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Title: Quantum phase transition of correlated iron-based superconductivity in $\text{LiFe}_{1-x}\text{Co}_x\text{As}$

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Abstract: The interplay between unconventional Cooper pairing and quantum states associated with atomic scale defects is a frontier of research with many open questions. So far, only a few of the high-temperature superconductors allow this intricate physics to be studied in a widely tunable way. We use scanning tunneling microscopy (STM) to image the electronic impact of Co atoms on the ground state of the $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ system. We observe that impurities progressively suppress the global superconducting gap and introduce low energy states near the gap edge, with the superconductivity remaining in the strong-coupling limit. Unexpectedly, the fully opened gap evolves into a nodal state before the Cooper pair coherence is fully destroyed. Our systematic theoretical analysis shows that these new observations can be quantitatively understood by the nonmagnetic Born-limit scattering effect in a $s\pm$ -wave superconductor, unveiling the driving force of the superconductor to metal quantum phase transition.

In the research of high- T_c superconductors, chemical substitution is a powerful way to manipulate electronic phases [1-5]. Meanwhile, chemical substitution also creates imperfections at the atomic scale, which break the unconventional Cooper pairing [4,5]. Although the single atomic impurity pair-breaking effect has been demonstrated in certain superconducting systems [4,5], it is challenging to study its collective many-body manifestation (the finite-density-impurity problem) in a widely tunable way, due to the existence of competing orders or inhomogeneity from strong electron correlation [1-5]. In this regard, the $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ is a rare case in which Co substitution monotonically suppresses the homogeneous superconductivity in LiFeAs without generating other competing orders [6-12], making it a versatile platform to quantitatively test many-body theories. Intriguingly, photoemission, optical and magnetic response experiments [7-11] reveal that Co substitution changes the Fermi surface and enhances the Fermi surface nesting along with the associated low-energy spin fluctuation, while the spin fluctuation is generally believed to be beneficial for the Cooper pairing in this material [13-15]. This contrast implies a striking, yet not understood de-pairing mechanism associated with Co substitution. Unexpectedly, previous STM experiments found no detectable local pair-breaking effects associated with a single Co impurity [16,17]. There is also no direct spectroscopic data measured deep in the superconducting state demonstrating how a finite density of Co impurities collectively suppresses Cooper pairing. Therefore, a systematic microscopic examination of the effect of the Co substitution on the ground state of $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ across the whole superconducting phase diagram is demanded.

LiFeAs crystallizes in a tetragonal unit cell ($P4/nmm$) as shown in Fig. 1(a) with a superconducting transition temperature T_c of $\sim 17\text{K}$. In momentum space, it features hole-like Fermi surfaces at the Brillouin zone center and electron-like Fermi surfaces around the zone boundary, with two extra Dirac cones at the zone center being recently observed [12] (Figs. 1(b)). We first probe the superconducting ground state of the pristine material at $T = 0.4\text{K}$. Our atomically resolved high resolution STM image reveals a tetragonal lattice which is the Li-terminating surface (Fig. 1(c)). A line-cut of the differential conductance spectra probing the local density of state (DOS) shows a spatially homogenous double-gap structure, with a larger gap of 6.0meV and a smaller gap of 3.3meV (Fig. 1(d)). Based on previous photoemission data

[18] measured at 8K, the large gap likely arises from the electron bands and the inner hole-like band, and the smaller gap likely arises from the outer hole-like band.

As the Fe lattice is systematically substituted with Co atoms, the T_C decreases linearly and reaches zero around $x = 16\%$ (Fig. 2(a)) [6-11]. Based on the photoemission data [12], the Fermi level can be systematically tuned by increasing Co concentration as illustrated in the inset of Fig. 2(a). Upon bulk substitution of 1% Co atoms, STM topographical scans reveal new dumbbell-like defects randomly scattered on the surface (Fig. 2(b)) that are different from various native defects in LiFeAs. The concentration of these defects is consistent with the nominal Co substitution. The dumbbell-like defects are also randomly aligned along two orthogonal directions, with its local two-fold symmetry arising from the structural geometry. The center of each such defect is located at the middle of two Li atoms (Fig. 2(c)), which corresponds to the position of the Co atom in the underlying (Fe, Co) lattice (Fig. 2(d) inset), and altogether they possess a local two-fold symmetry. Thus, these defects are likely caused by the atomic Co substitution [17]. Directly above these dumbbell defects, we observe a state near the smaller gap at the positive energy while the overall gap structure remains almost unchanged compared with the far away spectrum (Fig. 2(d)). The weak in-gap state is consistent with earlier calculations [19] based on the band structure and impurity potentials of Co obtained from density functional theory. We note that the observation of the small local electronic variation may benefit from our lower temperature (0.4K) and more dilute impurity concentration compared with previous STM studies [16,17]. Our observation indicates that the dilute Co substitution has a limited local impact on the superconducting order parameter or causes only very weak pair-breaking scattering.

With increasing Co concentration, the Co induced weak in-gap states overlap spatially, making them difficult to be visualized individually [16,17]. On the other hand, the finite concentration of Co impurities collectively suppresses bulk superconductivity. To study the global effects on the superconducting ground state, we systematically probe the spectra away from the apparent surface defects for a wide range of Co concentrations at base temperature 0.4K. We observe a strong variation of the superconducting gap structure in the tunneling conductance which correlates strongly with the T_C reduction (Fig. 2(e)). As the Co concentration increases, the large superconducting gap size decreases progressively until no gap remains at $x = 16\%$ where $T_C = 0$. Meanwhile, the superconducting coherence peak grows progressively weaker. Evidently, the spectral bottom evolves from a U-shape to a V-shape and then gradually elevates to the normal state value.

The Co induced gap reduction and scattering can also be qualitatively reflected in the vortex excitation. We extensively study the vortices (Fig. 3) for different Co concentrations at 0.4K with c-axis magnetic fields. In the pristine sample (Fig. 3 (a)), the vortices form an ordered hexagonal lattice under a zero-field cooling method [20,21], as can be clearly seen in the autocorrelation of the real-space mapping at 2T (Fig. 3(a) inset). As the Co concentration x increases, we find the vortex lattice symmetry to remain hexagonal like (Figs. 3(b) inset), while the vortex core size increases. The persistent hexagonal vortex lattice symmetry indicates that the randomly distributed Co dopants do not distort the vortex lattice significantly. As the core size is related with the coherence length which is proportional to the reverse of the gap in the BCS theory, the increment of the vortex core size is consistent with the aforementioned gap reduction. Moreover, measuring the conductance within a vortex under an applied c-axis field of 0.5T

reveals sharp in-gap bound states at $|E| \approx 1\text{meV}$ (Figs. 3(b)) [20,21], in agreement with the estimate of vortex core states energies in the quantum limit, which should be on the order of a non-topological superconducting vortex state (in the energy order of $\pm\Delta^2/E_F$). As the doping concentration increases, these sharp bound states become gradually less pronounced (Figs. 3(b)), consistent with the aforementioned increased scattering. For each concentration, we carefully examine at least six vortex core states, but do not find any that exhibits a pronounced zero-energy peak. This absence of localized zero-energy states is consistent with the detailed band topology of $\text{LiFe}_{1-x}\text{Co}_x\text{As}$. According to the photoemission study [12] and first-principles calculations (Fig. 1(b) and Fig. 2(a) inset), the surface Dirac cone (lower cone) is buried below the Fermi level in the three-dimensional bulk states, and hence does not form surface helical Cooper pairing and distinct Majorana bound states localized at the ends of the vortex line [22]. Moreover, the expected spectra of the vortex lines in superconductors with bulk Dirac states are not yet fully understood. Recently, there have been theoretical studies of the expected Majorana modes [23,24]. However, details of the vortex properties leave the possibility that these states are not localized at the vortex ends and the system might not feature zero energy bound states. These conclusions are not inconsistent with our experimental data, and we want to stress that it is a challenge to unambiguously distinguish the non-localized Majorana state by STM technique alone [23,24].

To quantify the Co induced gap reduction and scattering, we extract two key parameters from the raw data: the large energy gap size Δ_L and global zero-energy density of state $N(E=0)$. Remarkably, we find that Δ_L decreases linearly as a function of x and reaches zero around 16%, which scales linearly with the reducing T_C (Fig. 4(a)). In other words, the coupling strength $2\Delta_L/k_B T_C$ remains a constant (inset of Fig. 4(a)). In particular, $\text{LiFe}_{1-x}\text{Co}_x\text{As}$ remains in the strong coupling limit for all x as evidenced by $2\Delta_L/k_B T_C \approx 7.7$, much larger than the BCS value 3.5. These results suggest that the superconductivity is destroyed via a mechanism which decreases the pair susceptibility strength, but not the coupling strength. On the other hand, the extracted zero-energy state $N(E=0)$ exhibits an exponential like growth as shown in Fig. 4(b). The comparatively smaller rate of growth increase of $N(E=0)$ at low concentrations is consistent with the local effect of each Co atom individually (Fig. 2(d)) that each Co induces weak impurity state near the superconducting gap edge (Fig. 2(d)). As the concentration increases, the interference of their impurity wave functions becomes stronger and the global impurity states spread further in energy, and their tail states eventually contribute to the rapid rise of the global zero-energy state.

In our systematic first-principles calculations, we find that the Co dopants are essentially nonmagnetic with a relatively weak on-site potential of -0.43eV (Supplemental material [25]), consistent with previous experiments showing that they do not introduce a local magnetic moment [6,10,11,25]. According to the Anderson theorem, nonmagnetic impurities have little effect on the conventional s-wave superconductor. With a sign change in the order parameter, nonmagnetic impurity is then able to break the Cooper pairs [4,5,26-29]. Considering previous phase sensitive experiments [21] in this compound, the strongest pairing wave-function candidate is $s\pm$ (where the sign changes between the ordinary hole and electron Fermi surfaces). Crucially, the variation of the gap structure from U-shape to V-shape due to nonmagnetic scattering in the $s\pm$ pairing state has been predicted using the T-matrix theory [26]. Taking this two-band model from Ref. 26, we set both linear gap reduction and linear scattering rate enhancement with increasing x (Supplemental material [25]), and compute $N(E=0)$ under the

Born (weak scattering) limit and the unitary (strong scattering) limit [4,5] with the results shown in Fig. 4(b). We find that the experimental data is consistent with the former condition and deviates substantially from the latter. Figure 4(d) displays the calculated DOS in the Born limit, which gradually evolves from a fully opened gap to a less coherent V-shaped structure, in consistency with our experimental observation (Fig. 2(e)). In this model, such behavior is due to the impurity states residing near the gap edge (which can be qualitatively identified from the imaginary part of the quantum many-body self-energy, as detailed in Supplemental material [25]) with their tail states gradually moving towards zero-energy. Therefore, this theory offers a heuristic understanding of our experiment, demonstrating the Born limit nonmagnetic scattering nature of Co and sign reversal of the gap symmetry.

To acquire a self-consistent and quantitative understanding of the quantum many-body effect of the Co dopants, we further perform real-space calculations using the Bogoliubov–de Gennes (BdG) approach. We first take a two-orbital effective model capturing the essence of its low energy multi-band structure and consider randomly distributed electron dopants with weak potential scattering as Co impurities in reference to first-principles calculation (Supplemental material [25]). The next-nearest-neighbor intra-orbital attraction is considered to cause the $s\pm$ wave Cooper pairing. The calculated DOS indeed shows a clear U-shape to a V-shape evolution as demonstrated in Fig. 4(f). This encourages us to further perform a fully realistic calculation with complete five-orbitals. The five-orbital model has successfully explained the vortex core states²⁰ and weak Co impurity states in pristine LiFeAs^{16,19}, where the $s\pm$ wave Cooper pairing is self-consistently obtained within spin-fluctuation mediated pairing. Considering similarly weak potential scattering, the calculated DOS and phase diagram are shown in Fig. 4(e), which reasonably agrees with the experiment in realistic energy units. We stress that the latter five-band theoretical study contains no free fitting parameters since the band, gap structure, and impurity potential are fixed by either experiment or first-principles calculations. In this respect, it constitutes a new level of quantitative disorder modelling of unconventional superconductors. Therefore, these realistic self-consistent calculations capture the essence of the experiments and embrace the same spirit of the T-matrix calculation, unambiguously demonstrating the scattering nature of Co in iron-based superconductivity.

Our systematic experimental-theoretical analysis of the impurity effect from a single impurity to the finite density case microscopically uncovers that the Born-limit nonmagnetic scattering is the driving force of the superconducting quantum phase transition in LiFe_{1-x}Co_xAs. Future characterization of the impurity effect by Bogoliubov quasi-particle interference imaging and vector field perturbations^{21,30} will be important for further exploring the orbital and band selectivity of the Born-limit nonmagnetic scattering.

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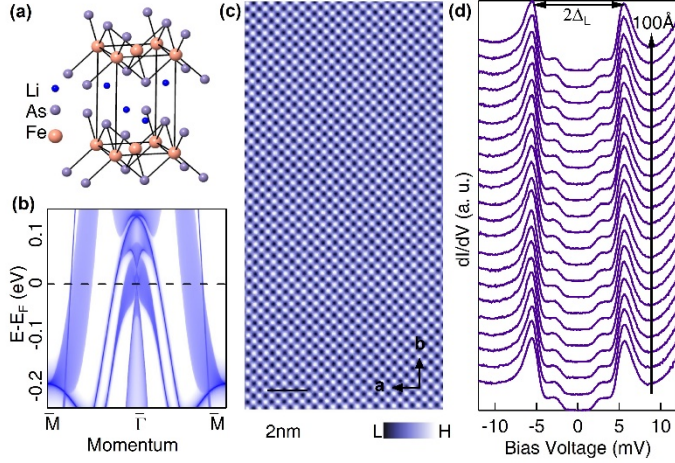


Fig. 1. (a) Crystal structure of LiFeAs. (b) First-principles calculation of the band structure for (001) surface. (c) Atomically-resolved topographic image of pristine LiFeAs showing clean tetragonal lattice. (d) Line-cut differential conductance spectra on pristine LiFeAs, showing a spatially homogeneous double-gap structure.

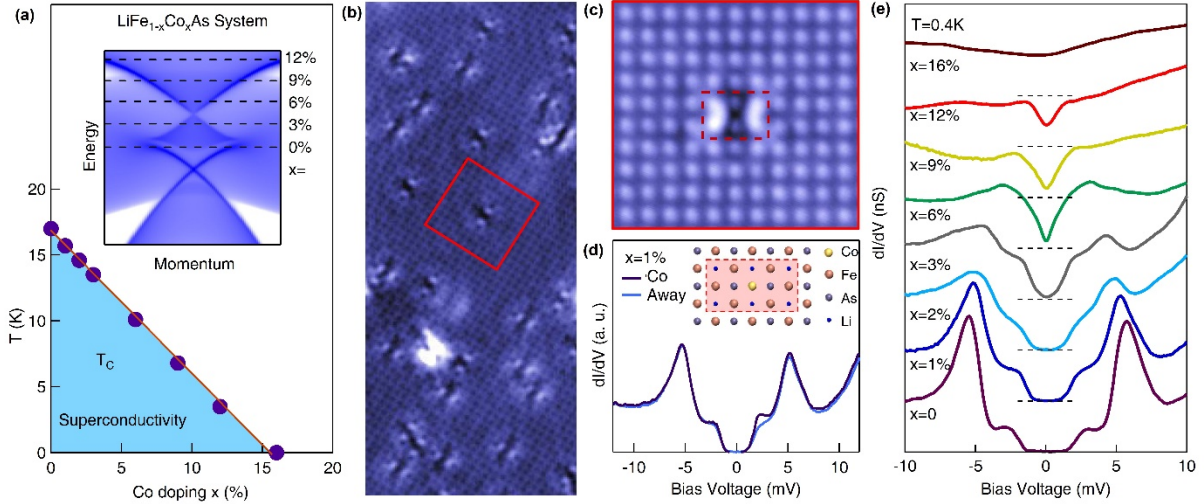


Fig. 2. (a) Phase diagram of $\text{LiFe}_{1-x}\text{Co}_x\text{As}$. The superconducting transition temperature is determined by the onset of zero resistivity. Inset: illustration of the Co doping effect on the bulk Dirac cone at the Brillouin zone center based on Ref. 12. (b) Atomically resolved topographic image of a sample with 1% Co substitution, showing randomly scattered dumbbell-like defects that do not exist in the pristine sample and with concentration consistent with the Co substitution level. (c) Enlarged image of single reproducible dumbbell-like defect. The center of the defect geometrically corresponds to a Co substitution atom in the Fe layer (in reference to Fig. 2D inset). (d) Differential conductance spectrum taken at the defect and far from the defect. Inset: crystal structure from top view. (e) Co concentration dependence on spatially averaged superconducting gap structure. The spectra are offset for clarity. The dashed lines mark the zero-intensity value for each case. 30 to 50 dI/dV curves taken away from apparent surface impurities

with the same junction set up ($V = -15\text{mV}$, $I = 750\text{pA}$) were averaged to obtain the dI/dV curve for each concentration.

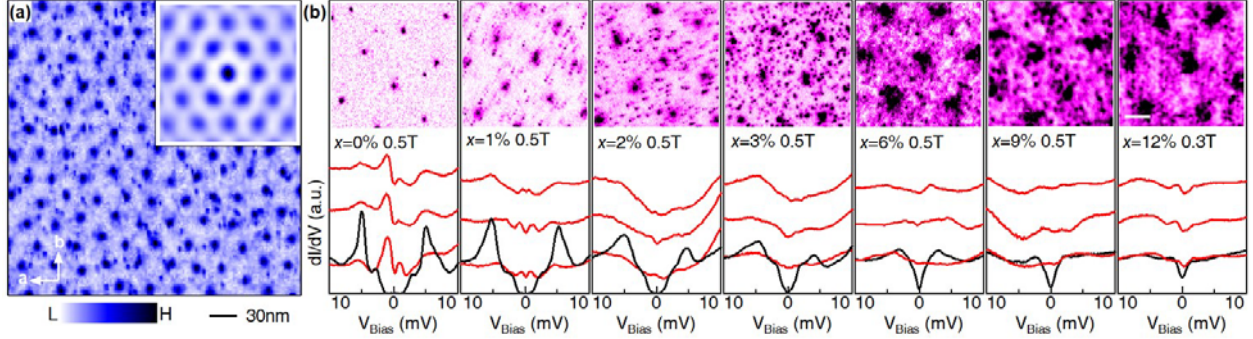


Fig. 3. (a) Left: real space mapping of vortices at the Fermi energy on pristine LiFeAs at $B = 2\text{T}$. Inset: auto-correlation of vortex mapping showing hexagonal lattice symmetry. (b) Spectra in the zero-field state (black) and at three representative vortices offset for clarity (red) for each concentration. The inset image in each panel shows the respective vortex lattice (the bar marks a length of 35nm).

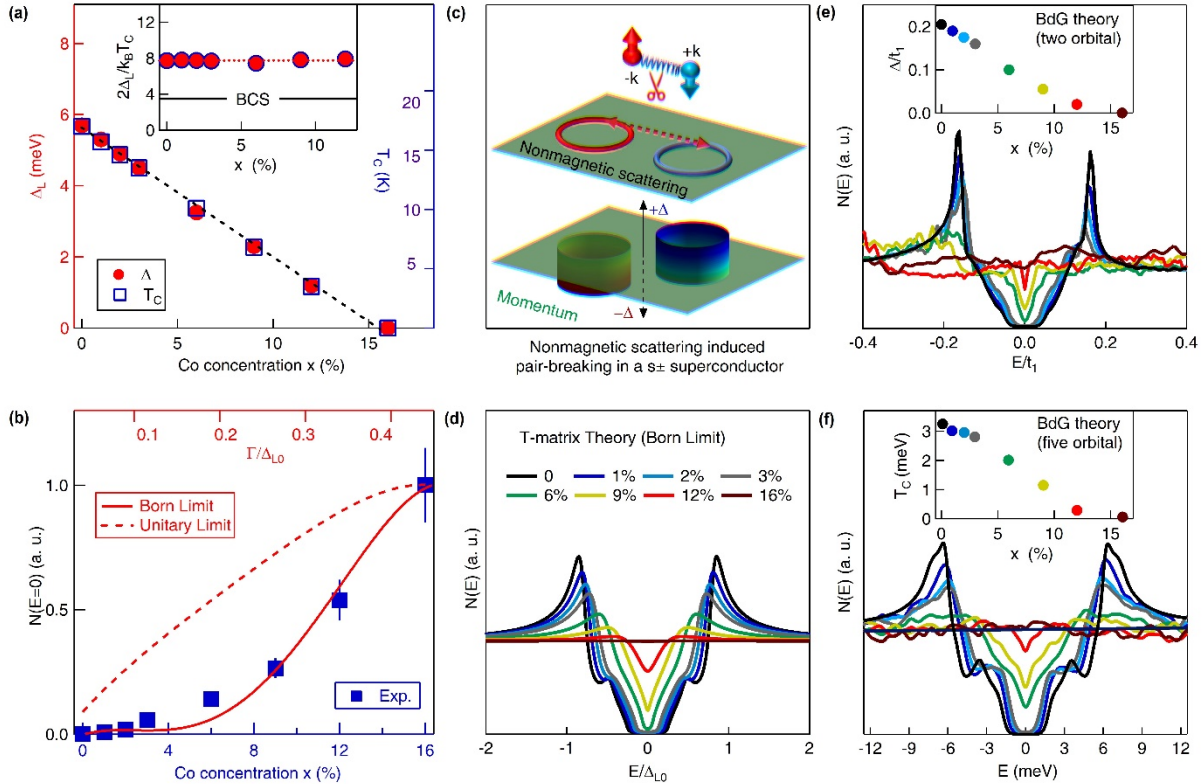


Fig. 4. (a) The large gap size Δ_L (left axis, red) and T_c (right axis, blue) both decrease linearly as a function of concentration x . Inset: $2\Delta_L/k_B T_c$ remains constant (~ 7.7) as a function of Co concentration. (b) Differential conductance at zero energy $N(E=0)$ as a function of Co concentration x in $\text{LiFe}_{1-x}\text{Co}_x\text{As}$. The experimental data is normalized by the normal state value.

The red solid and dashed lines denote $N(E=0)$ calculated based on Born and unitary limit scattering, respectively. (c) Schematic showing a sign reversal s-wave pairing on two Fermi surfaces (lower panel, $s_{\pm}$ gap symmetry) and the nonmagnetic impurities induced interband scattering causing pair-breaking (upper panel). (d) Calculated density of states evolution of the $s_{\pm}$ pairing state with nonmagnetic scattering at the Born limit with T-matrix theory. (e) (f) Calculated averaged DOS evolution with increasing Co concentration by BdG theory with two-orbital and five-orbital models, respectively. The inset shows the phase diagram plot.