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Article

Protonation induced high-T_c phases in iron-based superconductors evidenced by NMR and magnetization measurements

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ABSTRACT

Chemical substitution during growth is a well-established method to manipulate electronic states of quantum materials, and leads to rich spectra of phase diagrams in cuprate and iron-based superconductors. Here we report a novel and generic strategy to achieve nonvolatile electron doping in series of (i.e. 11 and 122 structures) Fe-based superconductors by ionic liquid gating induced protonation at room temperature. Accumulation of protons in bulk compounds induces superconductivity in the parent compounds, and enhances the T_c largely in some superconducting ones. Furthermore, the existence of proton in the lattice enables the first proton nuclear magnetic resonance (NMR) study to probe directly superconductivity. Using FeS as a model system, our NMR study reveals an emergent high-T_c phase with no coherence peak which is hard to measure by NMR with other isotopes. This novel electric-field-induced proton evolution opens up an avenue for manipulation of competing electronic states (e.g. Mott insulators), and may provide an innovative way for a broad perspective of NMR measurements with greatly enhanced detecting resolution.

1. Introduction

For both cuprate and iron-based superconductors, carrier doping into the parent compounds is crucial to suppress the magnetic ordering and induce high-temperature superconductivity [1–5]. However, doping in bulk materials is mostly achieved through chemical substitution upon reactions at high temperatures, a method that is constrained by the chemical solubility of the dopant. Ionic liquid (or electrolyte) gating method tunes the carrier density through electrostatic gating to achieve novel superconducting states [6–13]. A novel approach has been developed recently to use lithium ion electrolyte or conductive glass ceramics as medium to achieve the electric field induced lithiation in thin flakes [14–17]. However, all these techniques are only effective for thin material with carriers penetrating at nanometer scale, and gate voltage is required during measurements. Consequently, spectroscopic techniques, such as NMR and angle resolved photoelectron spectroscopy (ARPES), are not feasible because of the low effective volume of gated phases and the large impact of the ionic liquid.

Recently, it was discovered that ion liquid gating can also lead to oxygen and hydrogen evolution into the bulk form of a thin film [18], in which oxygen or hydrogen penetrates tens of nanometers within hours. More importantly the dopants reside in the sample permanently when the electrode voltage is switched off. This motivates us to tune the carrier density of bulk superconductors with extended gating time. In particular, for quasi-2D materials with large interlayer spacing, protons may be implanted into the interstitial sites with weak impurity scattering. If hydrogen is in

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a nonzero valence state, an effective charge doping effect is expected.

In this letter, we report our attempts to implant protons by this room-temperature ion liquid gating method into bulk iron-based superconductors with most common structures, including the 11 and the 122 structures. We found that protons are successfully doped into $FeSe_{0.93}S_{0.07}$ single crystals over a macroscopic length scale, whose T_c is enhanced from 9 to 42.5 K. For FeS, protonation enhances T_c from 4 to 18 K. These new protonated structures enable proton NMR measurements to give evidences for bulk superconductivity. Therefore, protons serve not only as a dopant for carrier doping, but also as a sensitive local probe for superconductivity, which is impossible for non-protonated compounds like FeS. To prove the generic nature of this approach, we also demonstrated that proton implantation induces superconducting for undoped non-superconducting $BaFe_2As_2$. We believe that our protonation methodology may be applied to a wide range of insulators, to tune for metal-insulator transitions, unconventional superconductivity, magnetism, etc., as well to allow for rich spectroscopy studies.

2. Techniques

The protonation to the iron-based superconductors was performed by the setup shown in Fig. 1a, following Ref. [18]. The ionic liquid is filled in a plastic container. Two platinum electrodes are separated by about 15 mm and connected to a 3 V voltage source. The single crystals were then attached to the negative electrodes by silver paint. Typical protonation peroid is about six days. We tested two types of ionic liquids, DEME-TFSI and FMIM-BF_4, and each produced the same enhancement of T_c. The single crystal X-ray data were performed on an XRD machines using Cu α and β lines. The magnetization was measured by a VSM-SQUID (Quantum Design) down to 2 K. The ac susceptibility is deduced from the shift of the resonance frequency of an untuned NMR circuit by $f = f_0\,(1 + \chi_{ac})^{-1/2}$, where χ_{ac} is the ac susceptibility of the sample. The proton NMR spectra were collected by the $\pi/2$-τ-π spin-echo pulse sequences, with $\pi/2$ pulse length of 0.3 μs and the inter-pulse delay τ of 8 μs. The proton spin-lattice relaxation time $^1T_1$ is measured by the standard inversion-recovery method.

3. Data analysis and discussions

Since these compounds have layered structure, protons are likely inserted into interstitial sites. The XRD patterns for three single crystals, $FeSe_{0.93}S_{0.07}$ (Sample S1), FeS (Sample S2) and $BaFe_2As_2$ (Sample B1), all after six days of protonation, are shown in Fig. 1b–d. The positions of all XRD peaks do not show an appreciable change after protonation, which suggests that the bulk crystal remains undamaged. Due to the small ratio of the protonated region (typically with micrometer thickness as discussed blow), the change of the lattice constant cannot be resolved from the current XRD method and would be an interesting problem for future studies.

We first show protonation effect in the 11 structure iron-based superconductor $FeSe_{0.93}S_{0.07}$ [19,20], as an example of enhanced T_c and sensitive NMR studies. The superconducting transition of the protonated sample is determined by both the dc and the ac susceptibility measurements shown in Fig. 2a and b. In Fig. 2a, the dc susceptibility χ_v under ZFC shows a primary drop at $T_{c1} \sim 9$ K, which

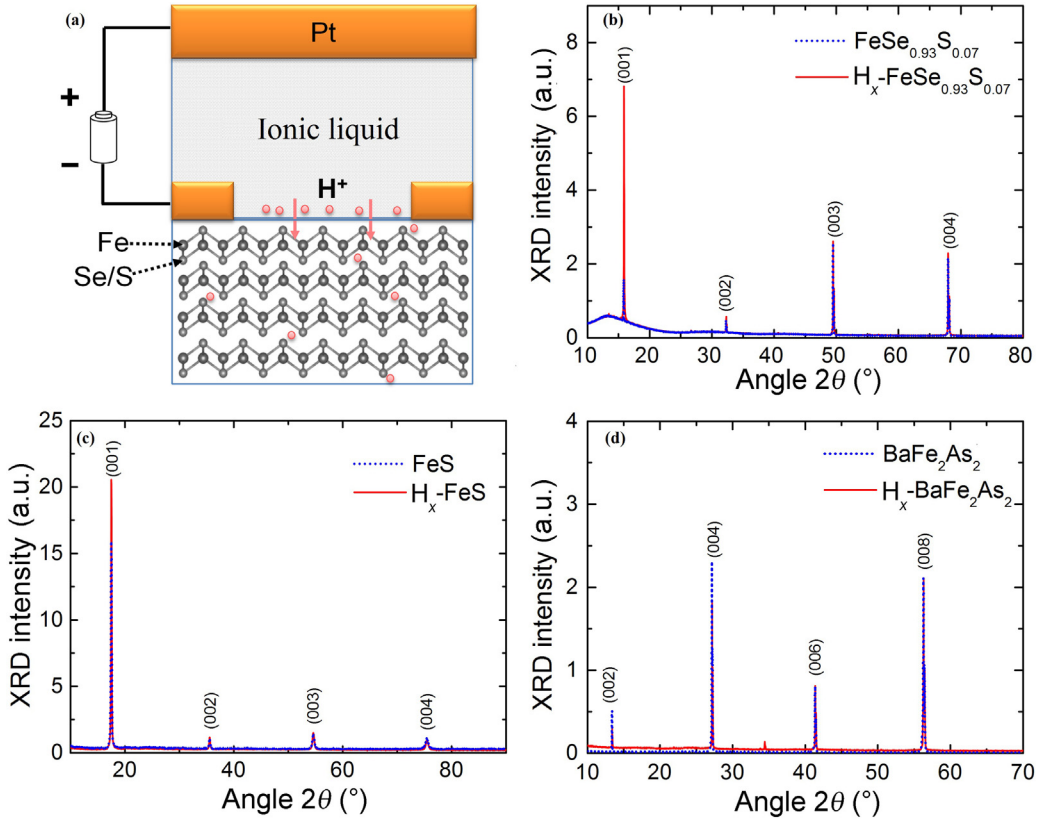

Fig. 1. (Color online) Sample protonation and structural characterization. (a) The configuration for protonation. Two parallel Pt electrodes are placed in the ionic liquid with a distance of 15 mm, applied with a 3 V voltage difference. The sample is attached to the negative electrode. (b) The single crystal X-ray diffraction (XRD) data of a $FeSe_{0.93}S_{0.07}$ single crystal (Sample S1, size ~3.24 mm × 1.54 mm × 0.28 mm) before and after six-day protonation. (c) The XRD data of a FeS single crystal (Sample S2, 2 mm × 2 mm × 0.1 mm), before and after protonation. (d) The XRD data of a $BaFe_2As_2$ single crystal (Sample B1, 2 mm × 4.4 mm × 0.2 mm) before and after protonation.

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