Observation of a bi-critical point between antiferromagnetic and superconducting phases in pressurized single crystal Ca$_{0.73}$La$_{0.27}$FeAs$_2$

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**A B S T R A C T**

One of the most strikingly universal features of the high-temperature superconductors is that the superconducting phase emerges in the close proximity of the antiferromagnetic phase, and the interplay between these two phases poses a long-standing challenge. It is commonly believed that, as the antiferromagnetic transition temperature is continuously suppressed to zero, there appears a quantum critical point, around which the existence of antiferromagnetic fluctuation is responsible for the development of the superconductivity. In contrast to this scenario, we report the observation of a bi-critical point identified at 2.88 GPa and 26.02 K in the pressurized high-quality single crystal Ca$_{0.73}$La$_{0.27}$FeAs$_2$ by complementary in-situ high pressure measurements. At the critical pressure, we find that the antiferromagnetism suddenly disappears and superconductivity simultaneously emerges at almost the same temperature, and that the external magnetic field suppresses the superconducting transition temperature but hardly affects the antiferromagnetic transition temperature.

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1. Introduction

Even after thirty years from the discovery of the copper oxide superconductors, how to understand the interplay between antiferromagnetism and unconventional superconductivity has been one of the most sophisticated issues in condensed matter physics [1–9]. Iron-based superconductors found in 2008 are a new family of high temperature superconductors [10,11], which provides new opportunity to clarify this issue. Among them, the iron pnictide superconductor Ca$_{1-x}$La$_x$FeAs$_2$ [10–17] has a monoclinic structure with the -FeAs-(Ca/La)-As-(Ca/La)-FeAs- stacking along c axis [12,14]. In particular, the presence of the metallic As-As zig-zag chains in the spacer layers make it structurally and electronically distinct from the archetype 122 Fe-based superconductor CaFe$_2$As$_2$ [18,19]. The superconductivity in Ca$_{1-x}$La$_x$FeAs$_2$ exhibits in the doping range from $x = 0.15$ to $x = 0.25$ [Refs. [13,14,20,21]]. Nuclear magnetic resonance measurements found that the superconducting phase coexists with the antiferromagnetic (AFM) phase in the above doping range and the AFM transition temperature is enhanced with increasing La concentrations [22]. However, beyond the doping level ~0.25, the sample becomes a poor metal with a stripe like AFM long-ranged order [20], which can be regarded as the “parent compound” of this family of superconductors. It is well-known that pressure is a “clean” way to realize a continuous tuning of the crystal structure and the corresponding electronic structure without introducing additional chemical complexity, being an ideal method to study the interplay between the AFM and superconducting phases [23,24].

2. Methods

In this study, by applying a Toroid (also known as the Paris-Edinburgh-type) high-pressure cell with the glycerin/water (3:2)
liquid as the pressure transmitting medium, which can maintain the sample in a hydrostatic pressure environment up to 5 GPa, we performed complementary in-situ hydrostatic pressure measurements of resistance, alternating current (ac) susceptibility and heat capacity on the high-quality Ca$_{0.73}$La$_{0.27}$FeAs$_2$ single crystals. Pressure inside the sample chamber measured by superconducting transition temperature of Lead (Pb).

### 3. Experimental results

The arrangement of the samples and the components on the lower part of the pressure anvil is shown in Fig. 1a. Under ambient pressure a resistivity drop at the temperature $\sim$54 K is observed (Fig. 1b), signifying an AFM transition ($T_M$) that is in fairly agreement with the reported results from neutron scattering measurements [20]. Above $T_M$, the first derivative of the resistance with respective to the temperature shows a weak kink which is associated with the monoclinic to a triclinic structural phase transition (inset of Fig. 1b), indicating that the stripe-like AFM is characterized by three-component order parameters [20]. The temperature of the structural phase transition is suppressed by applying pressure and gradually loses the resolution from the AFM transition. Under given pressures, the temperature dependence of electrical resistivity for the sample A is displayed in Fig. 1c. To confirm the pressure effect on antiferromagnetic transition temperature observed in the sample A, we performed our high-pressure measurements on the sample B, in which the evolution of $T_M$ with external pressure is confirmed (Fig. S1, Supplementary data). Our two independent measurements for the two samples consistently demonstrate that the $T_M$ shifts to lower temperature upon increasing pressure. At the pressure 2.85 GPa, the AFM phase transition occurs at 26.08 K, but suddenly disappears when pressure is higher than it. Furthermore, our high-pressure heat capacity measurements verify the above results and the detailed analysis is given in Fig. S2 (Supplementary data).

With further increasing pressure just greater than 2.85 GPa, a pressure-induced superconducting phase with a transition temperature ($T_C$) of 26.09 K is found at 2.95 GPa (sample A). The value of $T_C$ is determined by the onset temperatures of the resistivity drops. The zero resistant superconducting state is observed at 3.45 GPa and above (inset of Fig. 2a). To characterize the superconducting transition further, we applied magnetic field at 2.95 and 4.95 GPa, respectively. It is found that the onset-temperatures of the superconducting transition shift to lower temperatures (Fig. 2b), indicating that the resistivity drop is associated with a superconducting transition. To further confirm the pressure-induced superconductivity, we performed in-situ high pressure resistivity and alternating-current (ac) susceptibility measurements for the sample B. The results are shown in Fig. 2c and d, where the $T_C$ (ac) is determined by the intersection of the lines through the steep slope and the zero slope. By comparing the
amplitude of diamagnetic throw of the sample with that of the pressure gauge Pb (employed as a reference, placed next to the sample in the same coil, as shown in Fig. 1a) which is with the similar shape and mass to the sample, we can estimate the relative change of the superconducting volume, i.e. from $C_24$ at pressure of 2.99 GPa to $C_24$ at 3.53 GPa (Inset of Fig. 2d), implying that the pressure-induced superconductivity is abruptly turned on at the critical pressure. Because the Toroid high pressure cell can maintain the hydrostatic pressure conditions for the measurement as high as $P_{5 GPa}$, we performed our measurements below this pressure.

Our high-pressure X-ray diffraction measurements demonstrate that no pressure-induced crystal structural phase transition occurs throughout the pressure range investigated (Fig. S3, Supplementary data). Thus it can be regarded as that the pressure-induced suppression of AFM and emergence of superconductivity are caused by the electron-electron interactions. It is also possible that there is a significant change in the Fermi surface at the critical pressure. Because the Toroid high pressure cell can maintain the hydrostatic pressure conditions for the measurement as high as ~5 GPa [25], we performed our measurements below this pressure.

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4. Discussions and summary

We summarize the pressure dependence of the characteristic temperatures $T_M$ and $T_C$ in the phase diagram of Fig. 4a, in which there are two distinct low temperature regions representing the AFM phase and superconducting phase. In the AFM phase region, the $T_M$ is remarkably suppressed with increasing pressure and terminated at 26.08 K and 2.85 GPa. Then the superconductivity with $T_C = 26.09$ K appears at 2.95 GPa, where the $T_C$ is determined from the electrical resistance measurements. The values of the $T_C$ are unexpectedly close to the terminating point of $T_M$ (26.08 K) at 2.85 GPa, which implies that the AFM transition temperature and the superconducting transition temperature will meet together at a critical pressure. Extrapolations of the $T_M$-$P$ curve and $T_C$-$P$ curve yield an intersected point at 2.88 GPa and 26.02 K, which is denoted by the red star in the phase diagram. Such a special point is conventionally defined as a bi-critical point in phase transition.
In the superconducting phase region, the $T_C$ shows a weak response to pressure. Our deduced phase diagram is different from that obtained by the chemical doping in Ca$_{1-x}$La$_x$FeAs$_2$, whose superconducting phase coexists with the AFM phase [22,26]. This reveals a dramatic difference between these two tuning ways (lanthanum doping and applying pressure) for this compound.

It is noteworthy that Gati et al. [19] also found an intersection between $T_M$ and $T_C$ in the pressure-temperature phase diagram of Ca(Fe$_{0.972}$Co$_{0.028}$)$_2$As$_2$ sample, in which it demonstrates two first order transitions. One occurs below 0.03 GPa where the sample undergoes a transition from a paramagnetic (PM) phase to an AFM phase with cooling. The other appears at $\sim$0.03 GPa where the transition from the AFM phase to a superconducting phase is observed. These results indicate that the intersection is a tri-critical point. Naturally, this raises the question, why the nature of the intersected points is so different in the pressurized Ca(Fe$_{0.972}$Co$_{0.028}$)$_2$As$_2$ and Ca$_{0.73}$La$_{0.27}$FeAs$_2$. Here, we propose that the distinction between the crystal structures of these two compounds is responsible for their different high-pressure behaviors. It is found that the critical pressure for the tri-critical point is 0.03 GPa in the former, while for the bi-critical point is $\sim$3 GPa in the latter, about 100 times larger. Moreover, the ambient-pressure phase of the Ca(Fe$_{0.972}$Co$_{0.028}$)$_2$As$_2$ is a partially suppressed AFM phase which is quite close to the superconducting state, while that of the Ca$_{0.73}$La$_{0.27}$FeAs$_2$ is a peculiar AFM phase which is achieved by completely suppressing the superconducting phase ($La = 0.15 – 0.25$). These two types of intersected points found in the two different pressurized FeAs-based superconductors may provide significant constrains on the theory for understanding the FeAs based superconductors.
Twenty years ago, the SO(5) theory attempted to unify antiferromagnetism and superconductivity in the temperature-doping phase diagram of copper oxide superconductors and predicted a bi-critical point with emergent SO(5) symmetry [27,28]. If the bi-critical point with SO(5) symmetry exists, it can be expected that the application of magnetic field will not be able to separate the intersected point of the $T_M$ and $T_C$. To further understand the nature of the bi-critical point observed in Ca$_{0.73}$La$_{0.27}$FeAs$_2$, we applied different magnetic fields perpendicular to (100) plane of the sample. We find that, upon increasing magnetic field, the $T_C$ is suppressed to lower temperature in the pressure range of the superconducting phase (Fig. 4b–d), however, $T_M$ has no visible change to the applied magnetic field under the magnetic field up to 8 T (Fig. 4b–d and Fig. S4, Supplementary data). The field-induced separation of $T_M$ and $T_C$ at the critical pressure observed throughout our measurements implies that the SO(5) theory is not applicable to interpret the bi-critical point found in the pressurized Ca$_{0.73}$La$_{0.27}$FeAs$_2$. To the best of our knowledge, this is the first time that a bi-critical point between an AFM phase and a superconducting phase is observed experimentally in high temperature superconductors, which deserves further investigations from experimental and theoretical sides. Our observation in this study is expected to provide a valuable experimental foundation for understanding the interplay between the AFM and superconductivity.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.scib.2017.05.027.

References

[1] Keimer B, Kivelson SA, Norman MR, et al. From quantum matter to high-temperature superconductivity in copper oxides. Nature 2015;518:179.

[2] Scalapino DJ. A common thread: the pairing interaction for unconventional superconductors. Rev Mod Phys 2012;84:1383.
[3] Dai P, Hu J, Dagotto E. Magnetism and its microscopic origin in iron-based high-temperature superconductors. Nat Phys 2012;8:705.
[4] Sachdev S, Keimer B. Quantum criticality. Phys Today 2011;64:29.
[5] Norman MR. The challenge of unconventional superconductivity. Science 2011;332:196.
[6] Paglione J, Greene RL. High-temperature superconductivity in iron-based materials. Nat Phys 2010;6:645.
[7] Armitage NP, Fournier P, Greene RL. Progress and perspectives on electron-doped cuprates. Rev Mod Phys 2010;82:2421.
[8] Luetkens H, Klauss HH, Kraken M, et al. The electronic phase diagram of the LaO$_{1-x}$F$_x$FeAs superconductor. Nat Mater 2009;8:305.
[9] Monthoux P, Pines D, Lonzarich GG. Superconductivity without phonons. Nature 2007;450:1177.
[10] Rotter M, Tegel M, Johrendt D. Superconductivity at 38 K in the iron arsenide (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$. Phys Rev Lett 2008;101:107006.
[11] Kamihara Y, Watanabe T, Hirano M, et al. Iron-based layered superconductor La(O$_{1-x}$F$_x$)$_2$FeAs ($x = 0.05$–$0.12$) with $T_c = 26$ K. J Am Chem Soc 2008;130:3296.
[12] Yakita H, Ogino H, Okada T, et al. A new layered iron arsenide superconductor: (Ca, Pr)FeAs$_2$. J Am Chem Soc 2014;136:846.
[13] Kudo K, Mizukami T, Kitahama Y, et al. Enhanced superconductivity up to 43 K by P/Sb doping of Ca$_{1-x}$La$_x$Fe$_2$As$_2$. Phys Rev B 2014;90:134516.
[14] Gati E, Köhler S, Guterding D, et al. Hydrostatic-pressure tuning of magnetic, nonmagnetic, and superconducting states in annealed Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$. Phys Rev B 2012;86:220511.
[15] Jiang S, Liu C, Cao H, et al. Structural and magnetic phase transitions in Ca$_{0.7}$La$_{0.3}$FeAs$_2$ with electron-overdoped FeAs layers. Phys Rev B 2016;93:054522.
[16] Kudo K, Kitahama Y, Fujimura K, et al. Superconducting transition temperatures of up to 47 K from simultaneous rare-earth element and antimony doping of 112-type CaFeAs$_2$. J Phys Soc Jpn 2014;83:093705.
[17] Kawasaki S, Mabuchi T, Maeda S, et al. Doping-enhanced antiferromagnetism in Ca$_{1-x}$La$_x$FeAs$_2$. Phys Rev B 2015;92:180508.
[18] Jiang S, Liu L, Schütt M, et al. Superconductivity emerging from a suppressed large magnetoresistant state in tungsten ditelluride. Nat Commun 2013;6:7804.
[19] Sun L, Chen XJ, Guo J, et al. Re-emerging superconductivity at 48 Kelvin in iron chalcogenides. Nature 2012;483:67.
[20] Sidorov VA, Tsiok OB. Phase diagram and viscosity of the system glicerine-water under high pressure. Fiz Techn Vys Davlenyj 1991;1:74.
[21] Jiang S, Liu L, Schütt M, et al. Effect of interlayer coupling on the coexistence of antiferromagnetism and superconductivity in Fe pnictide superconductors: a study of Ca$_{0.74(1)}$La$_{0.26(1)}$(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals. Phys Rev B 2016;93:174513.
[22] Demler E, Zhang SC. Quantitative test of a microscopic mechanism of high-temperature superconductivity. Nature 1998;396:733.
[23] Zhang SC. A unified theory based on SO(5) symmetry of superconductivity and antiferromagnetism. Science 1997;275:1089.