models in which magnetic disorder only causes pair breaking scattering without affecting pairing coupling constants, as characteristic of electron-phonon superconductors like MgB_2 or the A-15 compounds represented in Fig. 4. Thus, the anomalously weak pair breaking by irradiation defects in Nd-1111 seems to indicate that, unlike electron-phonon superconductors, magnetic impurity scattering in pnictides is no longer decoupled from the pairing interaction but is intertwined with the superconducting pairing caused by spin excitations. Other mechanisms of $\Delta\rho(T) \propto \ln T$ such as the 2D weak localization [21] can be ruled out because of the moderate mass anisotropy of Nd-1111 [11].

In conclusion, we report the effect of α-particle irradiation on superconducting and nonsuperconducting properties of Nd-1111 single crystals. Our results indicate that irradiation defects produce both Kondo spin-flip and nonmagnetic scattering. Superconductivity in pnictides survives up to an unusually high concentration of irradiation defects for which magnetic intraband scattering would be expected to suppress T_c in multiband BCS superconductors.

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