Possible Phase Separation and Transport Properties in Large Superconducting Ca$_{0.77}$La$_{0.18}$Fe$_{0.90}$As$_2$ Crystals

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We synthesized large superconducting single crystal Ca$_{0.77}$La$_{0.18}$Fe$_{0.90}$As$_2$ (‘112’ type) of 2 millimeter size. Scanning electron microscopy (SEM) measurements revealed that bright and dark stripes alternately spread on the surface of crystals, indicating possible existence of intrinsic phase separation. Temperature ($T$)-dependent resistivity, Hall effect and magneto-resistance (MR) were measured with magnetic field ($H$) applied to different directions of crystal. The upper critical field ($H_{c2}$) anisotropy $\gamma$ was estimated with a moderate value around 2.8. Positive Hall coefficient ($R_H$) and anisotropic $MR$ were found and showed strong $T$-dependent feature. Below $T$ about 100 K, abnormal behaviors appear simultaneously in resistivity derivative, Hall coefficient and $MR$, which indicates that other scattering mechanisms more than conventional multiband effect may exist.

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The recent discovery of new superconductor Ca$_{1-x}$Re$_2$FeAs$_2$ (‘112’ type) sparks another interest on the research of iron-based superconductors (IBSs) which is mainly composed by '1111' (LaFeAs(O, F)), '122' (Ba, K)Fe$_2$As$_2$ '111' (LiFeAs) and '11' (Fe(Se, Te)) systems. The new superconductor with superconducting transition temperature $T_c$ around 43 K is crystallized in a monoclinic structure with the space group $P2_1$ (No. 4). Different from the most IBSs, the alternately stacked layer between two adjacent FeAs layers consists of an arsenic zigzag bond layer. Band structure calculation indicates that four hole-like bands around the zone center $\Gamma(0,0)$ and two electron-like bands near the zone corner $M(\pi, \pi)$ exist in the parent phase (CaFeAs$_2$) of this new superconducting category, which is much different from the previous IBSs.

Theoretical calculation pointed out that the high $T_c$ in IBSs may be closely related to the nesting between electron and hole bands based on the scenario of s$^\pm$ pairing, which yells out multiband effect. Actually, numerous and complicated phenomena resulted from multiband feature were reflected in IBSs, such as non-Fermi-liquid $T$-linear resistivity, $T$-dependent $R_H$ and even possible Dirac state. Conventional multiband scenario has ever been used to explain the transport properties of iron pnictides and seems working well. However, recent studies indicate interband antiferromagnetic (AFM) fluctuation rather than multiband effect may be more responsible to the strong $T$-dependent $R_H$. The discovery of '112' type IBSs provides another chance to recognize the previous debates. Comparable studies between the new type superconductor and the previous IBSs may pave new ways to explore mechanism of high temperature superconductivity (HTS) and even to discover new HTS superconductors. For this new category of IBSs (‘112’ type), it’s urgent to clarify its electronic behavior. However, to date, given the lack of single crystals of sufficient size (the general sizes of existing crystals are less than 0.5 mm.), almost no systematical transport studies of this new IBSs has been reported. In this report, for the first time large plate-like single crystals of 2 mm were obtained and detailed transport measurements were performed. The $H_{c2}$ anisotropy $\gamma$ closely related to superconductivity is estimated with a moderate value around 2.8. Hall and $MR$ results imply the electronic behavior can’t be simply ascribed to conventional multiband effect. Our data provide detailed information about the electronic behavior of this new type IBSs.

Single crystals with nominal composition Ca$_{0.9}$La$_{0.1}$FeAs$_2$ were grown using flux method similar as reported before. The quality of crystals was first characterized. Figure 1 (a) shows the elements distribution detected by energy dispersive X-ray spectroscopy (EDXS). All the measured values are located in the range of 10% uncertainty, which means small fluctuation of elements distribution. The actual composition determined from the mean value is Ca$_{0.97}$La$_{0.18}$Fe$_{0.90}$As$_2$. In fig. 1 (b), single crystal X-ray diffraction pattern was shown. Only (00l) peaks were observed, indicating good c-axis orientation and high sample quality. From fig. 1 (e) one can see, bright and dark stripes exist alternately on the crystal surface. Similar phenomenon has also been observed in another IBSs K$_2$Fe$_2$Se$_2$ which was ascribed to intrinsic phase separation. However, the element distribution for the present crystal seems uniform. In fact, targeted measurements for the bright and dark stripes were performed on many crystals, while no obvious difference was found. The small difference may be caused by the stack of stripes for different layers along the crystal c-axis. Indeed, stack of stripes was found in some SEM images, as shown in fig. 1 (f).

Temperature dependences of resistivity ($\rho - T$) for two samples were shown in figure 2 (a). No AFM/spin-density-wave-like (SDW) transition as in many other
un/under-doped IBSs was observed. The general shapes of \( \rho - T \) curves, similar as '1111' type IBSs, do not show a good linear behavior and also clearly deviate from standard Fermi-liquid theory where the resistivity \( \rho \) follows \( T^2 \) dependence in the upper-left and bottom-right corners, \( \rho - T \) curves under different fields were shown. Small shifts were found for \( \rho \) up to 9 T in both directions, indicating high \( H_{c2} \). It should be noticed that there exist of kinks in all \( \rho - T \) curves. The kinks may be aroused by the stripes observed in SEM images. Possibly, the bright and dark strips represent two phases with different \( T_c \)s and thus lead to the broad superconducting transition and existence of kinks. In fig. 2 (b), \( H_{c2} \) phase diagram was established. Here the \( H_{c2} \) were defined by 90\% of normal state resistivity. Upward curvature near \( T_c \) in \( H_{c2}(T) \) curves was observed, which was common in many IBSs and usually explained based on two-band theory. Nevertheless, the usual Werthamer-Helfand-Hohenberg (WHH) linear \( T \) dependences of \( H_{c2} \) were followed in field above 1 T. According to WHH model, \( H_{c2} \) values at zero temperature are estimated to be 28.4 T (\( H//c, H_{c2} \) slope=11 kOe/K) and 79.6 T (\( H//ab, H_{c2} \) slope=32 kOe/K), respectively. The corresponding coherence lengths \( \xi_c = 12.2 \) Å, \( \xi_{ab} = 34.1 \) Å. The \( H_{c2} \) anisotropy at zero temperature \( \gamma(0) = 2.8 \). Such \( \gamma \) value is moderate, lying between '122' type \( \text{Ba}_1\tau_2\text{K}_x\text{Fe}_2\text{As}_2 \) (\( \gamma \approx 1.5 \)) and '1111' type NdFeAs\( \text{O}_{1-x}\text{F}_x \) (\( \gamma \approx 5 \)). As can be seen in the bottom-left inset of fig. 2 (b), \( \gamma \) changes little against \( T \) near \( T_c \). Similar \( T \) dependence of anisotropy \( \gamma(\gamma) \) was found in '1111' crystal.

To get a deeper insight to the electronic behavior of this new type IBSs, Hall and MR measurements at various temperatures were performed. As shown in figure 3 (a), at \( T \) above 50 K, the transverse resistance \( R_{xy} \) follows good linear dependence with magnetic field. At 30 K, \( R_{xy} (\mu_0H) \) curve becomes bended, which may be resulted from vortex motion or depairing effect of magnetic field in the superconducting state. Positive Hall coefficients \( R_H \) determined by the slopes of \( R_{xy} (\mu_0H) \) curve were shown in fig. 3 (b). The dominated charge-carrier was demonstrated to be hole-type, which is also consistent with simple valence calculation. As we can see, although La doping introduces extra electron to the parent phase \( \text{CaFeAs}_2 \), hole-pockets are still predominant. Ad-
FIG. 3. (a) Measured Hall resistance against magnetic fields at different temperatures. (b) Temperature dependences of Hall coefficient $R_H$ and charge-carrier density $n$.

Additionally, $R_H$ decreased fast below 100 K. This behavior is quite elusive because no AFM/SDW like transition was witnessed. In Fermi liquid theory, the Hall coefficient $R_H$ in metallic material is usually constant against $T$. For multiband material or samples with non-Fermi liquid behavior, $T$-dependent $R_H$ may occur. Strong $T$-dependent $R_H$ has also been observed in many other IBSs and seems unreasonable even by taking into account multiband model. Different from the most IBSs, the density of dominated charge-carrier $n$ increases with lowering $T$ in the present superconductor if simply considering a single-band approximation $n = 1/eR_H$, as shown in fig. 3 (b).

Figure 4 shows the MR ($MR = \frac{R(H) - R(0)}{R(0)}$) results. Anisotropic MR is found for $H$ applied in crystal’s $c$-axis and $ab$-plane. In both directions, the current $I \perp H$ keeps to ensure the same Lorentz force. The large anisotropy over 200 may be caused by weakening of MR resulted from mixing the transport components of different crystallographic axes when $H || ab$. As can be seen, the large MR ($H || c$) can be well fitted by the semiclassical quadratic field-dependence law for multiband material, in which $MR \propto \mu_0 H^2$. This result supports the idea of multiband effect. However, the single band Kohler’s law seems effective in the middle $T$ range (150 K, 200 K, 250 K). For metallic materials with a symmetric Fermi surface, Kohler’s law gives that $MR = f(B\tau) = F(B/\rho_0)$ with the assumption that the single band scattering rate $1/\tau(T) \propto \rho_0(T)$. Here $\rho_0(T)$ is the zero-field resistivity. As shown in fig. 4 (b), the MR data disobey Kohler’s scaling in both ends of the measured temperatures. In BaFe$_{2-\delta}$Ru$_\delta$As$_2$, Kohler’s law was also found to recover in the heavy-doped region, which was regarded as a strong evidence for inaccuracy of conventional multiband interpretation.

Additionally, abnormal behaviors were found to occur simultaneously in $T$-dependent $\rho - T$ derivative $(d\rho/T)$, $R_H$ and $MR$ curves at $T$ about 100 K, which also degrades the conventional multiband effect. As shown in figure 5, when $T < 100$ K, $d\rho/T$ and $R_H$ increases and decays much more rapidly with decreasing $T$, respectively. While, unlike the continuous increase of $MR$ for the other IBSs, $MR$ in the present system at low $T$ reaches a maximum value and then tends to decrease. If considering the two-band theory, $\rho$, $R_H$ and $MR$ at certain $T$ in low field region can be expressed in the following forms: $\rho = 1/e(n_e\mu_e + n_h\mu_h)$, $MR = \frac{n_e\mu_e n_h\mu_h (\mu_h - \mu_e) B^2}{(n_e\mu_e + n_h\mu_h)^2}$
and $R_H = \frac{\mu_e^2 n_{h} - \mu_h^2 n_e}{\epsilon n_{h} + \mu_{h} n_{h}}$, respectively. Here $n_{c(h)}$, $\mu_{c(h)}$ represent the carrier concentrations, mobilities and electronic conductivity of the electrons (holes), and $e$ is the electron charge. Because the abnormal behaviors take place almost at the same $T$, the origin may come from the shared term $n_{c} + \mu_{c} n_{c}$ of the three forms mentioned above. Considering the continuous evolution of $n_{c(h)}$ and $\mu_{c(h)}$ with lowering $T$ under conventional multiband theory, such drastic changes in low $T$ can’t happen. Possibly, other special scattering mechanism stands behind, such as the anisotropic charge carrier scattering due to interband AFM fluctuations proposed in ref. [10].

In summary, regular bright and dark stripes were first observed in the plane surface of the new superconductor Ca$_{0.77}$La$_{0.18}$Fe$_{0.90}$As$_2$, which indicates possible existence of phase separation. Also, we primarily studied the anisotropic upper critical field, Hall and $MR$ effect on single crystals of superconducting Ca$_{0.77}$La$_{0.18}$Fe$_{0.90}$As$_2$ samples of large size. Upper critical anisotropy at zero $T$ limit in the present superconductor is moderate with value around 2.8. Positive $R_H$ indicates hole-dominated transport behavior. Large $T$-dependent $R_H$ and $MR$ were found. Detailed transport analysis gives evidences that other scattering mechanisms more than conventional multiband effect may work in the present IBGs.

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