CHIN. PHYS. LETT. Vol. 36, No. 7 (2019) 077401 **Express Letter**

# Ionic-Liquid-Gating Induced Protonation and Superconductivity in FeSe, $FeSe_{0.93}S_{0.07}$, ZrNCl, 1*T*-$TaS_2$ and $Bi_2Se_3$ *

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*We report protonation in several compounds by an ionic-liquid-gating method, under optimized gating conditions. This leads to single superconducting phases for several compounds. Non-volatility of protons allows post-gating magnetization and transport measurements. The superconducting transition temperature $T_c$ is enhanced to 43.5 K for $FeSe_{0.93}S_{0.07}$, and 41 K for FeSe after protonation. Superconducting transitions with $T_c \sim 15$ K for ZrNCl, ∼7.2 K for 1T-$TaS_2$, and ∼3.8 K for $Bi_2Se_3$ are induced after protonation. Electric transport in protonated $FeSe_{0.93}S_{0.07}$ confirms high-temperature superconductivity. Our $^1H$ nuclear magnetic resonance (NMR) measurements on protonated $FeSe_{1-x}S_x$ reveal enhanced spin-lattice relaxation rate $1/^1T_1$ with increasing $x$, which is consistent with the LDA calculations that $H^+$ is located in the interstitial sites close to the anions.*

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Carrier doping is an effective method for tuning metal-insulator transitions and superconductivity. In addition to chemical substitution, electric gating also emerged as an efficient method for tuning carrier density in thin films.[1−3] With the development of various room-temperature ionic liquids, the transistor-like gating method[4−9] was found to induce a large carrier density for thin films or crystal flakes, through charge polarization. Lithium doping by ionic solid gating was also found to enhance the superconducting transition temperature of thin flakes of FeSe.[10] Recently, tuning of proton or oxygen concentration, using ionic-liquid-gating as a medium, was introduced to modify the lattice structure and magnetism of $SrCoO_{2.5}$.[11] This $H^+$ implantation method was later applied in iron-based superconductors, to induce superconductivity or enhance the superconducting transition temperature in bulk crystals due to an electron doping effect.[12]

It is important to note that $H^+$ originates from water contamination in the ionic liquid by this method.[11] The advantages of this technique are that $H^+$ is nonvolatile and the gating is performed near the ambient conditions, which allow various post-gating measurements. However, multiple superconducting phases in protonated $FeSe_{1-x}S_x$ emerge, indicating that proton concentration is inhomogeneous across the bulk crystals. The magnetization data in the protonated $FeSe_{0.93}S_{0.07}$ show that the volume fraction of the superconducting phase is very low under the reported gating conditions.[12]

In this Letter, we report our optimized protonation conditions with this ionic-liquid-gating method, to improve the superconducting volume ratio and the doping homogeneity. The best protonation temperature is found to be 350 K (higher than the room temperature), with a gating period of 12 days. For $FeSe_{0.93}S_{0.07}$, the superconducting volume ratio is largely enhanced compared to the room temperature

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gating, as determined by the magnetization measurement. Transport measurement is also succeeded to confirm superconductivity. We also apply the optimized protonation on various layered compounds, including FeSe, insulating ZrNCl, 1$T$-$TaS_2$, and $Bi_2Se_3$, where protonation either induces superconductivity or enhances the $T_c$ largely. In particular for 1$T$-$TaS_2$, we achieve a $T_c$ higher than the regular gating method.

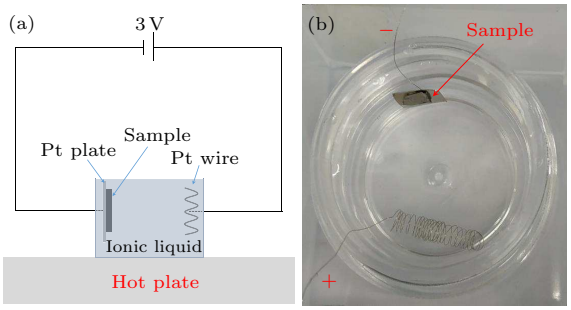


**Fig. 1.** (a) An illustration of the protonation setup. Platinum electrodes are placed in a container filled with the ionic liquid. The gating voltage is set to be about 3.0 V. The ionic liquid is heated up to 350 K by a hot plate. (b) A picture of the positive and negative platinum electrodes, with the sample attached on the negative electrode.

In our experiment, pristine FeSe and $FeSe_{0.93}S_{0.07}$ single crystals were made by the vapor transport method.[13,14] ZrNCl powders were made by the high-pressure synthesis.[15] The 1$T$-$TaS_2$ single crystal was grown by the chemical vapor transport method.[16] $Bi_2Se_3$ was grown by the flux method.[17] FeS single crystal was made by the hydrothermal method.[18] We employ the protonation technique as illustrated in Fig. 1. As shown in Fig. 1, samples are attached to the negative electrodes, and a voltage of 3.0 V is applied as the gating voltage. The ionic liquid EMIM-BF4 is used. The gating temperature is optimized to be 350 K, which improves proton diffusion efficiency in the crystal. Typical gating period is 12 days when water is nearly fully electrolyzed. The dc magnetization is measured with a magnetic property measurement system (MPMS), and the transport is measured with a physical property measurement system (PPMS). These measurements were successfully performed after gating was removed at the room temperature, which indicates nonvolatile protons are inserted, in contrast to conventional ionic-liquid gating where gating cannot be removed during measurements. The proton NMR is performed by the spin-echo method, and the spin-lattice relaxation rate $1/^1T_1$ is measured by the inversion recovering method.

In the following, we present protonation measurements on these compounds.

FeSe: Recently, FeSe has attracted a great deal of research attention because of its highly tunable superconductivity. Its $T_c$ is enhanced from 8.5 K to above 40 K under high pressure,[19,20] by chemical intercalation,[21–24] by ionic-liquid/solid gating,[25,10] or by dimensional reduction into a single-layer phase.[26]

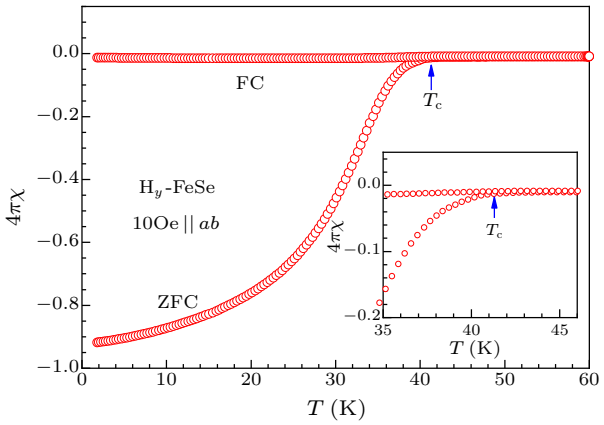


**Fig. 2.** The dc susceptibility of a protonated FeSe single crystal (5 mm×5 mm×1 mm) measured under the field-cooled (FC) and zero-field-cooled (ZFC) conditions with a magnetic field of 10 Oe. The arrows are located at the superconducting transition. Inset: an enlarged view of the susceptibility data close to $T_c$.

Figure 2 shows the dc susceptibility $\chi(T)$ of a protonated FeSe single crystal. A rapid drop of $\chi$ at 41 K is clearly seen, indicating the onset of superconductivity. Therefore, the $T_c$ of FeSe is also largely enhanced by the protonation technique.

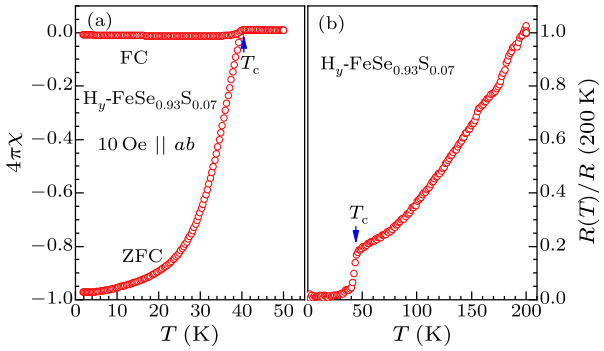


**Fig. 3.** (a) The dc susceptibility of a $H_y$-$FeSe_{0.93}S_{0.07}$ single crystal as a function of temperature, measured under ZFC and FC conditions. (b) The resistance of the crystal as a function of temperature. The arrows mark the onset temperature of superconductivity.

$FeSe_{0.93}S_{0.07}$: $FeSe_{1-x}S_x$ is a series of compounds, whose $T_c$ ranges between 8 K and 13 K for $x < 0.12$.[27] Previously, two superconducting transitions at 25 K and 42.5 K were reported in the protonated samples. Here we show that with increased protonation temperature at 350 K, a single high-$T_c$ phase is realized. Figure 3 shows the dc susceptibility $\chi(T)$ and the resistance data $R(T)$ of a protonated $FeSe_{0.93}S_{0.07}$ single crystal. The susceptibility data shows $T_c \approx 41$ K, seen by the drop of $\chi$ (Fig. 3(a)). By contrast, the resistance data show a higher onset $T_c$ of 43.5 K as indicted in Fig. 3(b), by a sudden drop of resistance upon cooling.

ZrNCl: ZrNCl is a layered material with electric gating or lithium doping. Superconductivity can be induced in ZrNCl by electric gating or lithium doping.[3,4,28] We pressed ZrNCl powders into thin pellets and then doped $H^+$ with the current ionic-

liquid-gating method. The samples turn from blue into black upon proton doping. Figure 4 shows the dc susceptibility of the proton-doped ZrNCl. The sharp drop of $\chi$ below 15 K shows the onset of superconductivity, with field up to 1000 Oe. The volume ratio of the superconducting phase, estimated from the ZFC data at 10 Oe field, is about 12%. This suggests that proton doping is very efficient. We note that an ionic-liquid gating on ZrNCl at low temperatures is also reported, which proposes that the depletion of $Cl^-$ concentration causes superconductivity.[29]

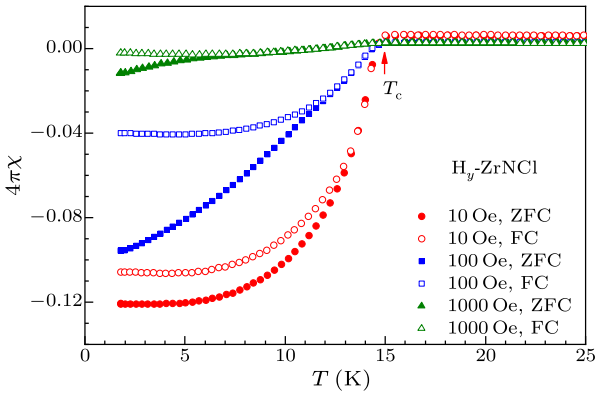


**Fig. 4.** The dc susceptibility $\chi$ of $H_y$-ZrNCl pellets, measured under FC and ZFC conditions with different fields. The arrow marks the onset temperature of superconductivity.

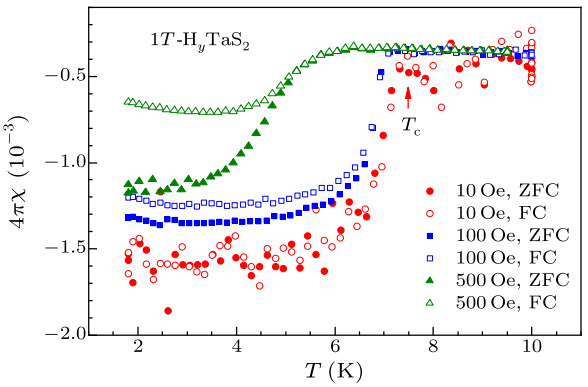


**Fig. 5.** The dc susceptibility $\chi$ of a protonated 1$T$-$TaS_2$ single crystal, measured under FC and ZFC condition, at various fields. The arrow marks the onset of the superconducting transition.

1$T$-$TaS_2$: 1$T$-$TaS_2$ is a layered compound with a triangular lattice. It goes through a series of charge-density-wave (CDW) transitions upon cooling.[30,31] Superconductivity can be achieved by chemical doping, where the highest $T_c$ is achieved at 3.5 K.[32] Here we performed protonation on 1$T$-$TaS_2$ single crystals. The dc magnetization of a protonated sample is shown in Fig. 5, measured under FC and ZFC conditions at different fields. The superconducting transition temperature $T_c$ is found to be ∼7.2 K under 10 Oe field. We note that this transition temperature is higher than that achieved by the chemical doping. With an applied field of 500 Oe, the superconducting transition is still observed.

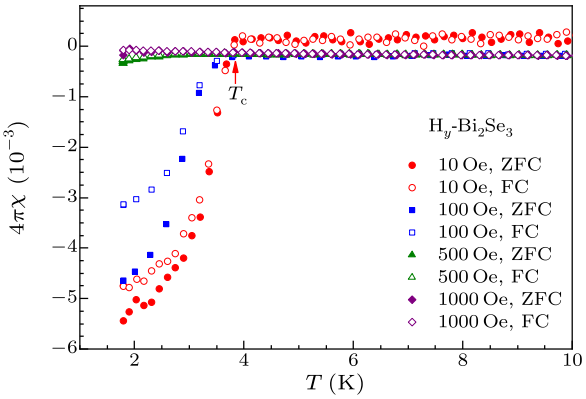


**Fig. 6.** The dc susceptibility $\chi$ of a protonated $Bi_2Se_3$ single crystal, measured under FC and ZFC condition at different fields. The arrow marks the onset of superconducting transition at $T_c$.

$Bi_2Se_3$: As a topological insulator, $Bi_2Se_3$ has caused a lot of research interests.[33,34] Superconductivity can be achieved upon Cu or Sr doping into this material.[35,36] Here we find that by protonation, superconductivity can also be achieved. As seen in Fig. 6, the superconducting transition temperature $T_c$ is found to be 3.8 K, which is close to that reported by the chemical doping. With an applied field of 500 Oe, superconductivity is highly suppressed. Since protonation does not induce chemical substitution, our study indicates that chemical doping in the interstitial sites is important for the occurrence of superconductivity. Further studies on the protonation of induced superconductivity in this compound, regarding to possible topological superconductivity, are demanded.

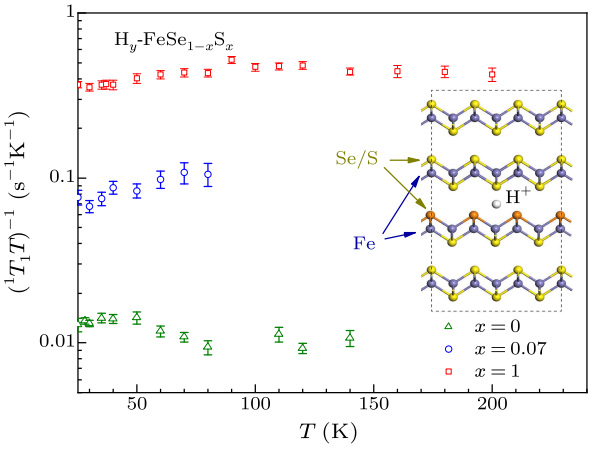


**Fig. 7.** The $^1$H spin-lattice relaxation rate divided by temperature $1/^1T_1T$ of $H_yFeSe_{1-x}S_x$ single crystals, measured with a magnetic field of 5 T along the $c$-axis. Inset: the proton position in the lattice obtained by the LDA calculations.

$^1$H NMR studies on $H_yFeSe_{1-x}S_x$: In $H_yFeSe_{1-x}S_x$ compounds, intrinsic $^1$H NMR spectra was observed. Figure 7 shows the $^1$H spin-lattice relaxation rates divided by temperatures, versus temperature for protonated $FeSe_{1-x}S_x$ with $x$=0, 0.07

and 1. Above 50 K, $1/^1T_1T$ stays nearly constant but varies with $x$, which indicate that doped protons are detected by the current measurements. Indeed, the increase of $1/^1T_1$ with increasing $x$ is consistent with the LDA calculations that $H^+$ is inserted in the interstitial sites as discussed below. Since the $c$-axis lattice parameter is reduced with increasing $x$,[27] the hyperfine coupling between $^1$H and the FeSe plane increases with increasing $S^{2-}$ concentration.

Our LDA calculations indicate that $H^+$ is located in the interstitial sites close to the anion $Se^{2-}/S^{2-}$, as shown by the schematic drawing in the inset of Fig. 7. This can be understood as an effect of coulomb attraction between $H^+$ and $Se^{2-}/S^{2-}$. So far, we have found that this doping method is efficient in layered compounds, which indicates that $H^+$ is most likely doped between the layers as in $H_yFeSe_{1-x}S_x$.

Discussions and summary: Our XRD measurement did not resolve the change of lattice structure after protonation, which suggests that the chemical pressure effect of proton insertion is possibly very small. As a result, an electron-doping should be primarily responsible for the change of $T_c$.

**Table 1.** $T_c$ of the materials before and after protonation.

| Compound | FeSe | $FeSe_{0.93}S_{0.07}$ | ZrNCl | 1$T$-$TaS_2$ | $Bi_2Se_3$ |
|---|---|---|---|---|---|
| $T_{c,before}$ | 9 K | 8 K | 0 | 0 | 0 |
| $T_{c,after}$ | 41 K | 43.5 K | 15 K | 7.2 K | 3.8 K |

In Table 1, we summarize all the $T_c$ of different compounds, before and after protonation under the current optimized conditions. The optimization at 350 K suggests that the efficiency of proton doping is caused by a balance between proton diffusion into the sample and the evasion out of the sample, both of which increase with temperature. The current method supplies a universal electron doping method, which could be widely used in tuning and searching for superconductivity and metal-insulator transitions in the layered compounds.

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