

Ionic-Liquid-Gating Induced Protonation and Superconductivity in FeSe, FeSe_{0.93}S_{0.07}, ZrNCl, 1T-TaS₂ and Bi₂Se₃ *

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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 allow 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. Superconductivity properties with $T_c \approx 15$ K for ZrNCl, ≈ 7.2 K for 1T-TaS₂, and ≈ 3.8 K for Bi₂Se₃ are induced after protonation. Electric transport in protonated FeSe_{0.93}S_{0.07} confirms high-temperature superconductivity. Our ¹H NMR measurements on protonated FeSe_{1-x}S_x reveal enhanced spin-lattice relaxation rate $1/T_1$ with increasing x , which is consistent with the LDA calculations that H⁺ are 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 is 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 emerges, 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.

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65 For $\text{FeSe}_{0.93}\text{S}_{0.07}$, the superconducting value ratio is 107 phase.^[26]
 66 largely enhanced compared to the room temperature
 67 gating, as determined by the magnetization measure-
 68 ment. Transport measurement is also succeeded to
 69 confirm superconductivity. We also apply the opti-
 70 mized protonation on various layered compounds, in-
 71 cluding FeSe, insulating ZrNCl , $1T\text{-TaS}_2$, and Bi_2Se_3 ,
 72 where protonation either induces superconductivity or
 73 enhances the T_c largely. In particular for $1T\text{-TaS}_2$, we
 74 achieve a T_c higher than the regular gating method.

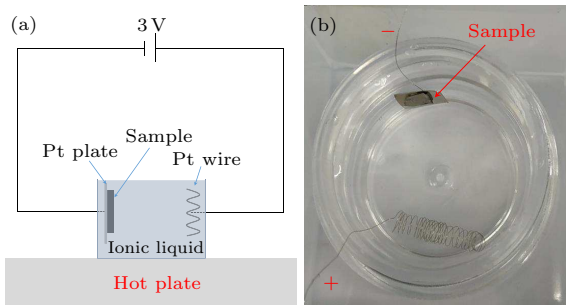


Fig. 1. (a) An illustration of the protonation setup. Platinum electrodes are placed in a container filled with the ionic liquid. The gating voltage is set to be about 3.1 V. The ionic liquid is heated up to 350 K by a hot plate. (b) A picture of the positive and negative platinum electrodes, with the sample attached on the negative electrode.

75 In our experiment, pristine FeSe and $\text{FeSe}_{0.93}\text{S}_{0.07}$
 76 single crystals were made by the vapor transport
 77 method.^[13,14] ZrNCl powders were made by the high-
 78 pressure synthesis.^[15] Also, $1T\text{-TaS}_2$ single crystal was
 79 grown by the chemical vapor transport method.^[16]
 80 Bi_2Se_3 was grown by the flux method.^[17] FeS single
 81 crystal was made by the hydrothermal method.^[18]
 82 We employ the protonation technique as illustrated in
 83 Fig. 1. As shown in Fig. 1, samples are attached to the
 84 negative electrodes, and a voltage of 3.0 V is applied
 85 as the gating voltage. The ionic liquid EMIM-BF4
 86 is used. The gating temperature is optimized to be
 87 350 K, which improves proton diffusion efficiency in
 88 the crystal. Typical gating period is 12 days when
 89 water is nearly fully electrolyzed. The dc magneti-
 90 zation is measured in an MPMS, and the transport
 91 is measured in a PPMS. These measurements were
 92 successfully performed after gating is removed at the
 93 room temperature, which indicates nonvolatile pro-
 94 tons are inserted, in contrast to conventional ionic-
 95 liquid gating where gating cannot be removed during
 96 measurements. The proton NMR is performed by the
 97 spin-echo method, and the spin-lattice relaxation rate
 98 $1/T_1$ is measured by the inversion recovering method.
 99 In the following, we present protonation measure-

100 ments on these compounds.

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

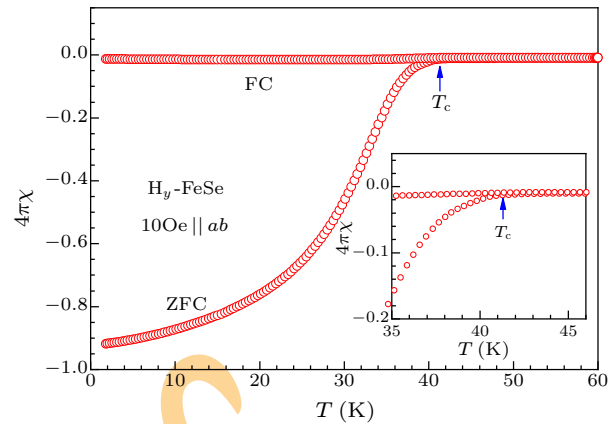


Fig. 2. The dc susceptibility of a protonated FeSe single crystal ($5\text{ mm} \times 5\text{ mm} \times 1\text{ mm}$) measured under the field-cooled (FC) and zero-field-cooled (ZFC) conditions with a magnetic field of 10 Oe. The arrows are located at the superconducting transition. Inset: an enlarged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

108 Figure 2 shows the dc susceptibility $\chi(T)$ of a pro-
 109 tonated FeSe single crystal. A rapid drop of χ at 41 K
 110 are clearly seen, indicating the onset of superconduc-
 111 tivity. Therefore, the T_c of FeSe is also largely en-
 112 hanced by the protonation technique.

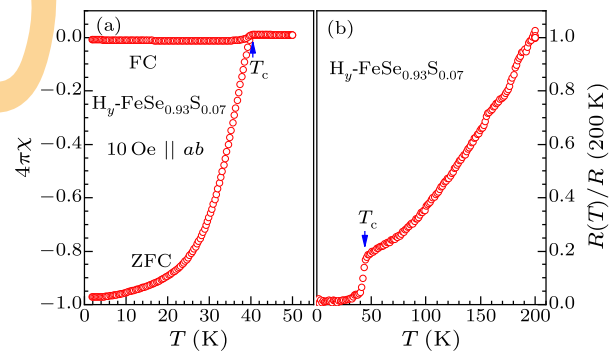


Fig. 3. (a) The dc susceptibility of a $\text{H}_y\text{-FeSe}_{0.93}\text{S}_{0.07}$ single crystal as a function of temperature, measured under ZFC and FC conditions. (b) The resistance of the crystal as a function of temperature. The arrows mark the onset temperature of superconductivity.

113 $\text{FeSe}_{0.93}\text{S}_{0.07}$: $\text{FeSe}_{1-x}\text{S}_x$ is a series of compounds,
 114 whose T_c ranges between 8 K and 13 K for $x < 0.12$.^[27]
 115 Previously, two superconducting transitions at 25 K
 116 and 42.5 K were reported in the protonated samples.
 117 Here we show that with increased protonation tem-
 118 perature at 350 K, a single high- T_c phase is realized.
 119 Figure 3 shows the dc susceptibility $\chi(T)$ and the re-
 120 sistance data $R(T)$ of a protonated $\text{FeSe}_{0.93}\text{S}_{0.07}$ sin-
 121 gle crystal. The susceptibility data shows $T_c \approx 41\text{ K}$,
 122 seen by the drop of χ (Fig. 3(a)). By contrast, the
 123 resistance data show a higher onset T_c of 43.5 K as in-
 124 dicated in Fig. 3, by a sudden drop of resistance upon
 125 cooling.

126 ZrNCl: ZrNCl is a layered material with elec-
 127 tric gating or lithium doping. Superconductivity can
 128 be induced in ZrNCl by electric gating or lithium

129 doping.^[4,28,29] We pressed ZrNCl powders into thin 153 than that achieved by the chemical doping. With an
 130 pellets and then doped H^+ with the current ionic- 154 applied field of 500 Oe, the superconducting transition
 131 liquid-gating method. The samples turns from blue 155 is still observed.
 132 into black color upon proton doping. Figure 4 shows
 133 the dc susceptibility of the proton-doped ZrNCl. The
 134 sharp drop of χ below 15 K shows the onset of super-
 135 conductivity, with field up to 1000 Oe. The volume
 136 ratio of the superconducting phase, estimated from
 137 the ZFC data at 10 Oe field, is about 12%. This sug-
 138 gests that proton doping is very efficient. We note that
 139 an ionic-liquid gating on ZrNCl at low temperatures
 140 is also reported, which proposes that the depletion of
 141 Cl^- concentration causes superconductivity.^[30]

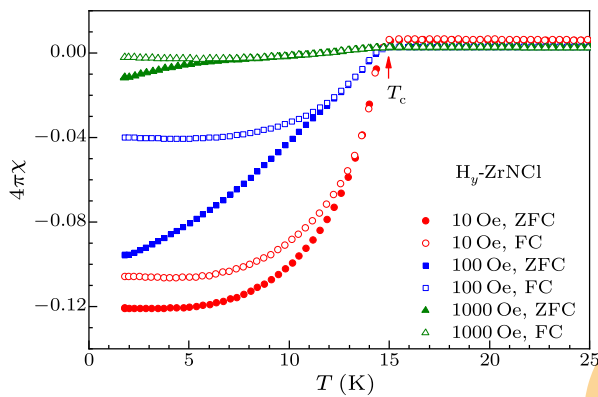


Fig. 4. The dc susceptibility χ of H_y -ZrNCl pellets, measured under FC and ZFC conditions with different fields. The arrow marks the onset temperature of superconductivity.

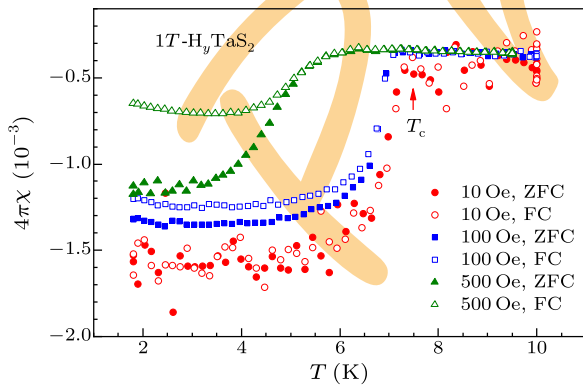


Fig. 5. The dc susceptibility χ of a protonated $1T$ -TaS₂ single crystal, measured under FC and ZFC condition, under various fields. The arrow marks the onset of the superconducting transition.

142 $1T$ -TaS₂: $1T$ -TaS₂ is a layered compound with a
 143 triangular lattice. It goes through a series charge-
 144 density-wave (CDW) transition upon cooling.^[31,32]
 145 Superconductivity can be achieved by chemical dop-
 146 ing, where the highest T_c is achieved at 3.5 K.^[33] Here
 147 we performed protonation on $1T$ -TaS₂ single crystals.
 148 The dc magnetization of a protonated sample is shown
 149 in Fig. 5, measured under FC and ZFC conditions at
 150 different fields. The superconducting transition tem- 171
 151 perature T_c is found to be ~ 7.2 K under 10 Oe field. 172
 152 We note that this transition temperature is higher 173

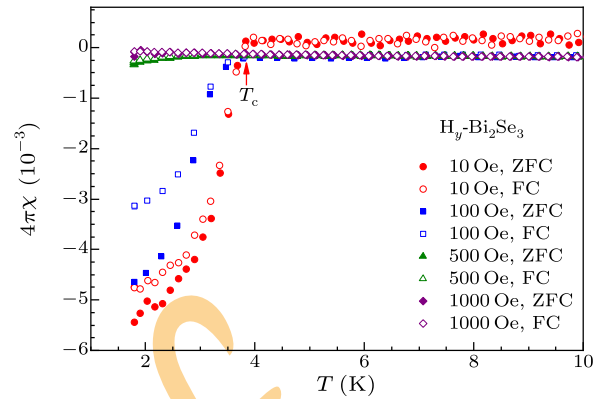


Fig. 6. The dc susceptibility χ of a protonated Bi₂Se₃ single crystal, measured under FC and ZFC condition at different fields. The arrow marks the onset of superconducting transition at T_c .

156 Bi₂Se₃: As a topological insulator, Bi₂Se₃ has
 157 caused a lot of research interests.^[34,35] Superconduc-
 158 tivity can be achieved upon Cu or Sr doping into
 159 this material.^[36,37] Here we find that by protonation,
 160 superconductivity can also be achieved. As seen in
 161 Fig. 6, the superconducting transition temperature T_c
 162 is found to be 3.8 K, which is close to that reported by
 163 the chemical doping. With an applied field of 500 Oe,
 164 superconductivity is nearly suppressed. Since pro-
 165 tonation does not induce chemical substitution, our
 166 study indicates that chemical doping in the interstitial
 167 sites is important for the occurrence of superconduc-
 168 tivity. Further studies on the protonation of induced
 169 superconductivity in this compound, regarding to pos-
 170 sible topological superconductivity, are demanded.

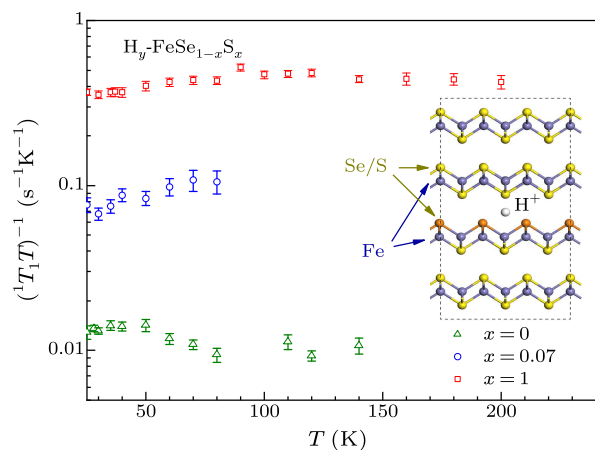


Fig. 7. The 1H spin-lattice relaxation rate divided by temperature $1/T_1T$ of $H_yFeSe_{1-x}S_x$ single crystals, measured in a magnetic field of 5 T along the c -axis. Inset: the proton position in the lattice obtained by the LDA calculations.

1H NMR studies on $H_yFeSe_{1-x}S_x$: In
 $H_yFeSe_{1-x}S_x$ compounds, intrinsic 1H NMR spec-
 tra was observed. Figure 7 shows the 1H spin-lattice

174 relaxation rates divided by temperatures, versus tem-
 175 perature for protonated $\text{FeSe}_{1-x}\text{S}_x$ with $x=0, 0.07$
 176 and 1. Above 50 K, $1/T_1T$ stays nearly constant
 177 but varies with x , which indicate that doped protons
 178 are detected by the current measurements. Indeed,
 179 the increase of $1/T_1$ with increasing x is consistent
 180 with the LDA calculations that H^+ is inserted in the
 181 interstitial sites as discussed below. Since the c -axis
 182 lattice parameter is reduced with increasing x ,^[27] the
 183 hyperfine coupling between ^1H and the FeSe plane
 184 increases with increasing S^{2-} concentration.
 185 Our LDA calculations indicate that H^+ is located
 186 in the interstitial sites close to the anion $\text{Se}^{2-}/\text{S}^{2-}$, as
 187 shown by the schematic drawing in the inset of Fig. 7.
 188 This can be understood as an effect of coulomb at-
 189 traction between H^+ and $\text{Se}^{2-}/\text{S}^{2-}$. So far, we have
 190 found that this doping method is efficient in layered
 191 compounds, which indicates that H^+ is most likely
 192 doped between the layers as in $\text{H}_y\text{FeSe}_{1-x}\text{S}_x$.
 193 Discussions and summary: Our XRD measure-
 194 ment did not resolve the change of lattice structure
 195 after protonation, which suggests that the chemical
 196 pressure effect of proton insertion is possibly very
 197 small. As a result, an electron-doping should be pri-
 198 marily responsible for the change of T_C .

199 **Table 1.** T_C of the materials before and after protonation.

Compound	FeSe	$\text{FeSe}_{0.93}\text{S}_{0.07}$	ZrNCl	1T-TaS ₂	Bi_2Se_3
$T_{C,\text{before}}$	9 K	8 K	0	0	0
$T_{C,\text{after}}$	41 K	43.5 K	15 K	7.2 K	3.8 K

200 In Table 1, we summarize all the T_C of different
 201 compounds, before and after protonation under the
 202 current optimized conditions. The optimization at
 203 350 K suggests that the efficiency of proton doping
 204 is caused by a balance between proton diffusion into
 205 the sample and the evasion out of the sample, both of
 206 which increase with temperature. The current method
 207 supplies a universal electron doping method, which
 208 could be widely used in tuning and searching for su-
 209 perconductivity and metal-insulator transitions in the
 210 layered compounds.

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Proofs