Strong anisotropy effect in an iron-based superconductor CaFe$_{0.882}$Co$_{0.118}$AsF

Yonghui Ma$^{1,2,3}$, Qiucheng Ji$^{1,2,3}$, Kangkang Hu$^{1,4}$, Bo Gao$^{1}$, Wei Li$^{1,2,5}$, Gang Mu$^{1,2}$ and Xiaoming Xie$^{1,2}$

$^1$State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, People’s Republic of China
$^2$CAS Center for Excellence in Superconducting Electronics (CENSE), Shanghai 200050, People’s Republic of China
$^3$University of Chinese Academy of Science, Beijing 100049, People’s Republic of China
$^4$Shanghai Key Laboratory of High Temperature Superconductors, Shanghai University, Shanghai 200444, People’s Republic of China
$^5$Department of Physics and State Key Laboratory of Surface Physics, Fudan University, Shanghai 200433, People’s Republic of China

E-mail: liwei@mail.sim.ac.cn and mugang@mail.sim.ac.cn

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Abstract
The anisotropy of iron-based superconductors is much smaller than that of the cuprates and that predicted by theoretical calculations. A credible understanding for this experimental fact is still lacking up to now. Here we experimentally study the magnetic-field-angle dependence of electronic resistivity in the superconducting phase of an iron-based superconductor CaFe$_{0.882}$Co$_{0.118}$AsF, and find the strongest anisotropy effect of the upper critical field among the iron-based superconductors based on the framework of Ginzburg–Landau theory. The evidence of the energy band structure and charge density distribution from electronic structure calculations demonstrates that the observed strong anisotropic effect mainly comes from the strong ionic bonding in between the ions of Ca$^{2+}$ and F$^{-}$, which weakens the interlayer coupling between the layers of FeAs and CaF. This finding provides a significant insight into the nature of the experimentally-observed strong anisotropic effect of electronic resistivity, and also paves the way for designing exotic two-dimensional artificial unconventional superconductors in the future.

Keywords: CaFe$_{0.882}$Co$_{0.118}$AsF, iron-based superconductors, anisotropy

(Some figures may appear in colour only in the online journal)

1. Introduction
Since the discovery of superconductivity at 26 K in a fluorine-doped quaternary compound LaFeAsO [1], studies of the mechanism of iron-based superconductors (FeSCs) have evoked enormous interest across the superconductivity and material science community. Huge experiments have revealed that the FeSCs belong to a family with an unconventional pairing mechanism within FeAs(Se) layers. Information regarding the upper critical field $H_{c2}$ and its anisotropy in superconductivity can be used as a fingerprint to understand the unconventional superconducting mechanism and to promote practical applications [2–4]. In addition, bidimensionality, which is represented by a rather high anisotropy between the $ab$-plane and c axis, is believed to be a very important factor for the occurrence of strong correlation physics and even high-$T_c$ superconductivity [5–9]. Generally speaking, the anisotropy parameter $\gamma$ of the FeSCs was found to be much smaller than that of the cuprates and that predicted by theoretical calculations [8, 10–16]. Although the Pauli-limit effects have been taken into account in understanding the low temperature behaviors of $H_{c2}$ [17–19], the nature of such a small value of anisotropy parameter $\gamma$ of the FeSCs remains unclear in the vicinity of superconducting transition.
temperature $T_c$. Interestingly, it has been found that the values of In($\gamma^2$) are linearly proportional to the distance $d$ of the adjacent conducting layers for both the cuprate superconductors and FeSCs [8, 11], which is understandable since a thicker insulating block layer weakens the interlayer hybridization; as a result the anisotropy will be enhanced. Quantitatively, the value $\gamma^2$ of FeSCs has a magnitude typically two orders lower than that of cuprate SCs with the same $d$.

Recently, high-quality single crystals of CaFeAsF and Co-doped compounds with a size above 1 mm were grown successfully by our group using a new flux CaAs [20, 21], which facilitates our research on the anisotropy effect of this system. Although the anisotropy parameter of the penetration depth were previously investigated by torque measurements [22, 23], it was found that the value of $\gamma$ obtained from the London penetration depth experiment is quite different from that based on the upper critical field in FeSCs [24, 25]. The nature of such a difference remains unclear. Considering this issue here, we thoroughly study the anisotropy of the superconducting single crystals CaFe$_{0.882}$Co$_{0.118}$AsF based on the upper critical fields. The magnetic-field-angular dependence of the electronic resistivity in the superconducting state is measured and the results are found to follow the scaling law of the anisotropic Ginzburg–Landau (GL) theory. The obtained anisotropy parameter is clearly larger than that of other FeSCs, and reaches the order of magnitude of the theoretical estimations [16]. Based on the charge density distribution calculations, it is found that this strange phenomena mainly stems from the nature of the strong ionic bonding in between the ions of Ca$^{2+}$ and F$^-$, which weakens the interlayer coupling between the FeAs and CaF layers.

2. Experimental details and calculations

The CaFe$_{1-x}$Co$_x$AsF single crystals were grown using the CaAs self-flux method [20, 21]. The crystal structure and lattice constants of the materials were examined by a DX-2700 type powder x-ray diffractometer using Cu K$_\alpha$ radiation. The electronic resistivity (including the magnetic field angle-resolved electronic resistivity) were measured using a four probe technique on the physical property measurement system (Quantum Design, PPMS) with a magnetic field up to 9 T. The angle $\varphi$ was varied in the range 0°–180°, where $\varphi = 0^\circ$ indicates the orientation with the magnetic field parallel to the c-axis of the sample. In addition, the current was always applied perpendicular to the magnetic field, as shown schematically in the inset of figure 2(a).

The first-principles calculations presented in this work were performed using the all-electron full potential linear augmented plane wave plus local orbitals method [26] as implemented in the WIEN2K code [27]. The exchange-correlation potential was calculated using the generalized gradient approximation as proposed by Pedrew, Burke, and Ernzerhof [28]. These calculations were performed using the experimental crystal structure [20], as shown in figure 1(a).

3. Results

The x-ray was incident on the ab-plane of the sample when carrying out the x-ray diffraction measurements. The diffraction pattern is shown in figure 1(b), which follows the tetragonal ZrCuSiAs-type structure. It is important to point out that only the sharp peaks along the (00l) orientation are observed, suggesting a high c-axis orientation. The actual doping level of the cobalt was determined to be 0.118 by energy dispersive x-ray spectroscopy. Detailed analysis and discussions regarding the crystal structure and the chemical composition have been reported in our previous paper [21]. The temperature dependence of the electronic resistivity is shown in figures 1(c) and (d). Under zero field, the sample exhibits a sharp superconducting transition at $T_c$ (onset) $= 21.6$ K (90%$\rho_0$) with a transition width $\Delta T_c = 1.7$ K (10%–90%$\rho_0$), where $\rho_0$ is the resistivity of the normal state before the superconducting transition, demonstrating the high quality of our single crystal samples. The slight semiconducting behavior just above $T_c$ along with the $T_c$ value indicates that the present sample locates on the slightly underdoped region near the optimal doped point of the phase diagram.

We perform the measurements of the temperature-dependent electronic resistivity with the magnetic field along various orientations to study the anisotropy effect of $H_{c2}$. As shown in figures 1(c) and (d), the superconducting transition point shifts to a lower temperature with the increase of the magnetic field for both the orientations parallel and perpendicular to the c-axis of the crystal structure. It is worth noting that the superconducting transition for the orientation of $H // c$ shifts more quickly than that of $H // ab$ by comparing the data from figures 1(c) and (d). Quantitatively, we use 90%$\rho_0$ to determine the upper critical field $H_{c2}$. The temperature dependence of $H_{c2}$ is shown in the inset of figure 1(d) for both the two orientations, and the value of the
For the FeSCs is two orders of magnitude lower than that reported on other FeSCs. Generally speaking, the value of $\gamma$ for the FeSCs is two orders of magnitude lower than that of the cuprate SCs with the same value of $d$.  

In figure 2(d), we also show the $\gamma^2$ values at 0.85 $T_c$ as a function of the distance $d$ between the neighboring conducting layers (FeAs layers or CuO$_2$ layers). The two dashed lines, respectively represent the tendency of the previously reported FeSCs and cuprate SCs [11]. Generally speaking, the value of $\gamma^2$ for the FeSCs is two orders of magnitude lower than that of the cuprate SCs with the same value of $d$.  

4. Discussion  

Although we have found the largest anisotropy parameter $\gamma$ of CaFe$_{0.882}$Co$_{0.118}$AsF in FeSCs, the experimental observation is consistent with the theoretical prediction by first-principles calculations. Previously, Singh et al [16] predicted the anisotropy to be about 15 for the parent phase of the 1111 system very soon after the discovery of the high-$T_c$ FeSCs. It is clear that the anisotropy is closely related to the electronic structure. Although, the Fermi surface of most of the FeSCs consists of five sheets, where two electron-like cylinders are centered around the M-A line and two hole-like cylinders around the Γ-Z line, as well as an additional small 3D hole-like pocket centered at the Z point, individual characteristics in the detailed electronic structure may have a remarkable influence on the anisotropic effect of the materials. As an example, the strong warping of the electron pockets in the 122, 111, and 11 systems, compared with the 1111 system [16, 32, 33], can be expected to increase the tendency of 3D characterizations, which may explain the fact that the anisotropy parameter of these three systems is smaller than that of the 1111 system.  

In order to examine the detailed electronic structure of CaFe$_{0.882}$Co$_{0.118}$AsF and to clarify the nature of the emergence of the strongest electronic anisotropy among the FeSCs, we carried out first-principles calculations. The electronic band structure should be merely changed slightly by the cobalt doping of 11.8% based on the rigid-band approximation. For simplicity, we only show the energy band and its Fermi surface topology of CaFeAsF in figures 3(a) and (b), respectively, which are in good agreement with previous report [34]. Firstly we examine the energy dispersions between the high symmetric k-points of Γ and Z; there are no band intersections across the Fermi level. This result indicates the absence of the 3D Fermi pocket around the Z point. In addition, it is found that all the Fermi surface sheets are almost ideal cylinders (see figure 3(b)). Previously, Nekrasov et al have pointed out that the fluorine-based 1111 system curve at a fixed temperature. In addition, the temperature dependence of the obtained anisotropy parameter $\gamma$ is also shown in figure 2(c). For comparison, we also show a consistent value of anisotropic parameter $\gamma$ estimated from $H^2_{GL}/H^2_{ab}$. Importantly, these anisotropic values are much larger than those reported on other FeSCs.  

Anisotropic GL theory, the effective upper critical field as a function of the azimuth angle $\varphi$ is expressed as [29]:  

$$H^2_{GL}(\varphi) = \frac{H^2_{ab}}{\sin^2 \varphi + \gamma^2 \cos^2 \varphi} \propto \frac{1}{\sin^2 \varphi + \gamma^2 \cos^2 \varphi}.$$  

Here, it should be noted that the resistivity in the superconducting state merely depends on the effective magnetic field $H/\gamma H^2_{GL}(\varphi)$, i.e. $\rho = \rho[H/\gamma H^2_{GL}(\varphi)],$ at a given temperature [30]. According to equation (1), we rewrite the resistivity as a function of $H/\gamma H^2_{GL}(\varphi)$, and show it in figure 2(b). It clearly demonstrates the universal behavior where all the magnetic-field-dependent electronic resistivity falls into one

Figure 2. (a) Magnetic-field-angular-dependence of electronic resistivity at 19 K under magnetic fields up to 9 T. The inset illustrates schematically the definition of angle $\varphi$, and the electron current is always perpendicular to the magnetic field. (b) Scaled resistivity at 18 K, 19 K, 20 K and 21 K as a function of $H \sin^2 \varphi + \gamma \cos^2 \varphi$. (c) Temperature dependence of the anisotropy parameters $\gamma$ obtained from GL theory and $H^2_{GL}/H^2_{ab}$. (d) Comparison of our anisotropy result with other FeSCs and cuprates. Here $\gamma^2$ is extracted at the temperature 0.85 $T_c$ and $d$ is the distance of the neighboring conducting layers. The two dashed lines representing the tendency of the previously reported FeSCs and cuprate SCs are reprinted from [11], with the permission of AIP Publishing. The value of the 42214 system was reported in [31], which implies a saturated tendency as $d$ becomes even larger.

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and the distribution of hybridization with the Pt topology of the Fermi surface stemming from the strong calculations have demonstrated a strong 3D character in the As for the 10-3-8 system with an even larger interlayer calculation for the system of LaFeAsO with the same crystal surfaces than the oxygen-based 1111 system LaFeAsO.

Figure 3. (a) Calculated band structure of CaFeAsF. The Fermi energy was set to zero (dashed line). There is no band intersecting the Fermi level between the Γ and Z points. (b) The Fermi surfaces of CaFeAsF. (c)–(d) The charge density distribution ρ(0) of the (110) and (010) planes for CaFeAsF and LaFeAsO respectively.

displays a much more perfect 2D character of the Fermi surfaces than the oxygen-based 1111 system LaFeAsO [35]. As for the 10-3-8 system with an even larger interlayer distance, both the ARPES measurements and first-principles calculations have demonstrated a strong 3D character in the topology of the Fermi surface stemming from the strong hybridization with the Pt d_{xy} orbitals [36]. This should definitely suppress the bidimensionality of the Fermi surface. The perfect bidimensionality of CaFeAsF may qualitatively explain the experimental fact of the strong anisotropy of CaFeO_{0.88}Co_{0.11}AsF.

Quantitatively, we calculated the charge density distribution ρ(r) of CaFeAsF, as shown in figure 3(c). For comparison, we also performed the charge density distribution ρ(r) calculation for the system of LaFeAsO with the same crystal structure of CaFeAsF, which is shown in figure 3(d). From the distribution of ρ(r) in the (110) plane, it displays no difference around the Fe–As bond between LaFeAsO and CaFeAsF, but ρ(r) in the area around La–As clearly has a much higher value than that in the area around Ca–As, suggesting the weakness of the interlayer coupling between the layers of FeAs and CaF. This result is also understandable because the strong electronegativity of F favors the formation of the much stronger ionic bonding with Ca, as revealed by the lower values of ρ(r) in between Ca^{2+} and F⁻ ions in the (010) plane, and weakens the interlayer coupling. This mechanism well explains the nature of such a strong electronic anisotropy observed in the experiments in the system of CaFeAsF.

5. Conclusions

In summary, the magnetic field angular dependence of the resistivity in the superconducting state was measured on the single crystals of CaFeO_{0.88}Co_{0.11}AsF. The obtained anisotropy parameter γ based on the anisotropic GL theory is much larger than that of other FeSCs. By the charge density distribution calculations, we found that the strong electronic anisotropy mainly comes from the strong intra-layer ionic bonding in the CaF layer, which weakens the interlayer coupling between the FeAs and CaF layers compared with that between the FeAs and LaO layers. Our results demonstrate that the fluorine-based 1111 system may be the most 2D superconducting material in the FeSCs from the viewpoint of electronic structure. The interplay between the strong electronic anisotropy and unconventional superconductivity is an important issue for understanding the mechanism of the unconventional SC, which deserves our attention in the future.

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