LETTER

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To cite this article: J. P. Sun et al 2020 EPL 130 67004

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Pressure-induced second high-\(T_c\) superconducting phase in the organic-ion-intercalated (CTA)\(_{0.3}\)FeSe single crystal

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received 21 April 2020; accepted in final form 17 June 2020
published online 21 July 2020

PACS 74.25.Dw - Superconductivity phase diagrams
PACS 74.70.-b - Superconducting materials other than cuprates

Abstract – Whether the pressure-induced second high-\(T_c\) superconducting phase (SC-II) is a universal phenomenon among the intercalated FeSe-derived superconductors deserves further investigations. Here, we report a high-pressure ac magnetic susceptibility study on the newly synthesized organic-ion-intercalated (CTA)\(_{0.3}\)FeSe single crystal, which has a high \(T_c\) \(\approx 45\) K at ambient pressure. We found that the superconducting transition is quickly suppressed to below 20 K upon increasing pressure to \(P_c \approx 2\) GPa, above which the SC-II phase emerges and its \(T_c\) increases gradually to a maximum of ca. 40 K at 5 GPa. For \(P > 5\) GPa, both \(T_c\) and the superconducting volume decline quickly, presumably due to the collapse of the hybrid structure against the higher pressure. Nevertheless, our results indeed evidenced the pressure-induced SC-II phase in (CTA)\(_{0.3}\)FeSe, in reminiscent of the situations observed in (Li,Fe)OHFeSe and Li\(_{0.36}\)(NH\(_3\))\(_2\)FeSe\(_2\). These results thus demonstrate that pressure-induced SC-II phase should be a universal phenomenon in the electron-doped intercalated FeSe-based superconductors.

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Introduction. – Recently, much attention has been paid to the FeSe-based superconductors due to the unique electronic structure and the wide range tunability of the superconducting transition temperature \(T_c\) within a simple structural framework. Bulk FeSe has a relatively low \(T_c\) \(\approx 8.5\) K at ambient pressure [1]. Interestingly, its \(T_c\) can be enhanced substantially to over 40 K through electron doping, which has been successfully realized via the interlayer intercalation (such as \(A_x\)Fe\(_{2-y}\)Se\(_2\) \((A = K, Rb, \ldots)\) [2,3], Li\(_x\)(NH\(_3\))\(_y\)Fe\(_2\)Se\(_2\) [4], and \((\text{Li,Fe})\)OHFeSe [5,6]), interface coupling or charge transfer in monolayer FeSe/SrTiO\(_3\) [7], surface K doping on thin films [8,9], or field-effect transistor gate-voltage regulation [10]. Very recently, much effort has been devoted to develop purely organic-ion-intercalated materials, such as (CTA)\(_{0.3}\)FeSe, with much larger interlayer distance and enhanced \(T_c\) [11]. Among the FeSe-derived bulk materials, however, the highest \(T_c\) achieved at ambient pressure remains below 50 K, and their \(T_c\) will decline or the sample even becomes insulating in the overdoped regime [12,13].

Given the inhibition to further raising \(T_c\) by electron doping, it is necessity to look for alternative means. The application of high pressure is always an important approach. Recent high-pressure studies on several intercalated FeSe-based materials, including \(A_x\)Fe\(_{2-y}\)Se\(_2\) \((A = K, Rb, \ldots)\) [14], Cs\(_{0.4}\)(NH\(_3\))\(_y\)FeSe [15], \((\text{Li,Fe})\)OHFeSe [16] and Li\(_x\)(NH\(_3\))\(_y\)FeSe\(_2\) [17], have evidenced the emergence of a second high-\(T_c\) superconducting phase above a critical pressure \(P_c\). Here, we denoted it as SC-II phase to distinguish from the ambient-pressure high-\(T_c\) SC-I
phase achieved via electron doping. The highest $T_c$ in the SC-II phase is usually about 10 K higher than that in the SC-I phase. Especially, we have achieved a record high $T_c(\text{onset}) \approx 55$ K in the SC-II of Li$_x$(NH$_3$)$_y$Fe$_2$Se$_2$ single crystal with a high electron doping level [17]. More interestingly, we found that the normal state of (Li,Fe)OHFeSe exhibits a sharp transition from a Fermi-liquid behavior for SC-I to a non-Fermi-liquid behavior for SC-II phase, which indicates that these two superconducting phases might have different pairing symmetry [16]. These results demonstrated that the application of high pressure can play a vital role to tune the normal- and superconducting-state properties of intercalated FeSe-derived materials.

To check whether the pressure-induced SC-II phase is a universal phenomenon among the intercalated FeSe-based superconductors, we turn to the newly synthesized organic-ion-intercalated (CTA)$_{0.3}$FeSe single crystal, which has an optimal $T_c \approx 45$ K at ambient pressure. The preliminary high-pressure measurements in ref. [11] have shown that its $T_c$ decreases to $\sim 40$ K at 1 GPa. By performing high-pressure ac magnetic susceptibility measurements up to 11 GPa, we indeed observed the reemergence of SC-II phase at a relatively low $P_c \approx 2$ GPa, similar with other intercalated FeSe-based superconductors mentioned above. Our present work thus demonstrate that pressure-induced SC-II phase should be a universal phenomenon among the intercalated FeSe-based materials.

Materials and methods. – The samples used in the present study were synthesized by an electrochemical intercalation method. Details about the sample preparation and characterizations at ambient pressure can be found in ref. [11]. Because the sample is very sensitive to air and becomes loosely packed after intercalation, we mainly measured the magnetic susceptibility to characterize the superconducting properties. To protect the sample from air, we covered the sample with Apizon-N grease in an Ar-filled glove box before taking out for magnetic susceptibility measurements. The dc magnetic properties at ambient pressure were recorded with a commercial MPMS-III from Quantum Design. Temperature dependences of ac magnetic susceptibility measured up to 11 GPa were measured with the mutual inductance method in the palm cubic anvil cell (CAC) apparatus [18]. The superconducting shielding fraction of the sample was estimated by comparing with the diamagnetic signal of Pb. Glycerol was used as the pressure-transmitting medium for the high-pressure measurements. The pressure values inside the CAC were calibrated by measuring the characteristic transitions of bismuth (Bi) and lead (Pb) at room temperature.

Results and discussion. – Figure 1 displays the temperature dependence of dc magnetization $M(T)$ of (CTA)$_{0.3}$FeSe measured upon warming up under 20 and 5 Oe after zero-field-cooled from room temperature. Two successive drops were observed at about 45 K and 32 K for $M(T)$ under 20 Oe, while one sharp drop at $\sim 45$ K was evidenced for $M(T)$ under 5 Oe. These results are consistent with those reported in the previous report [11].

Figure 2 shows the temperature dependence of ac magnetic susceptibility $\chi(T)$ below 60 K under various hydrostatic pressures up to 11 GPa for (CTA)$_{0.3}$FeSe. As shown in fig. 2(a) for $P \leq 4$ GPa, the superconducting diamagnetic signal can be clearly seen from the drop of $\chi(T)$ below $T_c^\Lambda$, which is indicated by the down-pointing arrow. At the first pressure $P = 2$ GPa, $T_c^\Lambda$ has shifted significantly down to $\sim 16$ K, in line with the previous high-pressure results [11]. Upon increasing pressure to 3 GPa, on the other hand, we start to see the drop of $\chi(T)$ at a higher $T_c^\Lambda = 22$ K, signaling the emergence of SC-II phase. In addition, the superconducting shielding fraction also increases from $\sim 38\%$ at 2 GPa to $\sim 60\%$ at 3 GPa. At 4 GPa, $T_c^\Lambda$ was further enhanced quickly to 36 K and the superconducting shielding fraction reaches about 75%, confirming the bulk nature for the observed SC-II phase under pressure. When we applied more pressure to 5 GPa, fig. 2(b), the enhancement of $T_c^\Lambda$ is quite minute and the superconducting drop in $\chi(T)$ becomes less sharp as compared to 4 GPa. As seen in fig. 2(b), further applying pressure to above 5 GPa causes a gradually decrease of $T_c^\Lambda$, and more profoundly the quick reduction of the superconducting shielding fraction. Although the onset of diamagnetic signal appears at a relatively high $T_c^\Lambda \approx 27$ K at 8 GPa, a sharper drop appears below $\sim 6$ K. No superconducting transition can be defined at 11 GPa.

Figure 3 shows the temperature-pressure phase diagram of (CTA)$_{0.3}$FeSe based on the above ac magnetic susceptibility measurements. The magnitude of
the \( \chi(T) \) is also superimposed on the phase diagram to illustrate the evolution of the superconducting shield fraction under pressure. The \( T-P \) phase diagram depicts explicitly the initial suppression of SC-I phase followed by the re-emergence of SC-II phase above \( \sim 2 \) GPa with a dome-shaped \( T_c(P) \) centered at \( \sim 5 \) GPa. The reemergence of SC-II phase under pressure is similar with other intercalated FeSe-based materials such as \( A_x Fe_{2−y}Se_2 \) [14], \( Cs_{0.4}(NH_3)_yFeSe \) [15], \( (Li_{1−x}Fe)OHFeSe \) [16] and \( Li_x(NH_3)_yFe_2Se_2 \) [17], thus pointing to a universal phenomenon in this class of materials. However, some differences are also noteworthy. For example, the critical pressure \( P_c \approx 2 \) GPa is nearly identical to that of \( Li_x(NH_3)_yFe_2Se_2 \), but the SC-II phase exists in a much narrower pressure range. In addition, the highest \( T_c \approx 38 \) K in the SC-II phase is lower than that at ambient pressure. Such an instability of the SC-II phase against pressure and the relatively low \( T_c \) that at ambient pressure. Such an instability of the SC-II phase in (CTA)\( _{0.3} \)FeSe is achieved via electron doping by intercalating organic-ion-(CTA\(^+\)) in between the FeSe layers [11]. The interlayer distance is as large as \( \sim 14.5 \) Å, thus enhancing its two-dimensional character. Although the weak bonding nature of (CTA\(^+\)) with FeSe layers renders a relatively narrower SC-II phase with a lower \( T_c \), the present work provides further positive evidences in support of pressure-induced SC-II phase as a universal phenomenon in the intercalated FeSe-based superconductors. Based on the previous high-pressure XRD on \( (Li,Fe)OHFeSe \) [16], the structural transition has been ruled out as the possible origin for the pressure-induced SC-II phase. Here, we have tried our best to measure the high-pressure synchrotron x-ray powder diffraction on (CTA)\( _{0.3} \)FeSe, but our attempt was hampered by the fact that the sample is very sensitive to air during the sample preparation, and we believe that the structure transition is unlikely to occur at such a low pressure of \( 2 \) GPa in (CTA)\( _{0.3} \)FeSe.

Although the pressure-induced SC-II phase seems to be a universal phenomenon among these FeSe-intercalated systems, the optimal \( T_c \) and the critical pressure for the emergent SC-II phase depends on the specific characters of each system, including the initial doping level, the interlayer bonding strength, structural stability, etc. For example, in comparison with \( (Li_{1−x}Fe)OHFeSe \), the higher doping level of \( Li_{0.36}(NH_3)_yFe_2Se_2 \) leads to a higher optimal \( T_c \), but the weaker interlayer interaction results in a lower critical pressure for the emergence of SC-II phase [16,17]. For the present case of (CTA)\( _{0.3} \)FeSe, the doping level is the highest, but the interlayer strength and the structural stability are the weakest among these three systems. These factors give rise to the specific phase diagram shown in fig. 3.

As mentioned above, the high-\( T_c \) SC-I phase in (CTA)\( _{0.3} \)FeSe is achieved via electron doping by intercalating organic-ion-(CTA\(^+\)) in between the FeSe layers [11].

![Fig. 2: The ac magnetic susceptibility \( 4\pi\chi(T) \) measured under different hydrostatic pressures: (a) from 2 to 4 GPa, (b) from 5 to 11 GPa. The superconducting transition \( T_c \)'s are marked by arrows.](Image 512x587 to 520x752)

![Fig. 3: Pressure dependence of the superconducting transition temperatures \( T_c \) and a contour color plot of the superconducting shielding fraction for the (CTA)\( _{0.3} \)FeSe single crystal.](Image 520x752 to 538x927)
In order to shed some light on the pressure-induced SC-II phase, we plotted the $T_c$ values of the parent FeSe and other intercalated FeSe-based superconductors [2,5,6,9,11,15,16] as a function of the electron doping level and the inter-FeSe-layer distance $d$ in fig. 4(a), (b). It has been well established that the electron doping plays an important role in raising the $T_c$ of the FeSe-based superconducting materials at ambient pressure. As shown in fig. 4(a), $T_c$ first increases quickly with increasing the electron doping and then keeps nearly constant upon further electron doping in the FeSe intercalated systems. As such, the heavily electron-doped (CTA)$_{0.3}$FeSe reaches an almost optimal $T_c \approx 45$ K at a considerable value of the electron doping level. A similar trend is also observed for $T_c$ vs. $d$ in fig. 4(b) at ambient pressure, even though the $d$ spacing is much enlarged in (CTA)$_{0.3}$FeSe. As seen in fig. 4(b), the application of high pressure on the intercalated FeSe materials that reduces $d$ monotonically produces a V-shaped $T_c (d)$, which indicates that the inter-FeSe-layer distance is not a vital factor governing the reemergence of the SC-II phase. Alternatively, the actual electron doping level or the electron carrier density near Fermi level that can be altered abruptly via the Fermi surface reconstruction or a Lifshitz transition might be a common factor responsible for this universal phenomenon. For both (Li$_{1-x}$Fe$_x$)$_2$OFeSe and Li$_{0.36}$(NH$_3$)$_y$Fe$_2$Se$_2$, the emergence of SC-II phase was found to be accompanied with a concomitant enhancement of the superconducting volume and thus enhanced carrier densities. This argument is consistent with the appearance of SC-II phase at ambient pressure in the heavily K-dosed FeSe ultrathin films, in which a Lifshitz transition associated with the emergence of an electron pocket at the $\Gamma$ point of the Brillouin zone center has been seen directly by the in situ ARPES measurements [8,9].

Theoretical investigations on $A_x$Fe$_{2-y}$Se$_2$ [19] and FeS [20] have proposed that the superconducting order parameters in the SC-I and SC-II phases should have distinct pairing symmetries associated with a Lifshitz transition. Although it is quite challenging to determine the pairing symmetry of the SC-II phase under high pressures, further investigations are needed in order to understand such an intriguing phenomenon. In particular, the study on pressure-induced SC-II phase might shed light on some other unconventional superconducting systems showing the double superconducting domes, such as heavy-fermion superconductor CeCu$_2$Si$_2$ [21] and LaFeAsO$_{1-x}$(H/F)$_x$ [22–24].

**Conclusions.** – In summary, we have performed ac magnetic susceptibility measurements on the newly synthesized (CTA)$_{0.3}$FeSe single crystal with cubic anvil cell apparatus under hydrostatic pressures up to 11 GPa. We found that the application of high pressure first suppresses the SC-I phase and then induces a second high-$T_c$ SC-II phase above $P_c \approx 2$ GPa, in reminiscent of the situations seen in other intercalated FeSe-based materials such as (Li,Fe)OHFeSe and Li$_{0.36}$(NH$_3$)$_y$Fe$_2$Se$_2$. However, the highest $T_c$ in the SC-II phase is limited to ca. 40 K at 5 GPa, above which both $T_c$ and the superconducting volume decrease quickly, presumably due to the collapse of the intercalated framework. Nevertheless, the observation of pressure-induced reemergence of SC-II in (CTA)$_{0.3}$FeSe demonstrates once again that it should be a universal phenomenon in the electron-doped intercalated FeSe-based superconductors presumably associated with a Fermi surface reconstruction under pressure.

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This work is supported by the National Science Foundation of China (Grant Nos. 11904391, 11834016, 11874400, 11904391, 11834016, 11874400).
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