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RAPID COMMUNICATION

Different behavior of upper critical field in $Fe_{1-x}Se$ single crystals*

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The temperature dependences of upper critical field (H_{c2}) for a series of iron-deficient $Fe_{1-x}Se$ single crystals are obtained from the measurements of in-plane resistivity in magnetic fields up to 9 T and perpendicular to the *ab* plane. For the samples with lower superconducting transition temperature T_c (< 7.2 K), the temperature dependence of H_{c2} is appropriately described by an effective two-band model. For the samples with higher T_c ($\gtrsim 7.2$ K), the temperature dependence can also be fitted by a single-band Werthamer–Helfand–Hohenberg formula, besides the two-band model. Such a T_c-dependent change in $H_{c2}(T)$ behavior is discussed in connection with recent related experimental results, showing an inherent link between the changes of intrinsic superconducting and normal state properties in the FeSe system.

Keywords: iron-deficient $Fe_{1-x}Se$ superconductors, upper critical field, magnetoresistivity

PACS: 74.70.Xa, 74.25.Op, 74.62.–c, 74.25.F– **DOI:** 10.1088/1674-1056/ab50b4

Among iron-based superconductors, the binary FeSe is the simplest in crystal structure and has been shown to display unique superconducting- and normal-state properties.[1,2] Study of the behavior of upper critical field (H_{c2}) can provide valuable information about the superconducting state. In a recent work,[3] H_{c2} of exfoliated FeSe thin flakes with varying superconducting transition temperature T_c has been studied, where T_c is suppressed by reducing the thickness of the flakes. However, previous studies of H_{c2} of bulk FeSe[4–7] were carried out mainly on the single crystals with a constant T_c (~ 9 K at ambient pressure). It is because these FeSe single crystals were grown by chemical vapor transport or other flux methods, so it was not easy to tune the electronic structure and superconducting property. So far, the measurements of upper critical field of the bulk samples with various T_c are still lacking. Recently, we have developed a hydrothermal ion-deintercalation (HID) method,[8] which is capable of producing phase-pure and sizable $Fe_{1-x}Se$ single crystals, and tuning the T_c from zero up to 9 K as well. Such a series of $Fe_{1-x}Se$ single crystals with tunable T_c provides a superior platform for experimentally studying the evolution of physical properties in the normal and superconducting states of the FeSe system.[9]

Here we report the different behavior of upper critical field $H_{c2}(T)$ observed in this series of $Fe_{1-x}Se$ single crystals from the magnetoresistivity measurements, with the applied field H parallel to the crystallographic *c*-axis. Interestingly, we find that, for the $Fe_{1-x}Se$ single crystals of $T_c < 7.2$ K, the temperature dependence of H_{c2} is appropriately described by an effective two-band model. For the samples of $T_c \gtrsim 7.2$ K, the temperature dependence can also be fitted by a single-band Werthamer–Helfand–Hohenberg (WHH) formula, in addition to the two-band model. We discuss that such a T_c-dependent change in the $H_{c2}(T)$ behavior of the FeSe system is inherently linked to a corresponding change in the normal-state properties just above T_c.

The single crystals of $Fe_{1-x}Se$ series studied here were synthesized by the HID method[8] (see also the schematic illustration of the HID process in Fig. 1(a)). These $Fe_{1-x}Se$ single crystals were characterized as nonstoichiometric, with just a few percent amount of variation in the Fe-deficiency x.[9] The in-plane electrical resistivity was measured in magnetic fields up to 9 T on a Quantum Design PPMS-9. The magnetic susceptibility measurements were carried out on a SQUID magnetometer (Quantum Design MPMS-XL1). The x-ray diffraction (XRD) experiments were performed at room temperature on Rigaku Ultima IV diffractometer. As can be seen from Fig. 1(b), all the $Fe_{1-x}Se$ single crystals exhibit a single preferred (001) orientation. And all the samples show a sharp superconducting transition and 100% superconducting shielding signal (see Fig. 2(a) for representative samples),

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indicating good quality and bulk superconductivity of the samples. The T_c of the $Fe_{1-x}Se$ samples was characterized by the onset temperature of superconducting transition in magnetic susceptibility, as shown in Fig. 2(a). Here H7.8, H6.4, and H4.6 stand for the representative HID $Fe_{1-x}Se$ single crystals with $T_c = 7.8$ K, 6.4 K, and 4.6 K, respectively.

The superconductivity of all the $Fe_{1-x}Se$ single crystal samples was further characterized by measuring the in-plane resistivity $\rho(T)$ under various magnetic fields up to 9 T, with the fields parallel to the c-axis. The corresponding data for the representative $Fe_{1-x}Se$ samples H7.8, H6.4, and H4.6 are shown in Figs. 2(b)–2(d), respectively. It is obvious that both the onset superconducting transition temperature (T_c^{onset}) in resistivity and the onset zero resistivity temperature shift simultaneously to lower temperatures with increasing magnetic field. Accordingly, there is no significant magnetic-field-induced broadening of the resistive transition, which is similar to the cases of FeSe-based "11" (Fe(Se, Te), Fe(Te, S))[10,11] and FeAs-based "122" ($BaFe_{2-x}Ni_xAs_2$)[12] superconductor systems. But this contrasts with FeSe-based "11111" ($Li_{1-x}Fe_xOHFe_{1-y}Se$)[13,14] and FeAs-based "1111" ($LnFeAsO_{1-x}F_x$, Ln = Nd, Sm) superconductors,[15,16] as well as cuprate superconductors.[17,18] In those iron-based and cuprate compounds, substantial broadening of their superconducting transitions with increasing magnetic field has been observed. It is therefore indicated that the field induced vortex-liquid state in the present $Fe_{1-x}Se$ superconductors is negligible or exists only in a much narrower temperature range, as compared with those iron selenide/arsenide and cuprate superconductors.

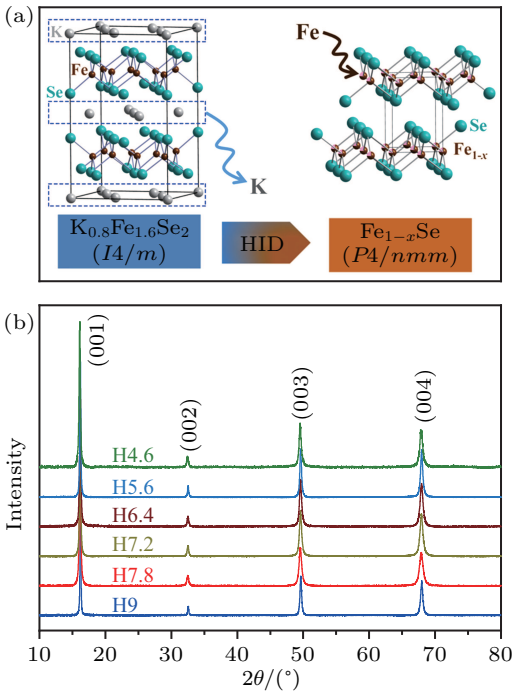


Fig. 1. (a) Schematic illustration of the soft-chemical HID method.[8] The $Fe_{1-x}Se$ single crystals are derived from the readily obtainable phase-pure matrix single crystals of $K_{0.8}Fe_{1.6}Se_2$ through the HID process. The original interlayer K ions and Fe vacancies (20% in concentration) in $K_{0.8}Fe_{1.6}Se_2$ are completely de-intercalated and substantially reduced, respectively, yielding the target $Fe_{1-x}Se$ single crystals with the left-over disordered Fe-vacancies of just a few percent in the concentration x.[9] (b) XRD θ–2θ scan indicates a single preferred (001) orientation for all the $Fe_{1-x}Se$ single crystal samples.

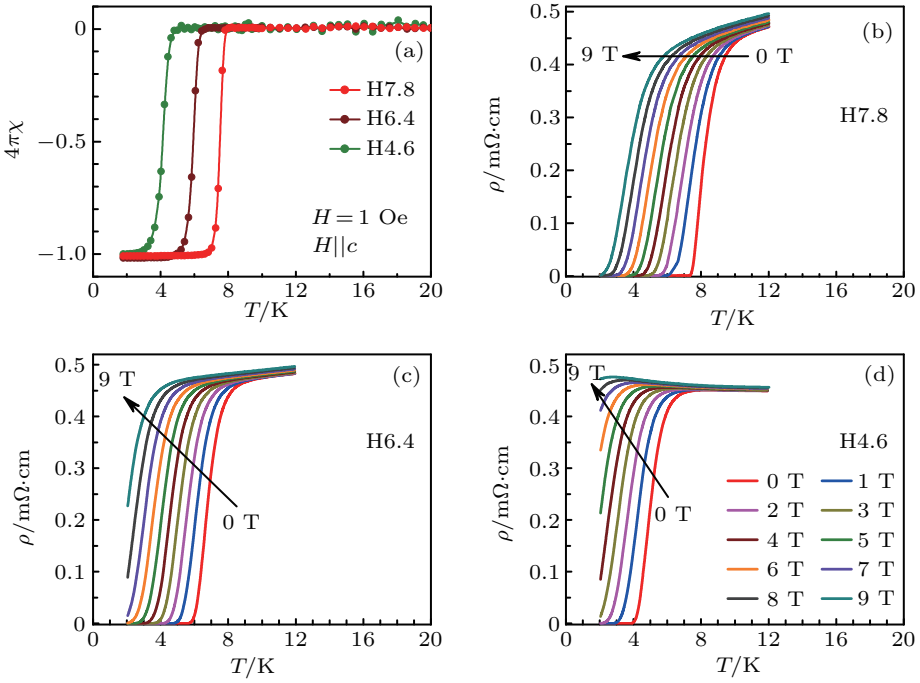


Fig. 2. (a) Temperature dependences of magnetic susceptibility near the superconducting transitions for the representative $Fe_{1-x}Se$ single crystal samples H7.8, H6.4, and H4.6. The data were measured in zero-field cooling mode and corrected for demagnetization factor. (b)–(d) Temperature dependences of in-plane resistivity near the superconducting transitions for these samples, measured under various magnetic fields up to 9 T, with the fields parallel to the c-axis.

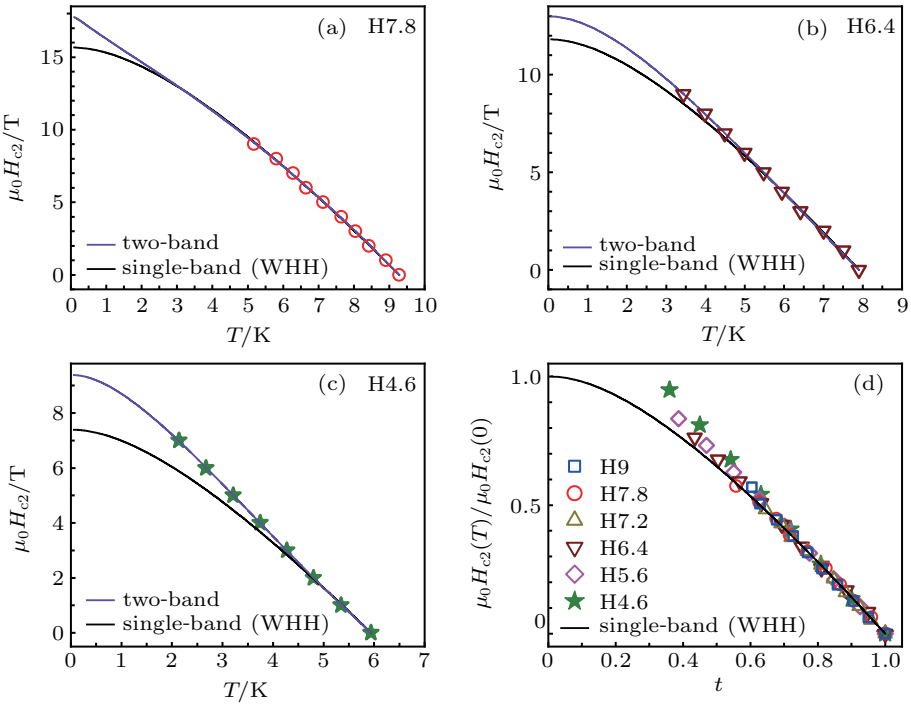


Fig. 3. (a)–(c) Temperature dependences of the upper critical field H_{c2} from the magnetoresistivity measurements, and corresponding fittings by the two-band (violet curves) and single-band WHH (black curves) models, for the representative samples. (d) Reduced upper critical field $H_{c2}(T)/H_{c2}(0)$ as a function of reduced temperature $t = T/T_c^{onset}$ for all the $Fe_{1-x}Se$ single crystal samples.

The temperature dependences of H_{c2} are extracted from the magnetoresistivity measurements for all the $Fe_{1-x}Se$ single crystals, the data for the representative samples are shown in Figs. 3(a)–3(c). Here the upper critical field H_{c2} is defined as 90% of the normal-state resistivity just above T_c at the temperature of initial upturn in the temperature derivative of resistivity, $d\rho(T)/dT$. We find that H_{c2} of the $Fe_{1-x}Se$ single crystals with $T_c < 7.2$ K shows a nearly linear temperature dependence. However, for the $Fe_{1-x}Se$ samples with $T_c \gtrsim 7.2$ K, the temperature dependence of H_{c2} exhibits a weakly downward-bend tendency. Accordingly, the behavior of $H_{c2}(T)$ of the lower-T_c (< 7.2 K) $Fe_{1-x}Se$ is more appropriately described by a two-band model[19] rather than the single-band WHH formula,[20] while that of the higher-T_c ($\gtrsim 7.2$ K) $Fe_{1-x}Se$ can be fitted by both the two-band and single-band models, as shown in Figs. 3(a)–3(c). In Fig. 3(d), we summarize the experimental data of $H_{c2}(T)$ for all the $Fe_{1-x}Se$ single crystals by a plot of reduced upper critical field $H_{c2}(T)/H_{c2}(0)$ versus reduced temperature $t = T/T_c^{onset}$. This reduced plot clearly shows the deviation from the single-band WHH fitting of the lower-T_c $Fe_{1-x}Se$ samples.

It has been shown that, in the exfoliated FeSe flakes, T_c is suppressed from ~ 9 K in the bulk samples to ~ 7 K in the thick (100 nm) flakes resembling the bulk behavior, and to $\lesssim 4$ K in the thinnest (14 nm) flakes characteristic of a reduced two-dimensionality.[3] However, the temperature dependence of H_{c2} (extracted also from the magnetotransport data with field H parallel to c-axis) can be fitted by the single-band WHH model for both the higher-T_c (~ 7 K) thick and lower-T_c ($\lesssim 4$ K) thinnest FeSe flakes. We note that the present T_c-dependent $H_{c2}(T)$ behavior is observed in the $Fe_{1-x}Se$ single crystals, which are characterized as bulk materials as compared with the exfoliated FeSe thin flakes.

It needs to be pointed out that the bulk FeSe system has been characterized as a nearly compensated semimetal in the normal state.[1,2,9] Therefore, the two-band model could be inherently more appropriate for describing the temperature dependence of the upper critical field, rather than the single-band WHH formula. Here we recall that signs of two-gap behavior in $H_{c2}(T)$ were also observed in iron arsenide $LaFeAsO_{0.89}F_{0.11}$ superconductor.[21] However, the results of two-band fitting were insensitive to the choice of the fitting parameters. In the present case of $Fe_{1-x}Se$ series, both the field and temperature spans of our experimental data are smaller, which do not allow the two-band fittings to yield the definite parameters either, including the diffusivity ratio η ($= D_2/D_1$) and coupling constants $\lambda_{i,j}$ ($i, j = 1$ or 2). But, it is qualitatively definite that the $H_{c2}(T)$ behavior changes in FeSe system depending on T_c.

The change in the behavior of upper critical field observed here can be further discussed in connection with our most recent transport study of the same series of $Fe_{1-x}Se$ single crystals.[9] It has been shown that, at low temperatures just above T_c, the hole-channel is more conductive than the electron-channel in the $Fe_{1-x}Se$ samples with the higher T_c. However, as the T_c of the $Fe_{1-x}Se$ samples is reduced, the contributions from the hole- and electron-channel become gradually comparable to each other. Therefore, in the $Fe_{1-x}Se$ sam-

ples of the higher T_c, the hole contribution predominates in the electronic conduction at low temperatures just above T_c, as compared with the samples of the lower T_c. In this sense, it is not surprising that, for the higher-T_c ($\gtrsim 7.2$ K) $Fe_{1-x}Se$ single crystals, the single-band WHH formula can also well fit to the temperature dependence of H_{c2}, and give the $H_{c2}(T)$ values at zero temperature consistent with previously reported results, while it is no longer suitable for the $Fe_{1-x}Se$ samples of the lower T_c (< 7.2 K).

Furthermore, given the applicability of the single-band WHH model in the $Fe_{1-x}Se$ samples of higher T_c, the initial slope of $H_{c2}(T)$ can be related to the effective mass m^*,[22] as $(-1/T_c^{\rm onset})(dH_{c2}/dT)|_{T=T_c^{\rm onset}} \propto (m^*)^2$. The corresponding values obtained from this simple picture for the $Fe_{1-x}Se$ samples are 0.22 T/K^2 for H9, 0.26 T/K^2 for H7.8, and 0.29 T/K^2 for H7.2. Namely, T_c is reduced as the effective mass is enhanced, an evident non-BCS superconductivity character. Here it is also important to note that our recent study of this Fe-deficient $Fe_{1-x}Se$ series[9] has revealed the strong enhancement of electronic correlation in the lower-T_c samples, particularly at low temperatures near T_c. By comparison, the scatterings from the disordered Fe-vacancies with quite a small concentration (just a few percent in x) have trivial effects on the strongly interacting quasiparticles. These results again point to a close correspondence between the intrinsic superconducting and normal state properties in the $Fe_{1-x}Se$ samples.

To summarize, our results highlight the change in upper critical field behavior in the FeSe system, which is intimately connected with the change in the normal-state properties just above T_c. These results have important implication for forthcoming investigation of the key ingredient for superconductivity. In particular, a microscopic interpretation of these important observations, including that from the related electronic structure, calls for further studies by various probes.

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