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# INVESTIGATION OF THE EFFECT OF SLOW NEUTRON IRRADIATION ON HALOGEN-DOPED HIGH-$T_C$ SUPERCONDUCTORS AND ITS MECHANISM*

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Irradiation effect of low-fluence ($\sim 10^8$ n/cm$^2$) slow neutrons on halogen-doped superconductors is presented in this paper. And the mechanism of the effect is also described from the viewpoint of nuclear physics for both fast and slow neutrons on high-temperature superconductors (HTSC). It is shown experimentally and theoretically that slow neutrons of low fluence has a similar irradiation effect to that of fast neutron beams with an energy $E_n > 0.1$ MeV and fluence $10^{16} - 10^{18}$ n/cm$^2$. However, quite different mechanisms are involved in them: Fast neutrons transfer their energies through elastic scattering in HTSC, whereas slow neutrons give off their energies during the slow neutron capture (n, $\gamma$) reaction.

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## I. INTRODUCTION

One of the critical factors for the practical applications of high temperature superconductors is to introduce effective pinning centers, which will thus increase the critical current density. Irradiation has been well established as a controllable way to increase the pinning center concentration. Experiments showed that neutron irradiation is not only more convenient but also more effective than electron, proton and ion irradiations. The 1 MeV neutrons can generate displaced atoms 2000 times as many as those generated by electrons of the same energy in the high-$T_c$ superconductors (HTSC)[1], and the flux pinning force created by neutron-irradiation induced defects is at least 1000 times greater than that by electron or proton induced ones[2].

Flux-pinning effects are greatly enhanced in the HTSC subjected to neutron irradiation, among which are included the fall of $J_c$ anisotropy, the shift of the irreversibility line to

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higher field and temperature, and the remarkable increase of $J_c$[2]; therefore, neutron irradiation has become a hot subject in the investigation of vortex dynamics. So far in most neutron irradiation experiments, nuclear reactor has been used as the source of neutrons[2-8], with energies greater than 0.1 MeV and fluence between $10^{16}-10^{18}$ n/cm$^2$. The complicated facility is difficult to shield and control, so they cannot be introduced to ordinary laboratories. In this work we study the irradiation effect of slow neutrons from an isotope neutron source at a low fluence of about $10^8$ n/cm$^2$ on HTSC, expecting to explore the mechanism of the effect from every aspect. It is found that both low-fluence slow neutrons and high-fluence fast neutrons are capable of enhancing flux pinning centers and critical current densities[9, 10].

Neutron irradiation effect is dertermined by the interaction between neutrons and superconducting materials. This interaction has nuclear properties, its strength being propotional to the nuclear reaction probability, i. e. cross section. According to the nuclear data for neutrons published recently by nuclear data center of Brookhaven National Laboratory[11], we note that nuclides $^{19}_{9}$F, $^{35}_{17}$Cl, and $^{127}_{53}$I have a total cross section with slow neutrons, $\sigma_{tot}$, close to or much greater than $^{16}_{8}$O (see Table 1), so a little amount of halogen doping can strengthen the irradiation effect of slow neutrons considerably.

**Table 1.** Total cross sections of O, F, Cl and I with slow neutrons.

| Nuclide | Percent abundance | $\sigma_{tot}$ (b) (0.01 eV$<E_n<$100 eV) |
|---|---|---|
| $^{16}_{8}$O | 99.76 | 4.05 – 3.75 |
| $^{19}_{9}$F | 100 | 3.9 – 3.65 |
| $^{35}_{17}$Cl | 75.97 | 56 – 5.5 |
| $^{127}_{53}$I | 100 | 13 – 4 |

Lagraff *et al.*[12] found, by X-ray and neutron diffraction analyses of F-doped samples, that F ions occupied oxygen vacancies, thus increased the carrier density and improved superconductivity. Moreover, much work has been done of the irradiation effect on pure YBCO samples. But to our knowledge, no such work has been done for anion-doped samples, for example, the halogen-doped Y-system superconductors.

## II. EXPERIMENTAL

The halogen-doped $YBa_2Cu_3O_{6+x}M_y$ ($M$ = F, Cl and I) samples were prepared by citrate pyrolysis. Since the raw materials for sample preparation are ultrafine particles, the process of thorough mixing and the subsequent sintering yields compact single-phase polycrystals with exact nominal composition, having a $T_c$ of about 91 K and a better morphology than that of the samples prepared by solid state reaction. Figure 1 shows the SEM micrographs of $YBa_2Cu_2O_{6+x}$ samples prepared by citrate pyrolysis and by solid state reacton for comparison.

X-ray analysis indicated that the samples prepared by citrate pyrolysis contain predominantly the orthorhombic 123 phase. Lattice constants of pure YBCO samples evaluated by Cohen's method from XRD data are $a$=3.822 Å, $b$=3.882 Å, and $c$=11.662 Å.

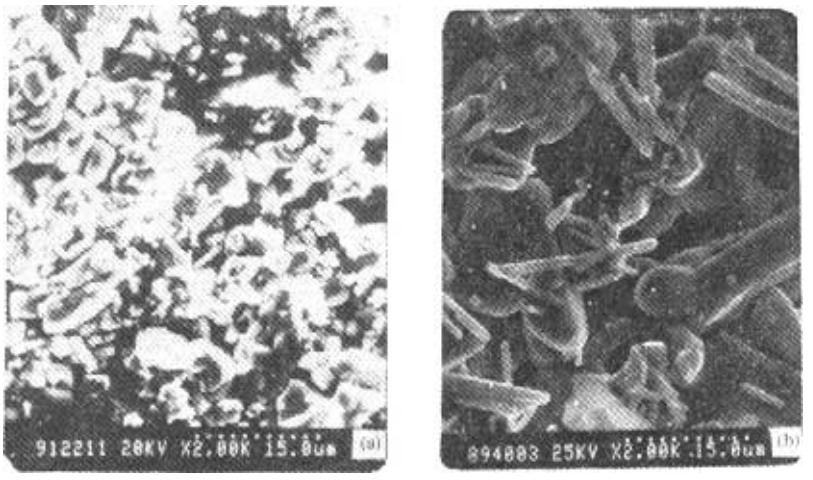

**Fig. 1.** SEM micrographs of $YBa_2Cu_3O_{6+x}$ samples (a) by citrate pyrolysis (b) by conventinal sintering process.

In the irradiation we used a 1 Ci Am-Be isotope source with an emissivity of $2.2 \times 10^6$ n/Ci · S, an average energy of 4.5 MeV, and a half period of 433 years. Neutron beams from the Am-Be source, which were slowed down by a deliberately-designed moderator acting upon the sample surface at room temperature. The total fluence of the slow neutron irradiation adds up to $5.18 \times 10^8$ n/cm$^2$ in this work.

Beckurtz *et al.* [13] pointed out that neutrons can reach approximately an equilibrium with the environment whenever they are moderated in bulk medium with little or no absorption. It follows that the energy of slow neutrons obeys Boltzmann distribution

$$f(E_n) = \frac{2}{\sqrt{\pi}\, kT} \sqrt{\frac{E_n}{kT}}\, e^{-E_n/kT},$$

where $E_n$ is the neutron energy, $k$ Boltzmann constant and $T$ the temperature of the medium. In the experiment the ratio of neutrons with $E_n < 0.5$ eV to those with $E_n > 0.5$ eV is 5 : 1, so the neutrons used in this experiment are in the range of slow neutrons.

## III. RESULTS

We measured the magnetic hysteresis loops of $YBa_2Cu_3O_{6+x}M_y$ ($M$ = F, Cl and I, $y$ = 0.01, 0.1; 0.05 and 0.05) samples at 77 K before and after the neutron irradiation with a

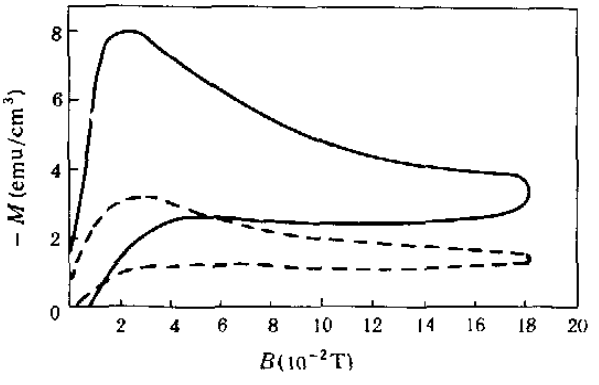


**Fig. 2.** Magnetic hysteresis loop of $YBa_2Cu_3O_{6+x}Cl_{0.05}$ sample before (– – –) and after (——) irradiation at 77 K.

vibrating samle magnetometer. Figure 2 is for $Cl_{0.05}$ (it stands for $YBa_2Cu_3O_{6+x}Cl_{0.05}$ hereafter) sample, and the hysteresis width can be seen broadened substantially after the irradiation. The other three samples have similar changes, as shown in Fig. 2. According to Bean model[14],

$$J_c = \frac{20(M^- - M^+)}{d},$$

where $M^+$ and $M^-$ (emu/cm$^3$) are magnetizations in the increasing and decreasing field branches, $d$(cm) is the average diameter of the grains in the sample, which was determined by SEM morphology.

The relationships between the derived $J_c$ and applied field $B$ for different samples $\varepsilon$ :

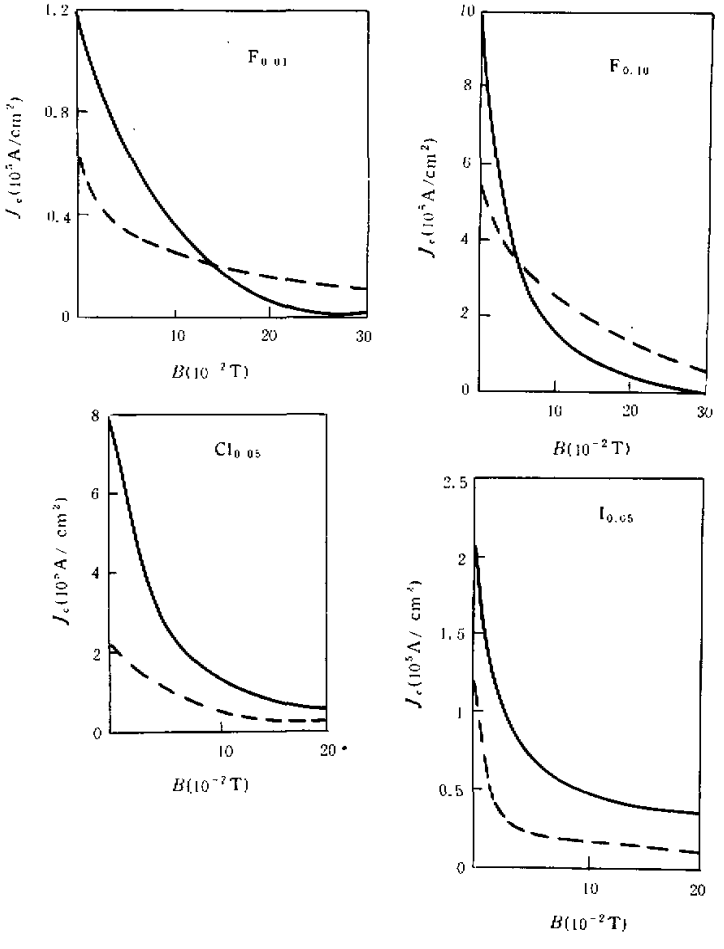


Fig. 3. Magnetization $J_c$ as a function of $B$ for different samples before (– – –) and after (——) irradiation.

shown in Fig. 3. The critical current density increases greatly in slow-neutron irradiated samples, especially the $Cl_{0.05}$ sample. Furthermore, the slow neutron irradiation decreases the normal state resistance $R$, for example, over 80% in F-doped samples. The values of $J_c$ and $R$ prior to and after the irradiation are listed in Table 2.

**Table 2.** $J_c$ and $R$ of $YBa_2Cu_3O_{6+x}M_y$ ($M$ = F, Cl, and I) before and after irradiation.

| Sample | $J_c$ (0 T, 77 K) ($\times 10^5$ A/cm$^2$) | | | $R$(m$\Omega$) | | | Percentage of drop of $R$ |
|---|---|---|---|---|---|---|---|
| | Nonirr. $J_{ci}$ | Irr. $J_{cf}$ | $J_{cf}/J_{ci}$ | Nonirr | Irr | $\Delta R$(m$\Omega$) | |
| $F_{0.01}$ | 0.64 | 1.2 | 1.88 | 23.2 | 4.6 | −18.6 | 80 |
| $F_{0.10}$ | 6.0 | 10.0 | 1.67 | 26.0 | 5.0 | −21.0 | 81 |
| $Cl_{0.05}$ | 2.20 | 8.00 | 3.64 | 16.6 | 4.0 | − 6.6 | 40 |
| $I_{0.05}$ | 1.15 | 2.15 | 1.87 | 12.0 | 7.2 | − 4.8 | 40 |

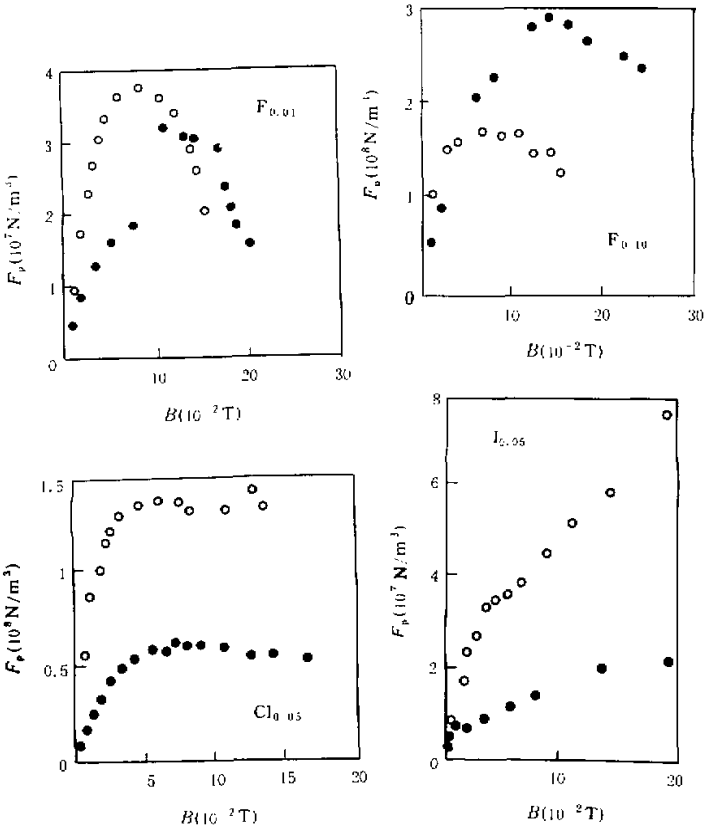


**Fig. 4.** Volume pinning force *vs* applied field for different samples before (·) and after (∘) irradiation at 77 K.

Flux pinning force per unit volume as a function of field induction was derived from $F_p = J_c \times B$ and is illustrated in Fig. 4. The neutron-irradiated samples evidently have a larger pinning force, indicating the presence of a series of new strong pinning centers, i. e. irradiation-induced defects[9, 10].

## IV. DISCUSSION

Bechtold *et al.*[2] studied systematically the relationship between the increase in $J_c$ and the dimension of irradiation-induced defects in $YBa_2Cu_3O_{6+x}$ samples, for electron, proton and neutron irradiation of different energies, and they found that the most effective pinning centers have a size of 30 – 100 Å (at least over 10 – 20 Å), based on the flux-pinning model and the measurement of coherence length of superconductors. Fast neutrons have stronger irradiation effects because they can produce larger defects in the sample, while electrons and protons can only produce such small defects that they are not clearly detectable even under TEM.

The TEM image (Fig. 5(b)) of a neutron-irradiated $YBa_2Cu_3O_{6+x}F_{0.1}$ sample shows some defects of 30 – 100 Å in size, which may become effective pinning centers. Therefore, the main cause for the increase of $J_c$ and $F_p$ due to slow-neutron irradiation can be attributed to these new pinning centers.

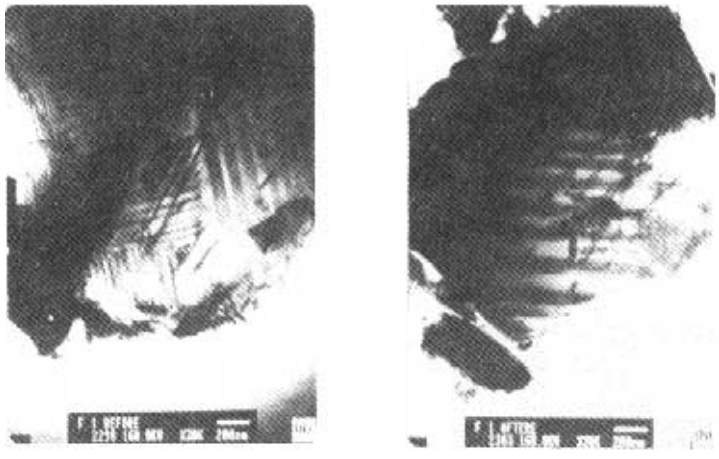

**Fig. 5.** TEM bright-field images of $YBa_2Cu_3O_{6+x}F_{0.1}$ samples before (a) and after (b) irradiation.

In addition, neutron beams can make the oxygen vacancies more uniformly distributed, consequently the phase fractions of metal, superconductor and semiconductor are adjustable and the superconducting volume fraction is increased in the samples with oxygen vacancy concentration lower than the optimum value. Superconducting percolating networks (filamentary

superconductors)[15] have been found to form, and this is one of the reasons why $R$ decreases as $J_c$ is increased. Another factor responsible for the drop in the normal resistance $R$ is that the slow neutrons could improve the superconductor-insulator-superconductor (SIS) conjunction in the intergranular weak links and depress the Coulomb potential at grain boundaries and consequently favor the electron tunneling.

Because of overdose of irradiation, part of defects due to irradiation will overlap to form irradiation-damaged areas (possibly F-rich regions), depressing the superconductivity of the samples.

The experimental results by Bechtold *et al.*[2] showed that the ionization energy loss is not essential to different types of particle irradiation over a broad range of energy. The irradiation effect determined by the density of total displaced atoms in the sample, which is proportional to the average recoil energy $\overline{E}_p$ of atoms collided at the initial stage. Moreover, the dimension of the defects is also an increasing function of $\overline{E}_p$.

In fast neutron irradiation, neutrons with energies from 1 to 200 keV[16] can create defects with the required size. According to nuclear physics the threshold energies of inelastic scattering of nuclides $^{89}_{39}Y$, $^{138}_{56}Ba$, $^{63}_{29}Cu$, $^{65}_{29}Cu$ and $^{16}_{8}O$ are 0.8, 0.3923, 0.6803, 0.7828, and 6.047 MeV, respectively. As for the $\gamma$-capture $(n, \gamma)$ reaction, its cross section $\sigma_{n,\gamma}$ follows a $1/V$ law ($V$ is the velocity of neutron), and for fast neutrons $\sigma_{n,\gamma}\approx 0$. Therefore, 1 – 200 keV fast neutrons can only have elastic scattering interaction, and in this case the (primary) recoil energy $E_{pf}$ transferred to a nuclide is

$$E_{pf}=\frac{4A}{(1+A)^2}\cos^2\theta E_n ,$$

where $A$ is the atomic mass of the recoil nucleus in atomic mass unit, $\theta$ the angle between the direction of recoil nucleus and that of the incident neutrons. Averaging the above equation over the directions, one gets $\overline{E}_{pf}=\frac{1}{2}E_{pf}$, as listed in Table 3 for each nucleus.

Slow neutrons, as we used in the irradiation, have quite lower energy than fast neutrons, so they can transfer too small an energy to the nucleus in the elastic collision to yield effective pinning centers. Nevertheless, the cross section of the slow neutron capture reaction (n, $\gamma$) $\sigma_{n,\gamma}$ is greatly increased according to $1/V$ law. Each neutron has an average binding energy of about 8 MeV, hence it is energetically favorable for the slow neutrons to be captured.

**Table 3.** $Q$, $\overline{E}_{pf}$ and $E_{ps}$ of the (n, $\gamma$) reaction of Y, Ba, Cu and halogens F, Cl and I.

| Nuclide | Percent abundance | $Q$(MeV) | $E_{ps}$ (keV) | $\overline{E}_{pf}$(keV) |
|---|---|---|---|---|
| $^{19}_{9}F$ | 100 | 6.60 | 1.17 | 0.10 – 19 |
| $^{35}_{17}Cl$ | 75.97 | 8.58 | 1.10 | 0.06 – 11 |
| $^{127}_{53}I$ | 100 | 6.80 | 0.19 | 0.02 – 3 |
| $^{16}_{8}O$ | 99.76 | 4.14 | 0.54 | 0.11 – 22 |
| $^{63}_{29}Cu$ | 69.09 | 7.91 | 0.53 | 0.03 – 6 |
| $^{65}_{29}Cu$ | 30.91 | 7.07 | 0.41 | 0.03 – 6 |
| $^{89}_{39}Y$ | 100 | 6.86 | 0.28 | 0.02 – 4 |
| $^{138}_{56}Ba$ | 71.66 | 4.72 | 0.09 | 0.02 – 3 |

Following relativistic kinetics, the nuclear reaction energy $Q$ and the energy transferred to the recoil nuclei, $E_{ps}$, for all elements in halogen-doped YBCO are calculated and tabulated in Table 3.

It is interesting to note from Table 3 that $E_{ps}$ falls in the range of $E_{pf}$ for 1 ~200keV fast neutrons. This leads naturally to the interpretation of the fact that quite large effective pinning centers are formed in both kinds of irradiation, as confirmed in the TEM bright-field image in Fig. 5, though quite different mechanisms are involved. In fast neutron irradiation the energy is transferred through elastic interaction, whereas the energy is given off in the slow neutron-capture reaction in slow neutron irradiation.

The cross sections $\sigma_{n,\gamma}$ of nuclides $^{19}_{8}$F and $^{35}_{17}$Cl are 50 and $2\times10^5$ times larger than that of $^{16}_{8}$O in (n, γ) reaction, respectively[11]. The energy transferred to F and Cl is nearly doubled compared to that to O in the slow neutron capture reaction (Table 3), so samples with a little amount of halogen doping may help to generate more pinning centers in them during the slow neutron irradiation, resulting in significant enhancement of $J_c$.

If the multiple scattering is neglected in the following, the probability $P$ of neutrons remaining in the sample of a thickness $x$ satisfies the exponential relation

$$P=1-e^{-\alpha_{tot}Nx}.$$

Here $N$ is the nuclear density, $\sigma_{tot}$ the total corss section of a neutron. According to the nuclear data for neutrons[11], $\sigma_{tot}$ increases significantly with decreasing $E_n$, thus a slow neutron has a much greater probability to stay in the sample than a fast one.

The duration of neutrons in the superconductors is $t \sim \frac{1}{\sqrt{E_n}}$ on neglecting the secondary and higher order scattering, and there would be 2 ~3 order-of-magnitude difference between the duration of fast and slow neutrons, and in turn the reaction chance of slow neutrons is increased additionally.

Actually the neutrons would be scattered many times in the sample. Wave properties can be applied to the elastic scattering of neutrons. De Broglie wavelength of slow neutrons is about $10^{-8}$cm, much greater than the nucleus radii, so the scattering of slow neutrons tends to be approximately isotropic. Nevertheless, the angular distribution of elastic scattering of fast neutrons is much concentrated on the forward direction, so that for slow neutrons the time of elastic interactions is much greater, that is to say, the transfer mean-free path is shorter and the reaction chance is increased.

In summary, slow neutron beams have a much greater propability of interaction, hence the slow neutrons of low fluence and fast neutrons of high fluence give rise to similar irradiation effects.

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