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Effects of Point Defects Introduced by Co-doping and Proton Irradiation in $CaKFe_4As_4$

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Abstract. Introduction of point defects into superconductors through proton irradiation enhances their critical current density (J_c). Similarly, chemical doping can also produce point defects, leading to the enhancement of J_c. Iron-based superconductors (IBSs) have been investigated as promising materials for practical applications because of their large J_c at high magnetic fields and temperatures. Recently, another promising IBS $CaKFe_4As_4$ (1144-type) was found, and attracts much interest due to its characteristic feature such as stoichiometric superconductivity and the presence of novel planar defects. We have grown single crystals of Co-doped $CaKFe_4As_4$ and clarified the effect of chemically-introduced point defects on J_c. We also introduced point defects through 3 MeV proton irradiation, and compared the effect of point defects to J_c.

1. Introduction

The critical current density (J_c) is determined by pinning of vortices in superconductors. In addition to the intrinsic pinning, pinning centers can be artificially engineered into superconductors through defects prompted by particle irradiations [1–4]. In 122-type iron-based superconductors (IBSs) point defects generated through proton irradiation have been recognized as effectively pinning centers, which enhance their J_c [5–8].

IBSs have been investigated as promising materials for practical applications because of their large J_c at high magnetic fields and temperatures. Recently, another promising IBS $CaKFe_4As_4$ (1144-type) was found [9]. Its crystal structure is similar to 122-type IBSs. $CaKFe_4As_4$ has a tetragonal structure (P4/mmm), where Ca and K layers stack alternatively along the *c*-axis [9, 10]. $CaKFe_4As_4$ shows similar superconducting properties to those in optimally doped 122-type IBSs [11-13], such as critical temperature (T_c) and upper critical field (H_{c2}) [14].

Here, we have successfully grown single crystals of Co-doped $CaKFe_4As_4$ with various doping levels, and characterized superconducting properties including the effect of chemically introduced point defects on J_c. We also investigated the effect of point defects generated by 3MeV proton irradiation into $CaKFe_4As_4$. We compare effects of two kinds of point defects, chemically and physically introduced, on J_c characteristics in $CaKFe_4As_4$.

2. Experimental Methods

$CaKFe_4As_4$ and $CaK(Fe_{1-x}Co_x)_4As_4$ single crystals were synthesized by FeAs self-flux method. Ca granules (99.5%), K ingots (99.5%), FeAs powder, and CoAs powder were used as starting materials. FeAs was prepared by sealing stoichiometric amounts of As grains (7N) and Fe powder (99.9%) in an evacuated quartz tube and reacting them at 700 °C for 40 h after heating at 500 °C for 10 h. We kept the temperature ramp rate always at 100 °C/h. CoAs was prepared by sealing stoichiometric amounts of As grains (7N) and Co powder (99%) in an evacuated quartz tube. It was heated up to 700 °C for 7 h and held for 6 h and then heated up to 1065 °C for 4 h and held for 10 h. A mixture with a ratio of Ca : K : FeAs : CoAs =1: 1.1: 10(1-*x*) : 10*x* was placed in an zirconia crucible in an argon-filled glove box. The alumina crucible was then sealed in a niobium tube using arc welding method. The niobium tube was sealed in an evacuated quartz tube. The whole assembly was heated up to 650 °C for 5 h and held for 5 h, and then heated up to 1180 °C for 5 h and held for 5 h. It was cooled down to 1050 °C for 5 h and slowly cooled down to 930 °C at a rate of 1.5 °C /h.

3 MeV proton irradiations were performed at room temperature at NIRS-HIMAC up to 5×10^{16} cm^{-2}. For this purpose, crystals were thinned down to 10-15 μm so that all protons pass through them.

Magnetization of the crystal was measured by a superconducting quantum interference device (SQUID) magnetometer (MPMS-5XL, Quantum Design). The single crystal was placed in a quartz sample holder and fixed with Apiezon N grease. T_c was estimated from zero-field cooling (ZFC) and field-cooling (FC) magnetizaition measurements for field perpendicular to the *ab*-plane. J_c was evaluated from the results of the magnetization measurements using the extended Bean model.

3. Results and Discussion

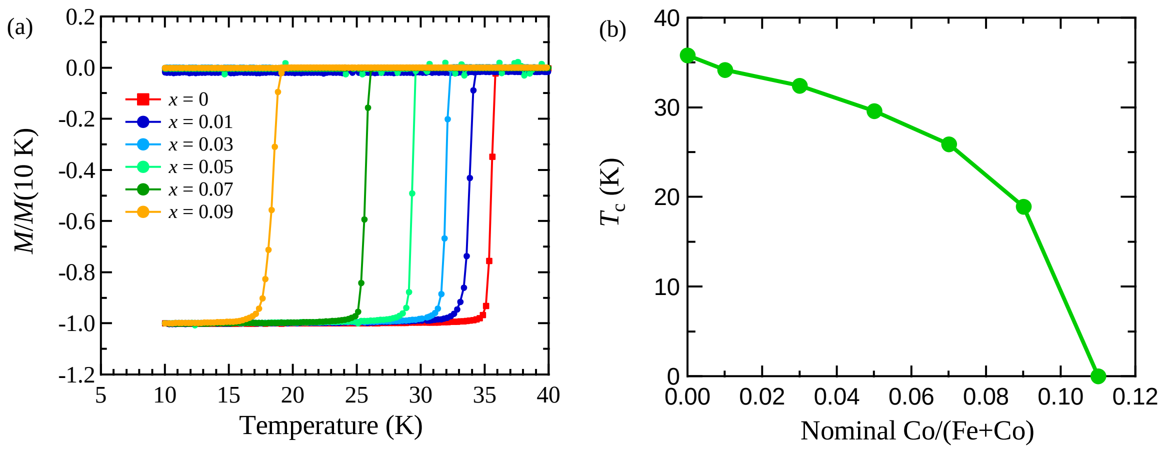

Figure 1. (a) Temperature dependence of normalized magnetization in $CaK(Fe_{1-x}Co_x)_4As_4$. (b) T_c as a function of Co-doping level in $CaK(Fe_{1-x}Co_x)_4As_4$.

Figure 1(a) shows the temperature dependence of magnetization in $CaK(Fe_{1-x}Co_x)_4As_4$. The superconducting transition is sharp even after Co-doping, and the magnetization at low temperatures is flat, indicating that quality of the grown crystals is high. It has been demonstrated that T_c in $CaK(Fe_{1-x}Co_x)_4As_4$, which is determined by the onset of diamagnetism, decreases with Co content. Co-doping level dependence of T_c is shown in figure 1(b). At small Co-doping levels, T_c decreases roughly at 1 K/(Co%). For the sample with $x = 0.11$, superconductivity does not show up above $T = 2$ K.

Figures 2(a)-(f) show the magnetic field dependence of J_c in $CaK(Fe_{1-x}Co_x)_4As_4$ with different x at different temperatures. In the pristine crystal, $x = 0$, non-monotonic temperature dependence of J_c at high magnetic fields is reproduced as reported in [14-15]. It is demonstrated that J_c at low temperatures increases with Co content, up to $x \sim 0.07$. It means that the substituted Co-doping introduces point defects. Figures 2(a)-(f) show that J_c is the largest when the Co-doping level is 0.03-0.07.

A close inspection of figures 2(a)-(f) show that the magnetic field dependence of J_c at low temperatures changes with Co-doing level. For the sample with $x = 0$, J_c at $T = 2$ K rapidly decreases with the field and it becomes less than that at $T = 15$ K at $H \sim 50$ kOe. On the other hand, for samples with $x > 0.03$, J_c does not decreases so much at $T = 2$ K, and the non-monotonic temperature dependence of J_c does not show up at high fields. In many superconductors, J_c changes as $H^{-\alpha}$ at low temperatures and high fields. This feature can be more clearly seen by making double-logarithmic plot of J_c - H as shown in the figures 2(g)-(i). Actually, in the case of pristine crystal, α at 2 K and 10 K are 0.84 and 0.62, respectively. On the other hand, for the sample with $x = 0.03$, α at 2 K and 10 K are 0.65 and 0.56, respectively, and for $x = 0.07$, α at 2 K and 10 K are 0.55 and 0.53, respectively. These values are closer to the value in the case of strong point pinning of 5/8~0.62 [16]. Hence, we speculate that the introduced Co atoms work as strong pinning centers.

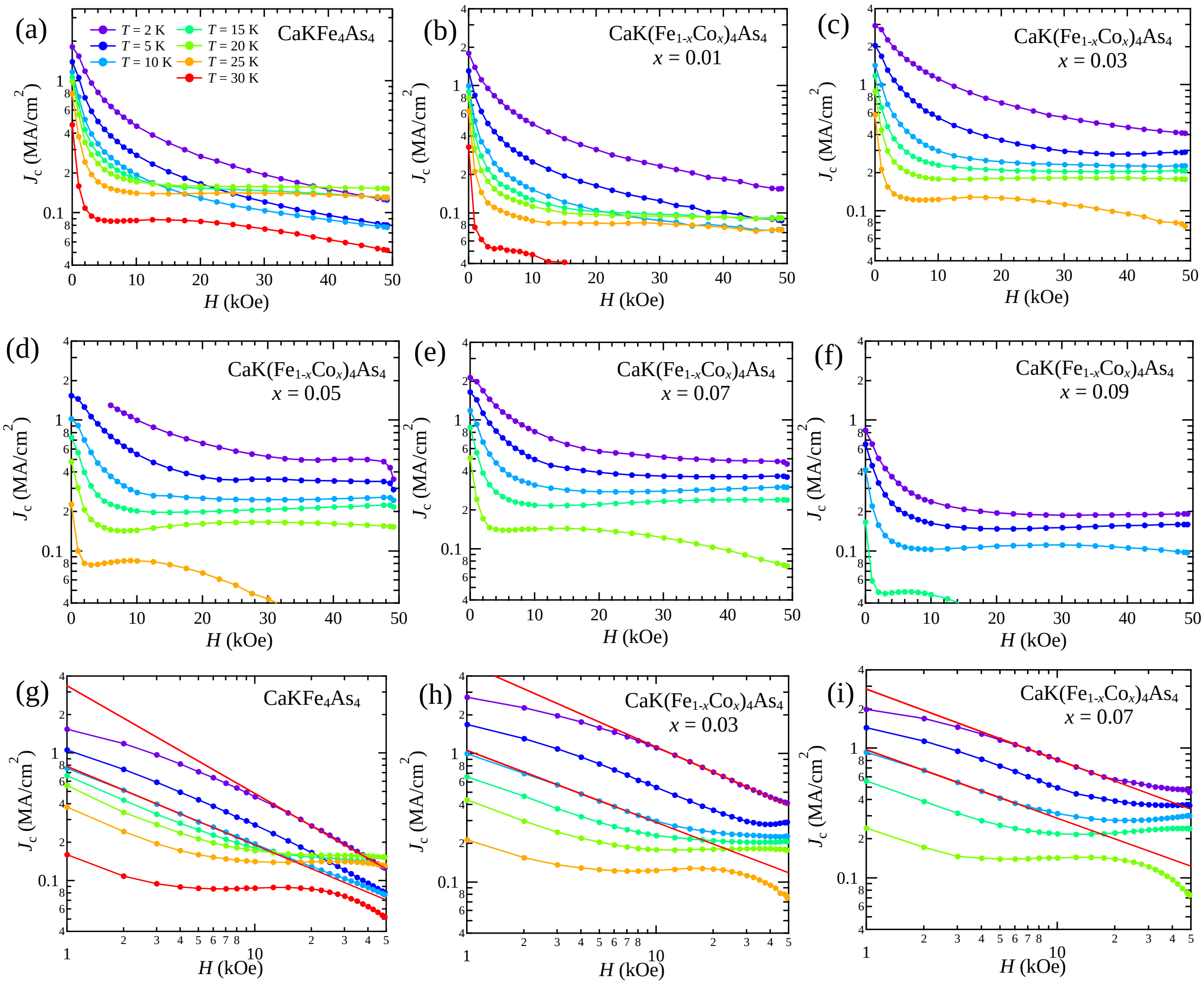

Figure 2. Magnetic field dependences of J_c at different temperatures in $CaK(Fe_{1-x}Co_x)_4As_4$ (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$, (e) $x = 0.07$, and (f) $x = 0.09$. (g)-(i) are the double logarithmic plot of J_c - H. Lines are fitting to the data at 2 K and 10 K in $CaK(Fe_{1-x}Co_x)_4As_4$ (g) $x = 0$, (h) $x = 0.03$, and (i) $x = 0.07$.

Figures 3(a)-(c) show that magnetic field dependences of J_c at different temperatures in $CaKFe_4As_4$ irradiated by 3 MeV protons at doses of (a) 0.01×10^{16} cm^{-2}, (b) 0.05×10^{16} cm^{-2}, and (c) 0.1×10^{16} /cm^2. They clearly demonstrate that J_c is enhanced by increasing proton dose up to 0.1×10^{16} cm^{-2} in almost all magnetic field and temperature range. In particular, J_c is enhanced more than a factor of 4 compared with the pristine sample at a dose of 0.1×10^{16} cm^{-2} at low temperatures and high fields. The power-law magnetic field dependence of J_c, $J_c \propto H^{-\alpha}$, is analyzed in figures 3(d)-(e). At a dose of 0.01 $\times 10^{16}$ cm^{-2}, α = 0.60 (T = 2 K) and α = 0.55 (T = 10 K), while it changes to α = 0.54 (T = 2 K) and α = 0.52 (T = 10 K) at a dose of 0.1×10^{16} cm^{-2}. It should be noted that T_c does not change at this low proton doses. This fact suggests that the origin of the non-monotonic temperature dependence of J_c at high fields is not due to the presence of secondary phase with low T_c, since proton irradiation at this low dose is not expected to destroy the secondary phase. It is remarkable that the anomalous non-monotonic temperature dependence of J_c at high fields is completely wiped out at a relatively low dose of 0.1 × 10^{16} cm^{-2}.

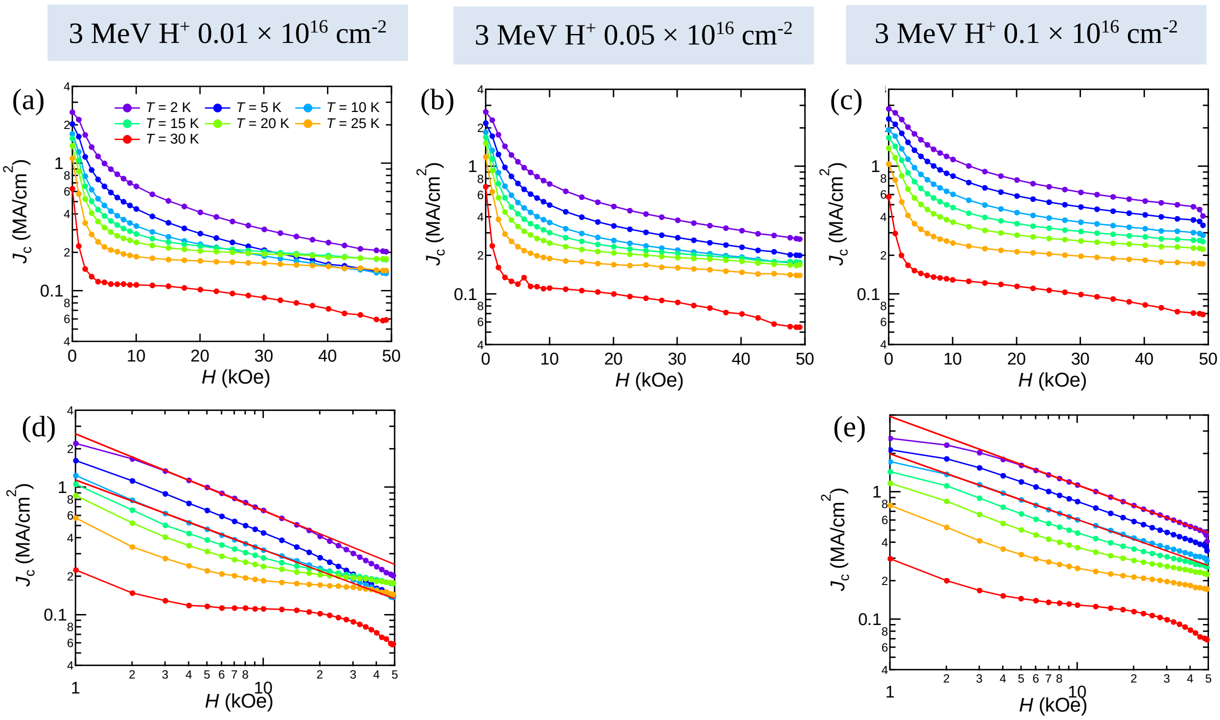

Figure 3. Magnetic field dependences of J_c at different temperatures in $CaKFe_4As_4$ irradiated with 3 MeV protons at doses of (a) 0.01 × 10^{16} cm^{-2}, (b) 0.05 × 10^{16} cm^{-2}, and (c) 0.1 × 10^{16} cm^{-2}. (d)-(e) are the double logarithmic plot of J_c - H. Lines are fitting to the data at 2 K and 10 K at doses of (d) 0.01 × 10^{16} cm^{-2} and (e) 0.1 × 10^{16} cm^{-2}.

Figures 4 and 5 show the magnetic field dependence of J_c at different temperatures in $CaK(Fe_{1-x}Co_x)_4As_4$ irradiated by 3 MeV protons. It demonstrates that J_c enhancement with the proton irradiation is weaker than that in $CaKFe_4As_4$. Actually, with 3 MeV proton irradiation up to 0.1 x 10^{16} cm^{-2}, J_c at T = 5 K is enhanced by a factor of ~2 for x = 0.03, while J_c is enhanced only by ~ 20 % for x = 0.07. The power-law exponent α of J_c is summarized in Table 1. α in most of the cases is close to 0.5, suggesting that the strong point pinning is dominant. Previous studies of 3 MeV irradiation into IBSs up to 1 x 10^{16} /cm^2 or more demonstrated that α changes from ~0.5 to ~0.3 [6,8]. These observations were reproduced by the large-scale TDGL simulation with large strong pinning centers [11]. However, in the present case, α remains ~0.5 in spite of the 3 MeV proton irradiation. This is probably due to the insufficient dose of protons. Further studies with much larger proton doses are desired.

Table 1. Values of the power-law exponent α of J_c.

	pristine		3 MeV H^+ 0.01×10^{16} /cm^2		3 MeV H^+ 0.1×10^{16} /cm^2	
	T = 2 K	T = 10 K	T = 2 K	T = 10 K	T = 2 K	T = 10 K
$CaKFe_4As_4$	0.84	0.62	0.60	0.55	0.54	0.52
$CaK(Fe_{1-x}Co_x)_4As_4$ x = 0.03	0.65	0.56	0.51	0.53	0.54	0.52
$CaK(Fe_{1-x}Co_x)_4As_4$ x = 0.07	0.55	0.53	0.52	0.48	0.48	0.48

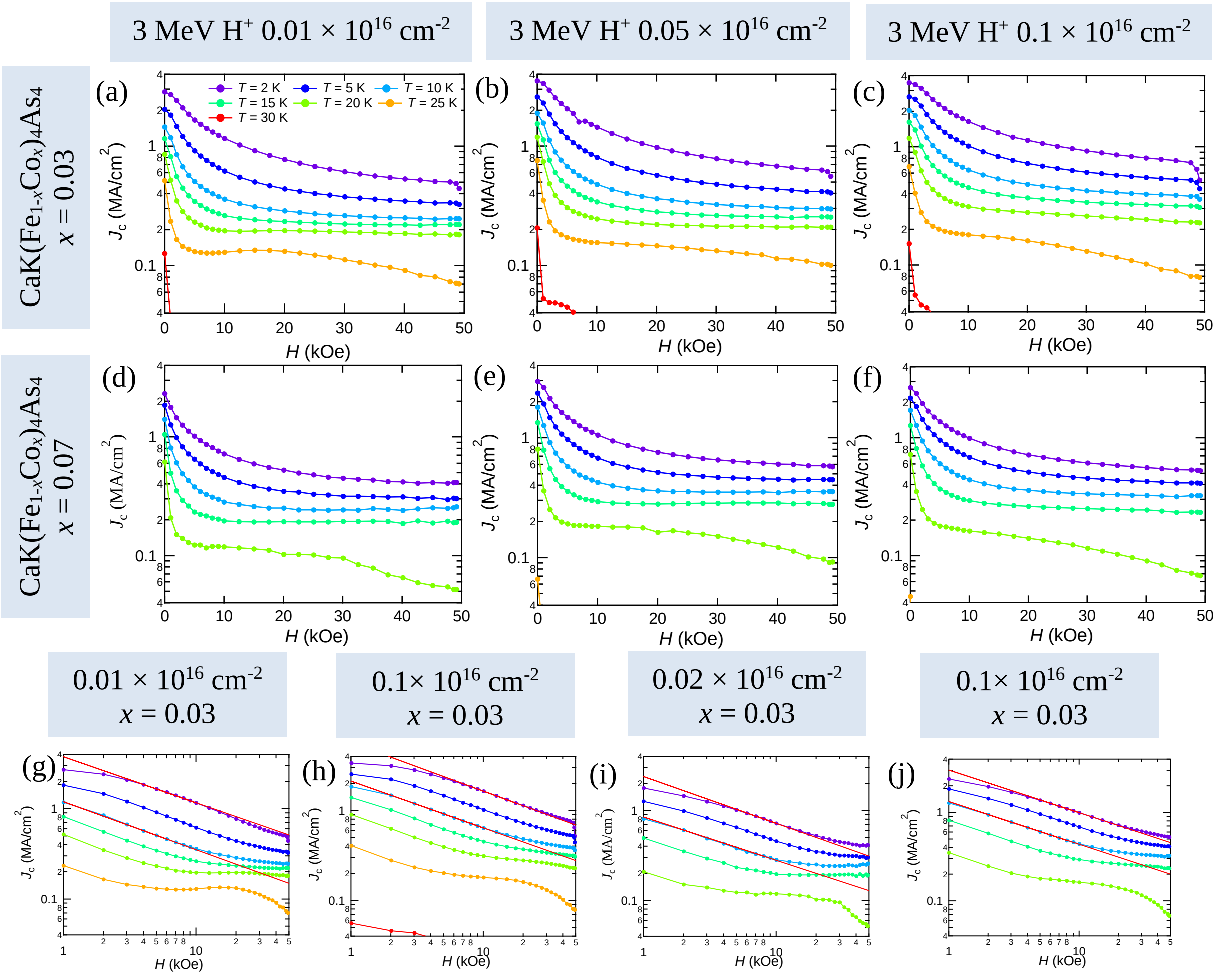

Figure 4. Magnetic field dependences of J_c at different temperatures in $CaK(Fe_{1-x}Co_x)_4As_4$ irradiated by 3 MeV protons at doses of (a) 0.01 × 10^{16} cm^{-2} (x =0.03), (b) 0.05 × 10^{16} cm^{-2} (x =0.03), (c) 0.1 × 10^{16} cm^{-2} (x =0.03), (d) 0.01 × 10^{16} cm^{-2} (x =0.07), (e) 0.05 × 10^{16} cm^{-2} (x =0.07), and (f) 0.1 × 10^{16} cm^{-2} (x =0.07). (g)-(j) are the double logarithmic plot of J_c - H in $CaK(Fe_{1-x}Co_x)_4As_4$ irradiated by 3 MeV protons at doses of (g) 0.01 × 10^{16} cm^{-2} (x = 0.03), (h) 0.1 × 10^{16} cm^{-2} (x = 0.03), (i) 0.01 × 10^{16} cm^{-2} (x = 0.07), and (j) 0.1 × 10^{16} cm^{-2} (x = 0.07). Lines in (g)-(j) are fitting to J_c - H at 2 K and 10 K.

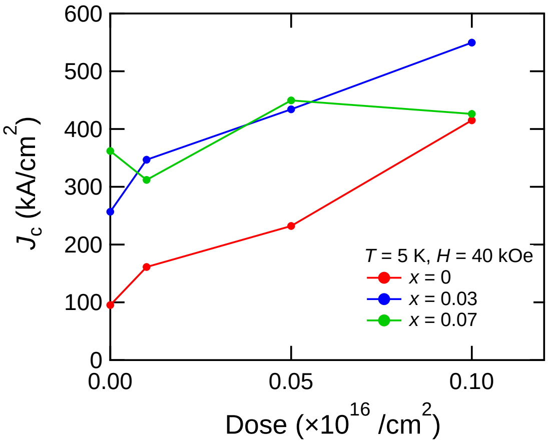

Figure 5. J_c at T = 5 K and H = 40 kOe for $CaK(Fe_{1-x}Co_x)_4As_4$ (x = 0, 0.03, and 0.07) as functions of 3 MeV proton dose.

4. Summary

We have studied the effect of point defects on J_c in $CaK(Fe_{1-x}Co_x)_4As_4$. While substitution of Co for Fe suppresses T_c, it enhances J_c by a factor of up to ~4 at low temperatures. In addition, the non-monotonic temperature dependence of J_c at high fields disappears for samples with $x > 0.03$. After Co substitution, the magnetic field dependence of J_c becomes weaker and shows a dependence characteristic of strong pinning centers. 3 MeV proton irradiation also introduces pinning centers in $CaKFe_4As_4$, and J_c is enhanced by a factor of 4 even at a dose of 0.1×10^{16} ions/cm^2. It also suppresses the non-monotonic temperature dependence of J_c at high fields. When $CaK(Fe_{1-x}Co_x)_4As_4$ is irradiated by 3 MeV protons, at a dose of 0.1×10^{16} /cm^2, J_c is enhanced by a factor of 2 for the sample with $x = 0.03$, while J_c is not enhanced for the sample with $x = 0.07$.

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