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Suppression of the critical temperature of superconducting $Ba(Fe_{1-x}Co_x)_2As_2$ by point defects from proton irradiation

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We report the effect of 3 MeV proton irradiation on the suppression of the critical temperature T_c in $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals at underdoping, optimal-doping, and overdoping levels. We find that T_c decreases and residual resistivity increases monotonically with increasing dose. We also find no upturn in low-temperature resistivity in contrast with the α-particle-irradiated NdFeAs(O,F), which suggests that defects induced by the proton irradiation behave as nonmagnetic scattering centers. The critical scattering rate for all samples estimated by three different ways is much higher than that expected in $s_{\pm}$-pairing scenario based on interband scattering due to antiferromagnetic spin fluctuation.

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Since the discovery of the high-T_c iron-based superconductors,[1] extensive studies for the superconducting gap structure have been performed because the gap structure is closely associated with the pairing mechanism. Theoretically, fully gapped s-wave state with opposite signs between different Fermi surfaces ($s_{\pm}$ wave) has been proposed.[2,3] The fully opened gap is suggested by some experiments, such as penetration depth measurements by microwave conductivity,[4,5] angle-resolved photoemission spectroscopy (ARPES),[6,7] and thermal conductivity.[8] However, whether the sign reversal is involved in the multigap structure is questioned. While the inelastic neutron measurements suggest *resonance peak* in magnetic excitation spectra $\chi''(\vec{Q},\omega)$, which is observed when the sign of the gap takes opposite values on different parts of the Fermi surface,[9,10] it is pointed out that such a hump structure of neutron-scattering intensity can be also explained by even s_{++} symmetry, which has the same sign of gaps on different Fermi surfaces.[11] In addition, several studies on the impurity effect indicate that the critical temperature T_c is robust against the introduction of nonmagnetic impurities, which is strikingly different from the suppression of T_c predicted in the $s_{\pm}$ wave.[12–14] Hence, these results lead us to consider that s_{++} symmetry should be added to one of the possible candidates for the gap symmetry of iron-based superconductors. Moreover, recent studies suggest that in some iron-based superconductors, such as LaFePO,[15] KFe_2As_2,[16] and $BaFe_2(As,P)_2$,[17] the gap is nodal in a part of the Fermi surface. In Co-doped $BaFe_2As_2$, it is reported that a fully opened gap structure changes to a nodal one when the Co concentration increases from optimal to overdoped region.[18] Further studies on the gap structure of iron-based superconductors have been desired.

To elucidate the superconducting gap structure, a detailed study on the effect of defects is very crucial because the pair-breaking effects due to scattering centers are phase sensitive. The conventional way to introduce impurities is chemical substitutions of constituent elements. It is well known that isotropic s-wave superconductivity is robust against nonmagnetic impurities due to Anderson's theorem while superconductivity with a sign change in the gap, such as d wave, is sensitive to nonmagnetic impurities. However, chemical substitutions may lead to inhomogeneity in the sample, change in carrier density and the Fermi-surface topology, which can mask the intrinsic impurity effect. Another way to introduce scattering centers is to create defects by the swift particle irradiation. Among them, a light element irradiation, such as proton and α particle, is very suitable for the study of artificially introduced scattering centers, since the irradiation can introduce point defects without providing inhomogeneity and changing electronic structure. So far, for single crystals, only one group reports α-particle irradiation experiments.[14] However, the irradiation produces Kondo-type upturn in the resistivity due to spin-flip scattering, which can mask the intrinsic nonmagnetic scattering effect on the superconducting gap of iron-arsenide superconductors.

In this paper, we address the issue of the superconducting gap structure in $Ba(Fe_{1-x}Co_x)_2As_2$ (x=0.045, 0.075, and 0.113) by detailed study of pair-breaking effect introduced by proton irradiation. We find monotonic increase in the resistivity with proton irradiation. The upturn of resistivity at low temperatures is not observed, which indicates that proton irradiation provides nonmagnetic scattering centers. The suppression of T_c is weaker than the expectation for a superconductor with sign-reversed gaps on/between the Fermi surfaces.

Single-crystalline samples of $Ba(Fe_{1-x}Co_x)_2As_2$ were grown by the FeAs/CoAs self-flux method and their fundamental properties are reported in Ref. 19. A mixture with a ratio of Ba:FeAs/CoAs=1:5 was placed in an alumina crucible. The whole assembly was sealed in a large silica tube and heated up to 1150 °C and kept there for 10 h followed by slow cooling down to 800 °C at a rate of 5 °C/h, which is slightly different from the synthesis reported before.[20] After cleaving, we can obtain shiny samples. The typical dimensions of the resulting crystals are $4\times4\times0.1$ mm^3. The

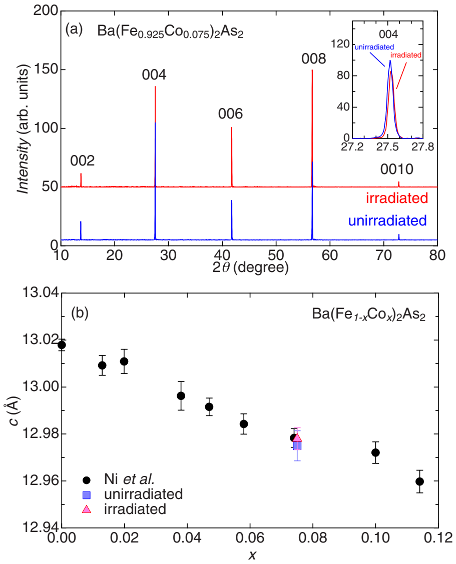

FIG. 1. (Color online) (a) X-ray diffraction patterns for the unirradiated and irradiated $Ba(Fe_{0.925}Co_{0.075})_2As_2$ using Cu $K\alpha_1$ radiation. Inset: peaks of the (004) reflection. (b) Lattice parameter c for the unirradiated (solid square) and irradiated (solid triangle) $Ba(Fe_{0.925}Co_{0.075})_2As_2$. Solid circles show c as a function of x obtained from Ref. 24.

average Co concentration in each batch was determined by energy dispersive x-ray spectroscopy measurements. The 3 MeV protons, which are known to create from one to few tens of displacements,[21] were irradiated into the samples at NIRS-HIMAC. The irradiation was carried out at 40 K avoiding the thermal annealing effect.[22] A total dose is 1.2×10^{16} cm^{-2}. To ensure the uniformity of damage throughout the sample, we used samples with thicknesses of 15–30 μm, which is smaller than the projected range of $\sim$50 μm obtained from the simulation using the stopping and range of ions in matter-2008.[23] Resistivity measurements were performed *in situ* after each irradiation by standard four-probe configuration. Similar results are confirmed in 6 MeV proton irradiation.

Figure 1(a) shows x-ray diffraction (XRD) patterns for the unirradiated and irradiated $Ba(Fe_{0.925}Co_{0.075})_2As_2$ using Cu $K\alpha_1$ radiation. We do not observe broadening of peaks for irradiated sample as shown in the inset of Fig. 1(a), which strongly support that disorder is so small to induce any structural changes. In addition, we confirm that no change in the lattice parameter c by the irradiation obtained from XRD measurements within experimental error. We note that these values are very close to that reported by Ni *et al.* in Ref. 24 as shown in Fig. 1(b).

Figure 2 shows the resistivity of $Ba(Fe_{1-x}Co_x)_2As_2$ with x=0.045, 0.075, and 0.113 as a function of temperature. With increasing dose, T_c decreases monotonically without significant broadening of the transition width while the resistivity increases monotonically. It should be noted that in the α-particle-irradiated NdFeAs(O,F) Kondo-type resistivity upturn at low temperatures is reported,[14] which is associated with the spin-flip scattering due to magnetic impurities. In contrast to the behavior in NdFeAs(O,F), no upturn is observed in the resistivity of proton-irradiated

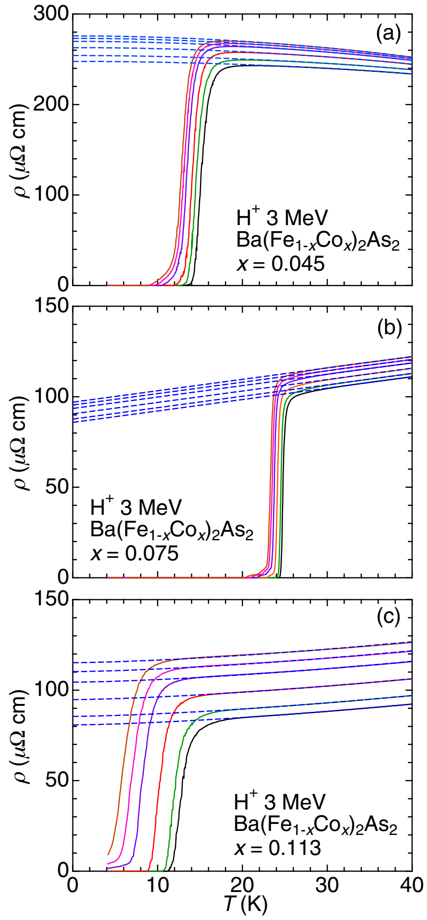

FIG. 2. (Color online) Temperature dependence of the resistivity for $Ba(Fe_{1-x}Co_x)_2As_2$ with (a) x=0.045, (b) 0.075, and (c) 0.113. The doses are 0, 0.1, 0.5, 0.8, 1.0, and 1.2×10^{16} cm^{-2} from the lowest curve. The dashed lines are fit to the data using the equation $\rho=\rho_0+AT^{\alpha}$ with α=2, 1, and 1.5 for x=0.045, 0.075, and 0.113, respectively.

$Ba(Fe_{1-x}Co_x)_2As_2$, which strongly suggests that defects produced by the irradiation act as nonmagnetic scattering centers. *We emphasize that only the contribution of nonmagnetic scattering centers to the pair breaking enable us to investi-*

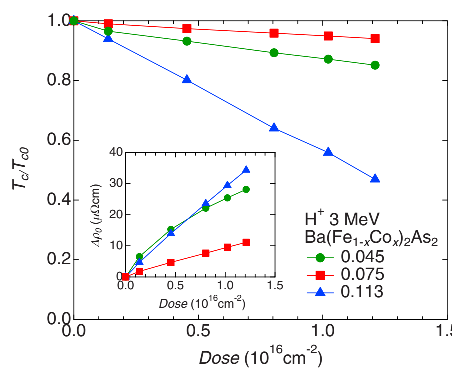

FIG. 3. (Color online) Dose dependence of the normalized critical temperature T_c/T_{c0} for $Ba(Fe_{1-x}Co_x)_2As_2$ with (a) x=0.045, (b) 0.075, and (c) 0.113. The T_{c0} is 15.1 K, 24.8 K, and 12.8 K for x=0.045, 0.075, and 0.113, respectively. Inset: increased residual resistivity by irradiation, $\Delta\rho_0=\rho_0^{irr}-\rho_0^{unirr}$, as a function of dose.

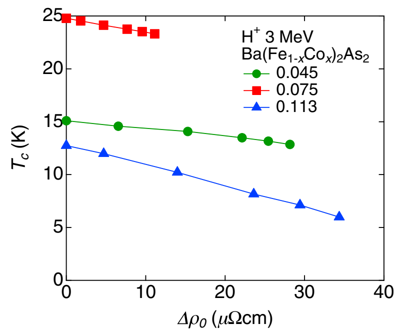

FIG. 4. (Color online) T_c as a function of $\Delta\rho_0$ for $Ba(Fe_{1-x}Co_x)_2As_2$ with x=0.045, 0.075, and 0.113.

gate the intrinsic nonmagnetic impurity effect on the order parameters of iron-arsenide superconductors.

Figure 3 shows the dose dependence of the normalized critical temperature T_c/T_{c0} for $Ba(Fe_{1-x}Co_x)_2As_2$, where T_{c0} is the transition temperature before the irradiation. T_{c0} obtained from the midpoint of resistive transition are 15.1 K, 24.8 K, and 12.8 K for x=0.045, 0.075, and 0.113, respectively. In all the samples, T_c/T_{c0} decreases linearly with increasing the dose in the present dose range. We note that the maximum dose of $\sim 1.2\times 10^{16}$ cm^{-2} in the present study is one fourth of that in the α-particle-irradiated NdFeAs(O,F). Interestingly, in the underdoped and optimally doped samples, the suppression of T_c is very small while in the overdoped sample the suppression is large down to the half of T_{c0}. We note that stronger suppressions of T_c in overdoped samples are also reported in Zn-doped $LaFeAsO_{0.85}F_{0.15}$ (Ref. 25) and $LaFeAsO_{0.85}$.[26] The increased residual resistivity by the irradiation $\Delta\rho_0$ as a function of dose is plotted in the inset of Fig. 3. $\Delta\rho_0$ is the difference of the residual resistivity between irradiated and unirradiated one, namely, $\Delta\rho_0=\rho_0^{irr}-\rho_0^{unirr}$, which corresponds to the density of defects introduced by the proton irradiation. We evaluate the residual resistivity ρ_0 by fitting the data using $\rho=\rho_0+AT^{\alpha}$, where α is an exponent of temperature. We fix α as 2, 1, and 1.5 for x=0.045, 0.075, and 0.113, respectively. $\Delta\rho_0$ increases almost linearly with dose, which ensures that the proton irradiation introduces defects systematically.

Figure 4 shows T_c as a function of $\Delta\rho_0$ for $Ba(Fe_{1-x}Co_x)_2As_2$. The suppression of T_c due to defects introduced by the irradiation is almost linear for samples with all doping levels. The slope $dT_c/d(\Delta\rho_0)$ is -0.08 K/$\mu\Omega$ cm, -0.13 K/$\mu\Omega$ cm, and -0.20 K/$\mu\Omega$ cm for x=0.045, 0.075, and 0.113, respectively. These values are slightly larger than the initial slope of the suppression in the α-particle-irradiated NdFeAs(O,F), ~ -0.04 K/$\mu\Omega$ cm.

To discuss the pair-breaking effect due to nonmagnetic scattering quantitatively, a key parameter is the normalized scattering rate $g=\hbar/2\pi k_B T_{c0}\tau$. Here, τ is the scattering time including both intraband and interband scattering contributions. To avoid ambiguity of estimation, we present g obtained from three different ways. In order to obtain the elastic scattering rate introduced by the irradiation, we use the relation $\tau^{-1}=ne^2\Delta\rho_0/m^*=e\Delta\rho_0/m^*R_H$, where n is the carrier number, R_H is Hall coefficient, and m^* is the effective mass. Figure 5(a) shows T_c/T_{c0} as a function of $g^H=\hbar/2\pi k_B T_{c0}\tau=\hbar\Delta\rho_0 e/2\pi k_B T_{c0} m^* R_H$ for x=0.045, 0.075, and 0.113. Assuming that electrons are dominant carriers, we use the R_H at 300 K obtained from Ref. 27 and $m^*\sim 3.5m_e$ in the electron pocket obtained from ARPES measurements for $Ba(Fe_{1-x}Co_x)_2As_2$.[28] It should be noted that the estimated $\tau_0=m^*R_H/e\rho_0$ for unirradiated sample with x=0.075 is $\sim$0.02 ps, which is consistent with the scattering time of $\sim$0.05 ps just above T_c obtained by microwave conductivity measurements for K-doped $BaFe_2As_2$ (Ref. 4) because the residual resistivity for unirradiated sample with x=0.075 is about twice as large as that of K-doped $BaFe_2As_2$. According to the $s_\pm$ scenario with equal gaps of opposite signs on different Fermi surfaces,[29] T_c obeys the equation, $-\ln t=\psi(1/2+g/2t)-\psi(1/2)$, where $t=T_c/T_{c0}$ and $\psi(x)$ is digamma function. This equation indicates that T_c vanishes at $g=g_c^{\pm}\lesssim 0.3$. To estimate critical values of normalized scattering rate for all samples, we linearly extrapolated the data for simplicity. The obtained values of critical g_c^H are $\sim$6.8, 3.8, and 2.5 for x=0.045, 0.075, and 0.113, respectively. Even in x=0.113, where T_c is most strongly suppressed

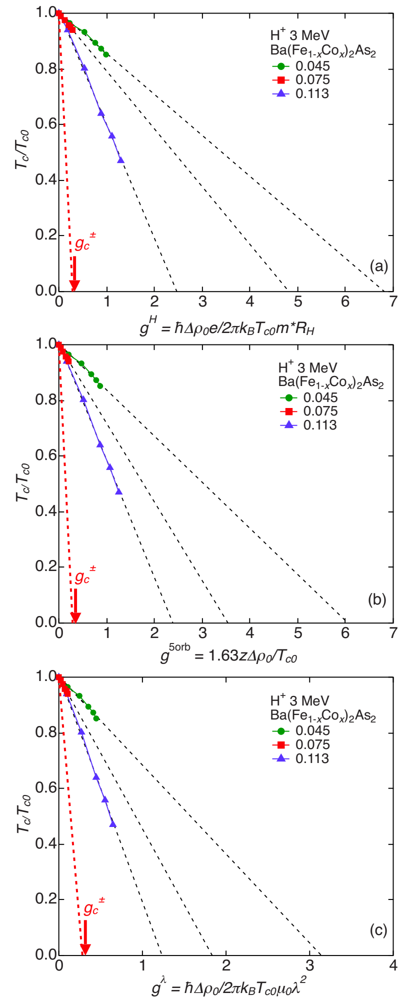

FIG. 5. (Color online) Normalized critical temperature T_c/T_{c0} as a function of normalized scattering rate (a) $g^H=\hbar\Delta\rho_0 e/2\pi k_B T_{c0} m^* R_H$, (b) $g^{5orb}=1.63z\Delta\rho_0/T_{c0}$, and (c) $g^{\lambda}=\hbar\Delta\rho_0/2\pi k_B T_{c0}\mu_0\lambda^2$ for $Ba(Fe_{1-x}Co_x)_2As_2$ with x=0.045, 0.075, and 0.113. Dashed lines are linear extrapolations. $g_c^{\pm}$ is the critical scattering rate expected in $s_\pm$ scenario.

among them, g_c^H is much larger than expected $g_c^{\pm}$ for $s_{\pm}$ scenario.

We show another way to estimate g_c based on the parameter obtained by theoretical calculation. According to the linear-response theory based on five-orbital model,[30,31] we can obtain the relation $\Delta\rho_0$ ($\mu\Omega$ cm)$=0.098\tau^{-1}$ (K) in $Ba(Fe_{1-x}Co_x)_2As_2$ with interplane distance $c=6.5$ Å and $n=5.8-6.1$. Figure 5(b) shows T_c/T_{c0} as a function of $g^{5orb}=z\hbar/2\pi k_B T_{c0}\tau=1.63z\Delta\rho_0/T_{c0}$, where $z=m/m^*$ is the renormalization factor. We use $z=1/3.5$ obtained by ARPES (Ref. 28) assuming $m\sim m_e$. Obtained critical values g_c^{5orb} by linear extrapolation are 6.1, 3.5, and 2.4 for $x=0.045$, 0.075, and 0.113, respectively, which are again much larger than $g_c^{\pm}$ for $s_{\pm}$ scenario. We note that the critical values g_c^{5orb} obtained from the parameter based on theoretical calculation is very similar to g_c^H obtained from experimental values of R_H and m^*.

To obtain carrier number and effective mass indirectly, we use the relation $\tau^{-1}=ne^2\Delta\rho/m^*=\Delta\rho/\mu_0\lambda^2$, where λ is the penetration depth, $\lambda=\sqrt{\mu_0 m^*/ne^2}$. Figure 5(c) shows T_c/T_{c0} as a function of $g^{\lambda}=\hbar\Delta\rho_0/2\pi k_B T_{c0}\mu_0\lambda^2$. Tunnel diode resonator measurements for Al-coated samples provides the absolute values of penetration depths in $Ba(Fe_{1-x}Co_x)_2As_2$.[32] Above $x=0.045$, the absolute value of penetration depth is almost independent of Co doping and is close to 200 nm with small scattering. Therefore, we use the value of the penetration depth $\lambda=200$ nm for all samples presented here. Obtained critical values g_c^{λ} by linear extrapolation are 3.1, 1.8, and 1.2 for $x=0.045$, 0.075, and 0.113, respectively. Although these values are roughly half of the previous two estimations, they are more than three times larger than $g_c^{\pm}$ expected for $s_{\pm}$ scenario.

Critical scattering rates obtained in the three different estimations in the present study are larger than that expected for $s_{\pm}$ scenario. It should be emphasized that proton irradiation provides only nonmagnetic scattering centers without changing electronic structure of $Ba(Fe_{1-x}Co_x)_2As_2$. Our present results definitely indicate that iron-arsenide superconductor $Ba(Fe_{1-x}Co_x)_2As_2$ is robust against nonmagnetic scattering. The weak suppression of T_c in $s_{\pm}$-wave superconductors could be understood by the details of scattering potential. Strikingly suppressed interband scattering introduced by the irradiation, which is rather unlikely in $Ba(Fe_{1-x}Co_x)_2As_2$ with both electron and hole pockets having d_{xz} and d_{yz} orbital characters, could explain the weak pair breaking. Further detailed theoretical model to understand the nontrivial weak suppression of T_c in $Ba(Fe_{1-x}Co_x)_2As_2$ should be required.

Finally we comment on the possibility of change in the gap structure with doping level in $Ba(Fe_{1-x}Co_x)_2As_2$. Thermal-conductivity measurements suggest the existence of nodes in overdoped sample.[18] The stronger suppression of T_c in overdoped sample than underdoped and optimally doped ones may suggest the different gap structures, for instance, nodal $s_{\pm}$-wave symmetry,[33] where the order parameter has d-wavelike nodes on the electron Fermi surface while others are fully open, or $s_{\pm}$ wave with *accidental* horizontal nodes.[18]

In summary, we present the suppression of T_c by defects introduced by 3 MeV proton irradiation in $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals with different doping levels. We find that T_c decreases and residual resistivity increases monotonically. No Kondo-type upturn in the low-temperature resistivity is observed which suggests that defects created by the irradiation act as nonmagnetic scattering centers. The critical scattering rates obtained from the three different estimations are much larger than that expected in $s_{\pm}$ scenario, which may contradict the theoretical expectation based on interpocket scattering due to antiferromagnetic spin fluctuations.

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