Superconductivity at 15.6 K in calcium-doped $\text{Tb}_{1-x}\text{Ca}_x\text{FeAsO}$: The structure requirement for achieving superconductivity in the hole-doped 1111 phase

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Abstract – Superconductivity at about 15.6 K was achieved in $\text{Tb}_{1-x}\text{Ca}_x\text{FeAsO}$ by partially substituting $\text{Tb}^{3+}$ with $\text{Ca}^{2+}$ in the nominal doping region $x = 0.40 - 0.50$. A detailed investigation was carried out on a typical sample with doping level of $x = 0.44$. The upper critical field of this sample was estimated to be 77 T from the magnetic–field–dependent resistivity data. The domination of hole-type charge carriers in the low-temperature region was confirmed by Hall effect measurements. The comparison between the calcium-doped sample $\text{Pr}_{1-x}\text{Ca}_x\text{FeAsO}$ (non-superconductive above 1.8 K) and the strontium-doped sample $\text{Pr}_{1-x}\text{Sr}_x\text{FeAsO}$ (superconductive) suggests that a large ion radius of the doped alkaline-earth element compared with that of the rare-earth element may be a necessary requirement for achieving superconductivity in the hole-doped 1111 phase.

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Introduction. – The discovery of superconductivity in iron pnictides has generated enormous interests in the community of condensed-matter physics [1]. Up to date, the iron pnictide superconductors have developed into several families with different structures, which were abbreviated as the 1111 phase (including the oxyarsenide [1] and fluorine-arsenide [2]), 122 phase [3,4], 111 phase [5–7], 11 phase [8], 42632 phase [9], and so on. It seems that each phase with different structure has a unique superconducting transition temperature $T_c$. As for the 1111 phase, most of the discovered superconductors are characterized as electron-doped ones [10–14], while the hole-doped superconductors were only reported in the strontium-doped $\text{La}_{1-x}\text{Sr}_x\text{FeAsO}$ ($\text{Ln} = \text{La, Pr, Nd}$) [15–18]. In general, it was found that the structures can be affected differently by electron doping and hole doping in the 1111 phase. On the electron-doped side, the lattice constants ($a$-axis and $c$-axis) shrink slightly when the system are doped by fluorine on the oxygen site [10] or by oxygen deficiency [19]. Whereas the lattice constants (especially that along $c$-axis) are expanded when hole-type charge carriers are doped to the system by strontium on the site of rare-earth elements [16,17,20]. The hole-doped superconductivity in 1111 phase by substituting other ion-dopants with valence of “+2”, such as barium or calcium, seems quite difficult to be achieved, at least in many of the rare-earth-element–based systems. Obviously, it is important to carry out more explorations in this direction in order to extend the family of the hole-doped superconductors in 1111 phase. And it is also significant to investigate the factors which govern the electronic properties (superconducting or non-superconducting) on the hole-doped side based on the 1111 phase. In this letter we report a new hole-doped superconductor in the 1111 phase, calcium-doped $\text{Tb}_{1-x}\text{Ca}_x\text{FeAsO}$, with the maximum superconducting transition temperature of 15.6 K (95% $\rho_n$). We estimated the upper critical field of the sample with $x = 0.44$ to be 77 T based on the Werthamer-Helfand-Hohenberg (WHH) formula [21]. The conducting charge carriers in this sample were characterized to be of hole type in a wide low-temperature region by Hall effect measurements. Meanwhile, we have also successfully synthesized the calcium-doped $\text{Pr}_{1-x}\text{Ca}_x\text{FeAsO}$, which also displays hole-type charge carriers in the low-temperature region.

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but does not exhibit superconductivity above 1.8 K. We attribute this different behavior to the sensitive electronic response to the relative radii of the doped ions compared with that of the rare-earth-element ions.

**Experimental details.** – The Tb$_{1-x}$Ca$_x$FeAsO samples were prepared using a two-step solid-state reaction method. In the first step, TbAs and CaAs were prepared by reacting Tb flakes (purity 99.99%) and CaAs flakes (purity 99.9%) at 500°C for 10 hours and then 700°C for 16 hours. They were sealed in an evacuated quartz tube when reacting. Then the resultant precursors were thoroughly ground together with Fe powder (purity 99.95%) and Fe$_2$O$_3$ powder (purity 99.5%) in stoichiometry as given by the formula Tb$_{1-x}$Ca$_x$FeAsO. All the weighing and mixing procedures were performed in a glove box with a protective argon atmosphere. Then the mixtures were pressed into pellets and sealed in an evacuated quartz tube. The materials were heated up to 1150–1170°C with a rate of 120°C/h and maintained for 40 hours. Then a cooling procedure was followed. After that, we can get the superconducting polycrystalline samples. The process of preparing Pr$_{1-x}$Ca$_x$FeAsO samples is quite similar to that of Tb$_{1-x}$Ca$_x$FeAsO.

The X-ray diffraction (XRD) measurements of our samples were carried out by a Mac-Science MXP18A-HF diffractometer with Cu-K$_\alpha$ radiation. The ac susceptibility of the samples was measured with the same sample Tb$_{0.56}$Ca$_{0.44}$FeAsO under 0 T and 9 T. The data under 0 T is shown up to 300 K. A clear superconducting transition can be seen in the low-temperature region. Taking a criterion of 95% $\rho_n$, the onset transition temperature is determined to be 15.6 K. A magnetic field of 9 T only suppresses the onset transition temperature about 1.6 K. In the high temperature region, no resistivity anomaly was observed, whereas only a flattening feature can be seen above 180 K. The similar behavior has been observed in other hole-doped 1111 systems Ln$_{1-x}$Sr$_x$FeAsO (Ln = La, Pr, Nd) [15–18]. The slender kink feature in the resistivity curve at about 70 K may come from the magnetic transition of the impurity FeAs, which has been reported to be an itinerant helimagnet [24].

Figure 1(c) shows the ac susceptibility data measured with $f = 333$ Hz and $H_{ac} = 0.1$ Oe. A rough estimate from
The diamagnetic signal shows that the superconducting volume fraction of the present sample is beyond 50%, confirming the bulk superconductivity in our samples. The onset critical temperature by magnetic measurements is roughly corresponding to the zero-resistance temperature.

**Upper critical field for Tb$_{0.56}$Ca$_{0.44}$FeAsO.** We attempted to estimate the upper critical field of the sample Tb$_{0.56}$Ca$_{0.44}$FeAsO from the resistivity data. Temperature dependence of resistivity under different magnetic fields is shown in the main frame of fig. 2. It is found that the onset transition point shifts more slowly than the zero resistance point to low temperatures under fields, resulting in a broadening behavior on the resistivity curves. For a polycrystalline sample, the zero resistance point is determined by the vortex flow behavior as well as weak links between the grains, while the onset transition point reflects mainly the upper critical field in the configuration of $H \parallel ab$-plane. We take a criterion of 95%$\rho_n$ to determine the onset transition points under different fields, which are represented by the red open circles in the inset of fig. 2. From these data we can determine the slope of $H_{c2}(T)$ vs. temperature near $T_c$, $dH_{c2}/dT|_{T_c} \approx -7.1$ T/K. By using the WHH formula [21] the value of the zero-temperature upper critical field $H_{c2}(0)$ can be estimated through

$$H_{c2}(0) = -0.693T_c \left( \frac{dH_{c2}}{dT} \right)_{T_c}. \quad (1)$$

Taking $T_c = 15.6$ K, we get $H_{c2}(0) \approx 77$ T. Regarding the relatively low value of $T_c = 15.6$ K in the present sample, this value of upper critical field $H_{c2}(0)$ is actually quite high.

Actually, in the strontium-doped Ln$_{1-x}$Sr$_x$FeAsO (Ln = La, Pr), the rather high $H_{c2}(0)$ and large slope of $dH_{c2}(T)/dT|_{T_c}$ ($\sim 4$ T/K) have been observed when comparing with the F-doped LaFeAsO sample, which was attributed to higher quasiparticle density of states (DOS) near the Fermi level in the hole-doped samples [17]. Surprisingly, the slope $dH_{c2}(T)/dT|_{T_c}$ found here is even larger than that of the strontium-doped samples. The essential physical mechanism for this behavior may still need more investigation in this system, including that from the theoretical side.

**Hall effect of Tb$_{1-x}$Ca$_x$FeAsO.** It is known that the Hall effect measurement is a useful tool to investigate the information of charge carriers and the band structure. For a conventional metal with Fermi-liquid feature, the Hall coefficient is almost independent of temperature. However, this situation is changed for a multiband material [25] or a sample with non-Fermi-liquid behavior, such as the cuprate superconductors [26]. To examine the type of the conducting carriers, we measured the Hall effect of the samples Tb$_{1-x}$Ca$_x$FeAsO. The main frame of fig. 3 shows the magnetic-field dependence of Hall resistivity ($\rho_{xy}$) at different temperatures for the sample with $x = 0.44$. In the experiment $\rho_{xy}$ was taken as $\rho_{xy} = |\rho(+H) - \rho(-H)|/2$ at each point to eliminate the effect of the misaligned Hall electrodes. We can see that all curves in fig. 3 have good linearity vs. the magnetic field. Moreover, $\rho_{xy}$ is positive at all temperatures below 160 K giving a positive Hall coefficient $R_H = \rho_{xy}/H$, which actually indicates that hole-type charge carriers dominate the conduction below 160 K in the present sample.

The temperature dependence of $R_H$ for two samples with $x = 0.44$ and 0.45 is shown in the inset of fig. 3. One can see that the evolutions of $R_H$ with temperature are quite similar for the two samples, indicating the reliability of the Hall data. The hump feature in low-temperature region is quite similar to that observed in strontium-doped...
Ln$_{1-x}$Sr$_x$FeAsO (Ln = La, Pr) samples [15–17]. However, there is still some differences obviously. Firstly, the Hall coefficient $R_H$ changes its sign at about 160 K which is remarkably lower than that observed in the strontium-doped systems (~250 K). This character seems to be quite common in the calcium-doped 1111 phase because the sign changing of $R_H$ was also found to occur at about 160 K in Pr$_{1-x}$Ca$_x$FeAsO (see fig. 5) and Nd$_{1-x}$Ca$_x$FeAsO (data not shown here). Secondly, the negative $R_H$ at about 200 K has a rather large absolute value. This feature seems to be unique in the calcium-doped superconducting samples, since it cannot be observed in Ln$_{1-x}$Sr$_x$FeAsO (Ln = La, Pr) or Pr$_{1-x}$Ca$_x$FeAsO. Assuming a simple two-band scenario with different types of carriers, we can express the Hall coefficient $R_H$ in the low-field limit as

$$R_H = \frac{\sigma_1 \mu_1 + \sigma_2 \mu_2}{(\sigma_1 + \sigma_2)^2},$$

where $\sigma_i$ and $\mu_i$ are the conductivity and the mobility of the $i$-th band, respectively. They are determined by the charge-carrier density and scattering rate of each band. We attribute the strong and complicated temperature dependence of $R_H$ in the present system to the competing effect of the scattering rate as well as the charge-carrier density in different bands.

The case in the calcium-doped Pr$_{1-x}$Ca$_x$FeAsO.

One may be curious to know what would happen if we substitute calcium to the systems based on other rare-earth elements. Actually, we have also tried the cases based on the light rare-earth elements. Here we show the results of Pr$_{1-x}$Ca$_x$FeAsO. No superconductivity was found in the calcium-doped Pr$_{1-x}$Ca$_x$FeAsO samples above 1.8 K in quite wide doping range (0.10 ≤ $x$ ≤ 0.50). In fig. 4, we show the temperature dependence of resistivity for two selected samples with $x$ = 0.20 and 0.40. In order to have a comparison, we also display the resistivity data for two strontium-doped Pr$_{1-x}$Sr$_x$FeAsO samples with different doping levels ($x$ = 0.05 and 0.25). It is clear that the resistivity anomaly from the AF or structural transition around 160 K is suppressed gradually with the increase of strontium contents. By having a closer scrutiny, we find that the behavior of the calcium-doped samples is between that of the two strontium-doped samples in the high-temperature region. This may suggest that the real doped charge carriers in the calcium-doped PrFeAsO are roughly corresponding to 0.10 ~ 0.20 of that of the strontium-doped PrFeAsO system and the AF order has been suppressed to a certain extent by the calcium doping.

To further investigate the conducting properties of the Pr$_{1-x}$Ca$_x$FeAsO samples, we have measured their Hall effect and display the data of one typical sample with $x$ = 0.40 in fig. 5. Non-linear behavior was observed in the field-dependent $\rho_{xy}$ data below 100 K. The hump feature and positive value of $R_H$ can be seen below about 160 K, which is rather similar to that observed in Tb$_{1-x}$Ca$_x$FeAsO (see fig. 3). This behavior indicates strongly that the hole-type charge carriers have been induced to the system and they dominate the conduction in low-temperature region.

In order to find the factors which prevent Pr$_{1-x}$Ca$_x$FeAsO from superconducting even if hole-type charge carriers have been doped into the system, we analyzed the structural details of one calcium-doped Pr$_{1-x}$Ca$_x$FeAsO with nominal $x$ = 0.4. Selected Rietveld refinement results are listed in table 1, and the refinement pattern is shown in fig. 6. Only small amounts of Pr$_2$O$_3$ and FeAs can be seen as impurities. From the refinement, we find that the actual doping concentration for the sample Pr$_{1-x}$Ca$_x$FeAsO with nominal $x$ = 0.4 is only

![Fig. 4](image-url) (Color online) Temperature dependence of resistivity for two calcium-doped samples Pr$_{1-x}$Ca$_x$FeAsO with $x$ = 0.20 and 0.40, along with two strontium-doped samples Pr$_{1-x}$Sr$_x$FeAsO with $x$ = 0.05 and 0.25 for comparison. It is clear that the behavior of the calcium-doped samples is between that of the two strontium-doped samples in the high-temperature region.

![Fig. 5](image-url) (Color online) Hall effect measurements for one sample Pr$_{0.60}$Ca$_{0.40}$FeAsO. The main frame shows a field dependence of the Hall resistivity $\rho_{xy}$ at different temperatures. Inset: Temperature dependence of the Hall coefficient $R_H$, which is positive in the temperature region below about 160 K.
The data of the latter two samples are cited from other reports [20,27].

The differences between observations and calculations.

Fig. 6: (Color online) The observed (red crosses) and calculated (green solid line) X-ray powder diffraction patterns of Pr$_{0.87}$Ca$_{0.13}$FeAsO. The three rows of vertical bars show the calculated positions of Bragg reflections for Pr$_2$O$_3$ (blue), FeAs (red) and Pr$_{0.84}$Ca$_{0.16}$FeAsO (black), respectively. The magenta solid line shown at the bottom of the figure indicates the differences between observations and calculations.

about 0.13, which is quite consistent with the argument we obtained from the resistivity data (see fig. 4). In order to have a comparison with the strontium-doped PrFeAsO system where superconductivity has been obtained, we also display the structural parameters of the parent phase PrFeAsO and strontium-doped Pr$_{1-x}$Sr$_x$FeAsO with $x=0.16$ (the value from refinement) [20,27] in table 1. Here we define $d_{\text{PrOPr}}$ and $d_{\text{AsFeAs}}$ as the vertical distance between the Pr atoms residing at the top and bottom of the PrO layer and that between the As atoms in the FeAs layer, respectively. And $d_{\text{inter}}$ is the interlayer space between the Pr-O-Pr block and the As-Fe-As block. It is clear that the lattice constant along a-axis remains nearly unchanged while that along c-axis expands clearly when calcium is doped to PrFeAsO. Both $d_{\text{PrOPr}}$ and $d_{\text{AsFeAs}}$ shrink slightly while $d_{\text{inter}}$ expands distinctly with the actual calcium doping of 0.13, resulting in the expansion behavior of the lattice along c-axis. Surprisingly, we find that calcium doping gives a rather similar influence to the crystal structure to that of strontium doping, when we compare the parameters of Pr$_{0.87}$Ca$_{0.13}$FeAsO and Pr$_{0.84}$Sr$_{0.16}$FeAsO as shown in table 1, even if the radius of Ca$^{2+}$ is smaller than that of Pr$^{3+}$ while the radius of Sr$^{2+}$ is larger (see fig. 7). We note that the sample Pr$_{0.84}$Sr$_{0.16}$FeAsO still does not superconduct and superconductivity was achieved in the samples with even higher doping, as reported in ref. [20]. However, the fact that the radius of Ca$^{2+}$ is smaller than that of Pr$^{3+}$ seems to prevent from doping even more calcium to PrFeAsO and consequently to prevent from achieving superconductivity in the Pr$_{1-x}$Ca$_x$FeAsO system, because the effect of doped calcium is to expand the lattice along the c-axis. This argument is reinforced by the fact that only 13% of calcium can be doped into the system even if the nominal doping concentration is 40%.

To validate our supposition, we have tried the case of other calcium-doped samples. In La$_{1-x}$Ca$_x$FeAsO, we found that it is quite difficult to dope charge carriers (probably also Ca) to the system and the Hall coefficient remains negative, and very similar behaviors to that of Pr$_{1-x}$Ca$_x$FeAsO were observed in Nd$_{1-x}$Ca$_x$FeAsO. Very small superconducting signal can be observed in Sm$_{1-x}$Ca$_x$FeAsO sometimes. Zero resistance can be obtained easily in Gd$_{1-x}$Ca$_x$FeAsO, but the diamagnetic signal is smaller than that of the Tb$_{1-x}$Ca$_x$FeAsO system. We cannot get the 1111 phase on the heavy rare-earth (Dy, Ho, etc.) side under ambient pressure. By summarizing

Table 1: Selected Rietveld refinement results of the calcium-doped Pr$_{0.87}$Ca$_{0.13}$FeAsO (0.13 is the value from the refinements) at room temperature, along with that of the parent phase PrFeAsO and strontium-doped Pr$_{0.84}$Sr$_{0.16}$FeAsO for comparison. The data of the latter two samples are cited from other reports [20,27].

| Sample          | $a$ (Å) | $c$ (Å) | Fe-As-Fe (°) | $d_{\text{PrOPr}}$ (Å) | $d_{\text{ASFeAs}}$ (Å) | $d_{\text{inter}}$ (Å) |
|-----------------|---------|---------|--------------|-----------------------|-------------------------|------------------------|
| PrFeAsO         | 3.985   | 8.595   | 111.968      | 2.405                 | 2.690                   | 1.750                  |
| Pr$_{0.87}$Ca$_{0.13}$FeAsO | 3.987 | 8.628 | 112.429 | 2.396 | 2.668 | 1.782 |
| Pr$_{0.84}$Sr$_{0.16}$FeAsO | 3.985 | 8.622 | 112.413 | 2.387 | 2.666 | 1.785 |

Fig. 7: (Color online) The data of ion radii for some selected rare-earth-element ions. The blue dotted and red dashed lines represent the value of Sr$^{2+}$ and Ca$^{2+}$, respectively.

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the phenomena mentioned above, we argue that the relationship between the ion radii of the rare-earth elements and the alkaline-earth elements may play a key role in achieving superconductivity in the hole-doped 1111 phase (see fig. 7). That is, superconductivity emerges only when the ion radius of the rare-earth element is smaller than that of the alkaline-earth element. At this time, we can say safely that it is rather difficult, if not impossible, to obtain superconductivity when the ion radius of the rare-earth element is larger. Moreover, it seems that superconductivity favors the situation when the difference between the two radii is larger, within the tolerance of crystal lattice. These arguments are quite consistent with that stated in the previous paragraph. This actually gives a restriction in exploring new superconductors on hole-doped side of 1111 phase.

Concluding remarks. – In summary, bulk superconductivity was achieved by substituting $\text{Tb}^{3+}$ with $\text{Ca}^{2+}$ in $\text{TbFeAsO}$ system. The maximum superconducting transition temperature $T_c = 15.6$ K is found to appear around the nominal doping level $x = 0.40–0.50$. The positive Hall coefficient $R_H$ in a wide low-temperature range suggests that the hole-type charge carriers dominate the conduction in this system. Surprisingly, the slope of the upper critical magnetic field vs. temperature near $T_c$ in calcium-doped $\text{Tb}_{1-x}\text{Ca}_x\text{FeAsO}$ is found to be much higher than that of the electron-doped and strontium-doped ones. Moreover, we have investigated the structural and conducting properties of other calcium-doped systems (taking $\text{Pr}_{1-x}\text{Ca}_x\text{FeAsO}$ for example). We found that the relationship between the ion radii of the rare-earth elements and alkaline-earth elements may play a key role in achieving superconductivity in the hole-doped 1111 phase.

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