Bound States of Defects in Superconducting LiFeAs Studied by Scanning Tunneling Spectroscopy

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Defects in LiFeAs are studied by scanning tunneling microscopy and spectroscopy. Topographic images of the five predominant defects allow the identification of their position within the lattice. The most commonly observed defect is associated with an Fe site and does not break the local lattice symmetry, exhibiting a bound state near the edge of the smaller gap in this multi-gap superconductor. Three other common defects, including one also on an Fe site, are observed to break local lattice symmetry and are pair-breaking indicated by clear in-gap bound states, in addition to states near the smaller gap edge. STS maps reveal complex, extended real-space bound state patterns, including one with a chiral distribution of the local density of states. The multiple bound state resonances observed within the gaps and at the inner gap edge are consistent with theoretical predictions for the $s^\pm$ gap symmetry proposed for LiFeAs and other iron pnictides.

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I. INTRODUCTION

Impurity physics plays a key role in superconducting systems, beginning with the remarkable feature that non-magnetic defects do not strongly impact superconductivity in conventional s-wave materials. In contrast to such single sign s-wave superconductors, where only magnetic defects cause pair-breaking and in-gap states, both potential and magnetic defects can induce in-gap states in d-wave and multi-band sign reversal s-wave superconductors. Not surprisingly then, a superconductor’s sensitivity to defects, plus the energetic and spatial characterization of bound states localized at defect sites have provided clues to the pairing symmetry of novel superconductors, and scanning tunneling microscopy (STM) and spectroscopy (STS) have proven invaluable tools for such studies. Since a sign change of the order parameter gives rise to sensitivity to defects, it has been suggested that the study of these impurity bound states in the iron arsenides could help close the on-going discussion regarding the gap structure.

The fact that most high temperature superconductors, cuprates as well as pnictides, require chemical substitutions to tune them into their superconducting states adds further importance to understanding the effect of defects in these systems. In the cuprates, this tuning is often achieved through cation substitution on sites away from the CuO$_2$ planes, doping them with holes or electrons, while largely avoiding strong scattering. Direct substitution onto the CuO$_2$ planes is typically pair-breaking, sometimes strongly, sometimes weakly. For many iron-based superconductors chemical substitution that suppresses extended magnetic order is an essential ingredient in achieving high temperature superconductivity. In BaFe$_2$As$_2$ it has been shown that certain elements such as Co and Ni substituted into the Fe-layer induce superconductivity, while other substituents (Mn) cause strong pair-breaking. Thus, the arsenides lack the easy distinction of off-plane substitution to promote superconductivity versus on-plane defects that are pair-breaking. This makes it particularly important to assess individual impurities and their influence on the surrounding electronic states.

STM study of the pnictides has proven difficult due to surface specific effects arising from a lack of natural cleaving planes, or from structural or electronic reconstruction caused by a polar catastrophe. Recently, stoichiometric examples within the pnictide and chalcogenide families that exhibit surfaces suitable for STM study such as cleaved LiFeAs crystal, and molecular beam epitaxy grown films of FeSe and KFe$_2$Se$_2$ have presented the opportunity to apply STM and STS to well-defined systems. All three also possess the advantage of being superconducting without chemical substitutions. In LiFeAs, STM has been used to measure the superconducting gaps of clean defect free areas, to study vortexes, and to determine band structure and gap symmetry through quasiparticle interference induced by defect scattering. A detailed investigation of the impurities themselves and their localized electronic effects has yet to be reported, though in-gap states have been observed for iron adatoms in FeSe and possibly iron vacancies in KFe$_2$Se$_2$.

In this letter we characterize defects arising from crystal growth in nominally stoichiometric LiFeAs. We identify their position in the crystal lattice and analyze the spatial and energetic distribution of their bound states.
II. EXPERIMENTAL METHOD

The LiFeAs single crystals were grown by the LiAs self-flux technique. Li₃As was pre-synthesized through the reaction of Li (99.9%) lumps and As (99.9999%) powder at 773 K for 10 hours. Fe₃As was pre-synthesized from mixed powders of Fe (99.995%) and As (99.9999%) at 973 K for 10 hours. Powders of Li₃As and Fe₃As were mixed in a composition of 1:2 and placed in an alumina crucible, which was sealed under 0.3 atm Ar in a quartz tube. A Mo crucible was used to encapsulate the alumina crucible to prevent Li attack on the quartz tube. All the mixing procedures were done in an Ar atmosphere glovebox. The mixture was heated slowly to 1323 K for 10 hours, then cooled to 1073 K at 4.5 K/hour. Finally, the samples were additionally annealed at 673 K for 12 hours before being removed from the furnace. Single crystals with typical dimensions $2 \times 2 \times 0.2$ mm$^3$ were mechanically extracted from the LiAs flux. Lattice parameters $a = (3.777 \pm 0.004)$ Å and $c = (6.358 \pm 0.001)$ Å were determined by x-ray diffraction, and $T_{c, onset} = 17$ K with a transition width of 1 K was determined by SQUID magnetometry with a 1 G magnetic field.

STM/STS measurements were performed in a Createc ultrahigh vacuum low temperature STM. The electrochemically etched tungsten tip was Ar sputtered and thermally annealed at the beginning of this experiment. After cleaving the sample in situ at a temperature of 20 K it was immediately transferred to the 4.2 K STM. The sample is identical to the one used in a previous study,$^{22}$ but it has been cleaved before we obtained the measurements presented here. All spectra shown in this report were recorded at a temperature of 2.2 K and were acquired by numerical differentiation of the I-V sweep. All topography scans and dI/dV maps were recorded at 4.2 K.

III. RESULTS AND DISCUSSION

Fig. 1 a) and c) to e) show atomic resolution topographic images with common types of defects at the surface of LiFeAs. Defects with similar topography and densities have been observed in STM studies of LiFeAs grown elsewhere.$^{23,24}$ STM scans of LiFeAs also show other types of defects, but we decided to focus on the most common ones with the largest effect on the electronic structure. For a clear identification of the Fe, Li and As positions, and thereby assignment of the visible defect sites, a close look at the crystallography and the defects is needed.

LiFeAs presents a layered crystal structure detailed in Fig. 1 b).$^{19}$ At its core is a square lattice of Fe atoms, each nested at the center of a tetrahedron of As. After cleaving between the weakly bonded Li layers, the surface consists of a top layer of Li in a square lattice followed by a square lattice of As of the same periodicity but translated by $[1/2, 1/2]$. The third layer is Fe arranged again in a square lattice but of twice the density and rotated 45° relative to the Li or As lattice, where neither As nor Li sits directly above or below an Fe site.

The most common defect (labeled Fe-D$_2$-1 in Fig. 1a) according to labeling principles described below), provides a key clue to the identification of the lattice observed by STM. Its distinctive feature is the dihedral D$_2$ symmetry exhibiting two bright lobes oriented either along [100] or [010]. The symmetries discussed in this work are based on the Schönfließ notation adapted for two dimensions, since STM provides a weighted 2D projection of the 3D crystal most sensitive to disruptions occurring on the upper rather than the buried planes.

The question is: Which chemical site in the lattice can generate the observed topography? To form the center of this D$_2$ defect, both the Li and As sites are unlikely as they present D$_4$ symmetry due to the four nearest neighbors within each plane as discussed above. Iron sites, however, would induce a D$_2$-symmetry of this D$_2$ defect. The question is: Which chemical site in the lattice can generate the observed topography? To form the center of this D$_2$ defect, both the Li and As sites are unlikely as they present D$_4$ symmetry due to the four nearest neighbors within each plane as discussed above. Iron sites, however, would induce a D$_2$-symmetry of this D$_2$ defect, even though other origins such as dimers or interstitial impurities cannot be completely excluded. The
four strongly polarizable nearest neighbor $\Delta_{2}^{pp}$ would be most significantly affected by an iron site defect through charge transfer. But STM is much more sensitive to changes on the upper two As above the Fe layer, resulting in a prominent charge density contrast along the direction of these two As atoms. Likely this defect arises from Fe vacancies or Li substitution of iron sites, as the crystal was grown from a Li-rich flux. In the following we refer to this defect as Fe-D$_{2}$-1 based on the apparent center position and symmetry.

The spatial assignment of the Fe-D$_{2}$-1 defect, centered on an iron site and extended along the line of the two As nearest neighbors lying above the Fe layer, allows the registry of the three atomic sublattices (Fe, As and Li) to the measured STM corrugation. In Fig. 1a) the STM topography is overlaid with a model of the (001) cleaved crystal structure of LiFeAs (Li: yellow, As: blue, and Fe: orange), where the Fe site sits at the center of the Fe-D$_{2}$-1 defect and the two topmost As are located at the lobes. This model works remarkably well across the full scan with no phase shift between the applied grid and the measured atomic periodicity matching the Fe periodicity.

Previously, atomic resolution STM images of LiFeAs have produced the periodicity of either Li or As$^{22-25}$ measured atomic periodicity matching the Fe periodicity. lobes. This model works remarkably well across the full topography is overlaid with a model of the (001) cleaved crystal structure of LiFeAs (Li: yellow, As: blue, and Fe: orange), where the Fe site sits at the center of the Fe-D$_{2}$-1 defect and the two topmost As are located at the lobes. This model works remarkably well across the full scan with no phase shift between the applied grid and the measured atomic periodicity matching the Fe periodicity.

FIG. 2. a) The top panel shows $dI/dV$ spectra taken at a Fe-D$_{2}$-1 defect (red and blue lines) and the average over 20 spectra measured about 2 nm away from the defect (black line). The thin red and blue lines in the lower panel correspond to the difference between the spectra taken at the defect and the average from the defect-free position. A bound state is visible at approximately 3 meV. Spectra were taken at the positions marked by single red and blue dots in the topographic image b). c) $dI/dV$ map at an energy of 3 ± 1 meV, i.e. averaged from 2 meV to 4 meV. The topography and the $dI/dV$ maps are overlayed with the top-view crystal structure. Spectra shown in a) were taken at a temperature of 2.2 K. Topography and $dI/dV$ map shown in b) and c) were recorded at 4.2 K with a constant height defined by $U_{bias} = 25$ meV, $I_0 = 260$ pA. Topography and $dI/dV$ maps have edge lengths of $\approx 3.4$ nm.
FIG. 3. Same as Fig. 2 but for the As-D$_1$ defect. Bound states are visible at approximately -1.5 meV and at +3.7 meV. The topography which indicates the location of the spectra is shown as an inset of a). b) and c) $dI/dV$ maps at energies of -1.5 and 3.7 ± 1 meV, respectively.

FIG. 4. Same as Fig. 2 but for the Li-D$_1$ defect. a) A bound state is visible at approximately +1.2 meV. The topography which indicates the location of the spectra is shown as an inset of a). b), c) and d) show $dI/dV$ maps at energies of -1, 1 and 3.7 ± 1 meV, respectively.

FIG. 5. Same as Fig. 2 but for the Fe-C$_2$ defect. a) Bound states are visible at approximately +1.0 meV and at about ±3.5 meV. The topography which indicates the location of the spectra is shown as an inset of a). b), c) and d) show $dI/dV$ maps at energies of -1, 1 and 3.7 ± 1 meV, respectively.
TABLE I. Summary of the five defect types. The approximate density is the number per LiFeAs formula unit and has been obtained for one sample cleaved two times. Other samples have shown the same types of defects, with similar relative densities, but sample-to-sample differences of absolute densities. $E_b$ is the bound state energy relative to $E_F$.

| Defect | Symmetry | Density $[10^{-3}]$ | $E_b [meV]$ | $|E_{b1}| \Delta_{pp}^1$ | $|E_{b2}| \Delta_{pp}^2$ |
|--------|----------|---------------------|-------------|----------------|----------------|
| Fe-D$_2$-1 | D$_2$ | $\gtrsim 1.2$ | $\approx 3.0$ | $0.5$ | $1$
| Fe-D$_2$-2 | D$_2$ | $\lesssim 0.2$ | $\approx 3.0$ | $0.5$ | $1$
| As-D$_1$ (*) | D$_1$ | $\lesssim 0.5$ | $\approx 3.7$ | $0.62$ | $1.23$
| Li-D$_1$ (*) | D$_1$ | $\lesssim 0.1$ | $\approx 3.7$ | $0.62$ | $1.23$
| Fe-C$_2$ | C$_2$ | $\lesssim 0.1$ | $\approx \pm 3.5$ | $0.58$ | $1.17$
|               |         |                     | $\approx 1.0$ | $0.17$ | $0.33$

The strong dependence on the bias voltage reveals different spatial localization of different resonance energies. Consequently, bound states in LiFeAs result in more complex patterns than those observed in the cuprates where the LDOS of particle and hole components shows complex patterns than those observed in the cuprates where the relative densities, but sample-to-sample differences of absolute densities. $E_b$ is the bound state energy relative to $E_F$. (*) indicates those defects where the spatial assignment is ambiguous.

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32 The energetic positions of bound-state resonances are not expected to be influenced by the tip state, which we have confirmed by comparing the data shown here for the Fe-D2-1 with 4 K spectra on this defect from our previous data,[22] showing the lower weight of Δ2.

33 We note that this normalization procedure may slightly shift energetic features especially if there is an overall redistribution of spectral weight, a gap suppression, or multiple peaks that are within our 200 µV resolution. Since these factors likely exceed the small statistical uncertainty of locating the peak position, we report only approximate values for bound state energies.

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