Effects of Point Defects Introduced by Co-doping and Proton Irradiation in CaKFe$_4$As$_4$

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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$_4$As$_4$ (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$_4$As$_4$ 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$_4$As$_4$ (1144-type) was found [9]. Its crystal structure is similar to 122-type IBSs. CaKFe$_4$As$_4$ has a tetragonal structure (P4/mmm), where Ca and K layers stack alternatively along the c-axis [9, 10]. CaKFe$_4$As$_4$ 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$_4$As$_4$ 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$_4$As$_4$. We compare effects of two kinds of point defects, chemically and physically introduced, on $J_c$ characteristics in CaKFe$_4$As$_4$.

2. Experimental Methods
CaKFe$_4$As$_4$ and Ca(Fe$_{1-x}$Co$_x$)$_4$As$_4$ 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: 10(1-x) : 10x was placed in a 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 5x10^16 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) magnetization 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](image_url)

**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/(Co9%). 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 $x = 0.07$. 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 $H = 50$ 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 $H^a$ 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, $\alpha$ at 2 K and 10 K are 0.84 and 0.62, respectively. On the other hand, for the sample with $x = 0.03$, $\alpha$ at 2 K and 10 K are 0.65 and 0.56, respectively, and for $x = 0.07$, $\alpha$ 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](image-url)

**Figure 2.** Magnetic field dependences of $J_c$ at different temperatures in CaK(Fe$_{1-x}$Co$_x$)$_4$As$_4$ (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$_x$)$_4$As$_4$ (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$_4$As$_4$ irradiated by 3 MeV protons at doses of (a) $0.01 \times 10^{16} \text{ cm}^2$, (b) $0.05 \times 10^{16} \text{ cm}^2$, and (c) $0.1 \times 10^{16} \text{ cm}^2$. They clearly demonstrate that $J_c$ is enhanced by increasing proton dose up to $0.1 \times 10^{16} \text{ cm}^2$ 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 $0.1 \times 10^{16} \text{ cm}^2$ 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 $0.01 \times 10^{16} \text{ cm}^2$, $\alpha = 0.60$ ($T = 2$ K) and $\alpha = 0.55$ ($T = 10$ K), while it changes to $\alpha = 0.54$ ($T = 2$ K) and $\alpha = 0.52$ ($T = 10$ K) at a dose of $0.1 \times 10^{16} \text{ cm}^2$. 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 $0.1 \times 10^{16}$ cm$^2$.

| 3 MeV H$^+$ 0.01 $\times 10^{16}$ cm$^2$ | 3 MeV H$^+$ 0.05 $\times 10^{16}$ cm$^2$ | 3 MeV H$^+$ 0.1 $\times 10^{16}$ cm$^2$ |
|--------------------------------------|--------------------------------------|--------------------------------------|

(Figure 3) Magnetic field dependences of $J_c$ at different temperatures in CaKFe$_4$As$_4$ irradiated with 3 MeV protons at doses of (a) 0.01 $\times 10^{16}$ cm$^2$, (b) 0.05 $\times 10^{16}$ cm$^2$, and (c) 0.1 $\times 10^{16}$ cm$^2$. (d)-(e) are the double logarithmic plot of $J_c$ vs. $H$. Lines are fitting to the data at 2 K and 10 K at doses of (d) 0.01 $\times 10^{16}$ cm$^2$ and (e) 0.1 $\times 10^{16}$ cm$^2$.

Figures 4 and 5 show the magnetic field dependence of $J_c$ at different temperatures in CaK(Fe$_{1-x}$Co$_x$)$_4$As$_4$ irradiated by 3 MeV protons. It demonstrates that $J_c$ enhancement with the proton irradiation is weaker than that in CaKFe$_4$As$_4$. Actually, with 3 MeV proton irradiation up to $0.1 \times 10^{16}$ 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 $\alpha$ of $J_c$ is summarized in Table 1. $\alpha$ 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 $1 \times 10^{16}$ /cm$^2$ or more demonstrated that $\alpha$ 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, $\alpha$ 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 $\alpha$ of $J_c$.

|                  | pristine | 3 MeV H$^+$ 0.01 $\times 10^{16}$ /cm$^2$ | 3 MeV H$^+$ 0.1 $\times 10^{16}$ /cm$^2$ |
|------------------|----------|--------------------------------------|--------------------------------------|
|                  | $T = 2$ K | $T = 10$ K                          | $T = 2$ K                           | $T = 10$ K                          |
| CaKFe$_4$As$_4$  | 0.84     | 0.62                                | 0.60                                | 0.55                                | 0.54                                | 0.52                                |
| CaK(Fe$_{1-x}$Co$_x$)$_4$As$_4$ | $x = 0.03$ | 0.65                                | 0.56                                | 0.51                                | 0.53                                | 0.54                                | 0.52                                |
| CaK(Fe$_{1-x}$Co$_x$)$_4$As$_4$ | $x = 0.07$ | 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$_x$)$_2$As$_4$ irradiated by 3 MeV protons at doses of (a) $0.01 \times 10^{16}$ cm$^{-2}$ ($x = 0.03$), (b) $0.05 \times 10^{16}$ cm$^{-2}$ ($x = 0.03$), (c) $0.1 \times 10^{16}$ cm$^{-2}$ ($x = 0.03$), (d) $0.01 \times 10^{16}$ cm$^{-2}$ ($x = 0.07$), (e) $0.05 \times 10^{16}$ cm$^{-2}$ ($x = 0.07$), and (f) $0.1 \times 10^{16}$ cm$^{-2}$ ($x = 0.07$). (g)-(j) are the double logarithmic plot of $J_c - H$ in CaK(Fe$_{1-x}$Co$_x$)$_2$As$_4$ irradiated by 3 MeV protons at doses of (g) $0.01 \times 10^{16}$ cm$^{-2}$ ($x = 0.03$), (h) $0.1 \times 10^{16}$ cm$^{-2}$ ($x = 0.03$), (i) $0.01 \times 10^{16}$ cm$^{-2}$ ($x = 0.07$), and (j) $0.1 \times 10^{16}$ 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$_x$)$_2$As$_4$ ($x = 0, 0.03$, 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$_x$)$_4$As$_4$. 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$_4$As$_4$, and $J_c$ is enhanced by a factor of 4 even at a dose of $0.1 \times 10^{16}$ ions/cm$^2$. It also suppresses the non-monotonic temperature dependence of $J_c$ at high fields. When CaK(Fe$_{1-x}$Co$_x$)$_4$As$_4$ is irradiated by 3 MeV protons, at a dose of $0.1 \times 10^{16}$/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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