Rapid Communication

Magnetic phase transitions and large mass enhancement in single crystal $CaFe_4As_3$*

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High quality single crystal $CaFe_4As_3$ was grown by using the Sn flux method. Unlike layered $CaFe_2As_2$, $CaFe_4As_3$ crystallizes in an orthorhombic three-dimensional structure. Two magnetic ordering transitions are observed at ~ 90 K and ~ 27 K, respectively. The high temperature transition is an antiferromagnetic(AF) ordering transition. However, the low temperature transition shows complex properties. It shows a ferromagnetic-like transition when a field is applied along *b*-axis, while antiferromagnetism-like transition when a field is applied perpendicular to *b*-axis. These results suggest that the low temperature transition at 27 K is a first-order transition from an AF state to a canted AF state. In addition, the low temperature electron specific heat coefficient reaches as high as 143 mJ/mol·K^2, showing a heavy fermion behavior.

Keywords: antiferromagnetic ordering transition, ferromagnetic ordering transition, canted antiferromagnetic state

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The discovery of superconductivity in iron pnictides with T_c over 50 K has generated tremendous interest in the scientific community.[1−6] Up to date, several different crystal structures of iron pnictides have been discovered to exhibit high T_c superconductivity by either electron- or hole-doping. They are *Ln*FeAsO (*Ln*=rare earth, the so-called 1111 system), AFe_2As_2 (*A*=Ca, Sr, Ba, 122),[7,8] LiFeAs(111)[9−11] and $FeSe_{1-\delta}$(11).[12] All these iron-pnictide superconductors have a layered structure with two-dimensional Fe*Pn* (*Pn*= pnictogen) conducting layers.

Except for a relatively high transition temperature, the systems display interesting magnetic properties. Most remarkably, the parent compounds show collinear antimagnetic type spin-density-wave (SDW) ordering. The superconductivity is found to be in the vicinity of the SDW.[13,14] In addition, recent inelastic neutron scattering experiments have found the presence of an incommensurate magnetic resonance peak around wave vector $Q = (0.5, 0.5, 0)$ position in the superconducting states of (BaK)Fe_2As_2 and $FeSe_{1-\delta}$ superconductors, similar to that of high T_c cuprates.[15,16] These observations reveal that magnetism plays a crucial role in understanding the superconductivity in iron pnictide superconductors.

Recently, Todorov *et al.* reported a novel metallic iron arsenide compound $CaFe_4As_3$.[17] Unlike the layered structure of $CaFe_2As_2$, $CaFe_4As_3$ crystallizes in the orthorhombic space group *Pnma* with a three-dimensional (3D) framework, where Fe and As form a channel-like network and Ca resides in the channels in the ac plane, which uniformly run along *b*-axis to form the orthorhombic cell, as shown in Fig. 1(a). The ac plane network consists of Fe_2As_2 ribbons that are also the building blocks of $CaFe_2As_2$. The Fe–As distances of $CaFe_4As_3$ are similar to that of $CaFe_2As_2$. Susceptibility measurement reveals complicated magnetic properties with two magnetic transitions at ~ 90 K and ~ 23 K, respectively. Zhao *et al.* also observed the two magnetic transitions and found that $CaFe_4As_3$ displays low-temperature Fermi-liquid behavior.[18] It would be interesting to understand the nature of the two magnetic transitions and to compare them with that of iron pnictide superconductors.

In this work, we present an extensive investigation of the physical properties of high quality single crys-

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tal $CaFe_4As_3$. We found that above 90 K, $CaFe_4As_3$ shows a metallic behavior in resistivity while a Curie–Weiss-like behavior in susceptibility. An antiferromagnetic (AF) ordering transition occurs at $\sim$ 90 K. However, the other magnetic transition at $\sim$ 27 K shows striking properties. Below 27 K, the transition is shown to be ferromagnetism-like when a field is applied along b-axis. However, when a field is applied perpendicularly to the b-axis, the transition is shown to be antiferromagnetism-like. Furthermore, a large thermal hysteresis is observed from magnetization and transport measurements, which show the properties of a first-order transition. The results show that the low temperature transition is a transition from an AF state to a canted AF. In addition, the low temperature electron specific heat coefficient reaches as high as 143 mJ/mol·K^2, showing a heavy fermion behavior.

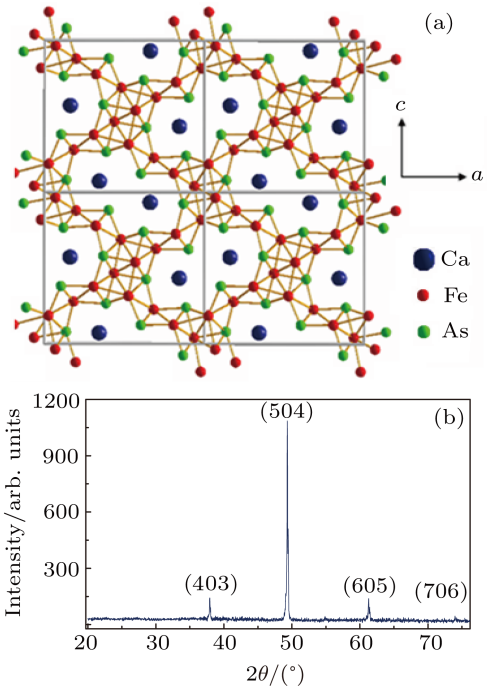


Fig. 1. (colour online) (a) Projection view of $CaFe_4As_3$ along b-axis. (b) X-ray diffraction patterns of a $CaFe_4As_3$ single crystal. The XRD patterns are well indexed on the base of the orthorhombic structure with the space group *Pnma* with lattice parameters a = 11.891 Å, b = 3.714 Å and c = 11.682 Å, respectively.

The crystals were grown using the Sn-flux method, similar to the procedure described in Ref. [14]. The starting materials Ca(99.9%), Fe(99.9%), As(99.99%) and Sn(99.99%) with a ratio of 1:4:3:40 were put into an alumina crucible and then sealed in a quartz ampoule under a reduced pressure of 10^{-3} Pa. The mixture was heated to 650 °C for 12 h and kept at this temperature for 6 h, and then heated to 850 °C for 12 h, kept for 10 h, and slowly cooled to 600 °C for 12 h. At this temperature, the Sn flux was decanted from $CaFe_4As_3$ crystals by centrifugation. The needle-like crystals were obtained with dimensions up to 0.5 mm × 0.5 mm × 5 mm. The resulting crystals were characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation at room temperature. Figure 1(b) shows the XRD patterns of a $CaFe_4As_3$ crystal. It is found that the XRD patterns are well indexed on the base of the orthorhombic structure with the space group *Pnma*. The lattice parameters are a = 11.891 Å, b = 3.714 Å and c = 11.682 Å, respectively, comparable to reported data.[17] The magnetic susceptibility was measured using an SQUID VSM Magnetometer of Quantum Design Company. The resistivity was measured by the standard 4-probe method. The specific heat measurement was carried out with a thermal relaxation calorimeter in a ^{3}He system down to 0.5 K. The temperature and magnetic field dependences of the thermometer and addenda were carefully calibrated before the experiment.

Figure 2 shows the magnetic susceptibility $\chi = M/H$ as a function of temperature T in a field of 0.2 T applied both along and perpendicular to the b-axis. At high temperatures, χ increases with decreasing T,

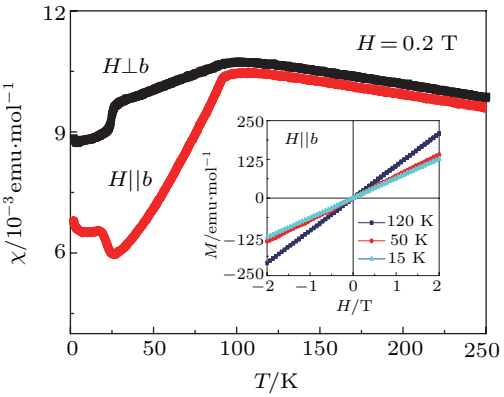


Fig. 2. (colour online) Magnetic susceptibility χ versus temperature T for $H \perp b$ and $H \parallel b$, respectively (1 emu = 10^{-3} A·m^2). The inset plots the magnetization M versus applied field H between −2 T and 2 T in fixed temperatures.

showing a Curie–Weiss-like behavior. This is in strong contrast to the parent of iron pnictide superconductors where susceptibility decreases linearly with decreasing T above the SDW temperature.[19,20] Below 90 K, χ drops sharply, indicating a long-range order transition from a paramagnetic state to an AF state. The drop in χ for $H \parallel b$ is over 2 times larger than that

for $H \perp b$, showing anisotropic magnetism for different field orientations. Below 27 K, the second magnetic transition occurs, which has complex magnetic properties. For $H \parallel b$, χ increases with decreasing T, showing behavior of a ferromagnetic ordering-like transition. However, for $H \perp b$, χ decreases with decreasing T, showing behavior of an antiferromagnetic ordering-like transition. Note that the susceptibility change (both for $H \parallel b$ and $H \perp b$) for the 27 K magnetic transition is much less than the drop in χ for the 90 K AF transition, which possibly suggests that only partial of the Fe moments experience the 27 K transition. The inset of Fig. 2 shows the field dependence of magnetization M from -2 to 2 T for $H \parallel b$ at fixed temperatures. M is linear with field in the measured field range.

The two magnetic phase transitions were clearly observed in transport measurements. Figure 3(a) shows the resistivity ρ_b ($I \parallel b$) between 2 K and 250 K in zero field. Similar to that reported by Zhao *et al.*,[18] ρ_b exhibits a metallic behavior above 90 K. Below 90 K, ρ_b increases with decreasing T and a minimum in ρ_b is observed. Generally, in a system with an AF ordering, the resistivity would increase below the transition temperature, because magnetic scattering is enhanced in the AF ordered state. The behavior of $\rho_b(T)$ shows that an AF ordering transition occurs at 90 K, consistent with the susceptibility measurement. On the other hand, an extremely steep resistivity drop is observed below 27 K. The value of ρ_b at 2 K is less than one-fourth of its value at 28 K, a temperature well above the transition. It suggests that the second transition at 27 K is different from the first transition at 90 K in nature. Figure 3(b) shows $\rho_b(T)$ at 0 T and 8 T applied both along and perpendicular to b-axis between 16 K and 30 K. All the three runs were performed with cooling down T. Strikingly, compared with that at zero field, the transition temperature T_m at 8 T for $H \parallel b$ notably increases by $\sim$ 1.3 K, while T_m at 8 T for $H \perp b$ decreases by $\sim$ 1.3 K. The inset of Fig. 3(a) shows magnetoresistance at 24 K in fields applied along and perpendicular to b-axis. Clearly, a large negative magnetoresistance is observed for $H \parallel b$ while a large positive magnetoresistance of ~ 8 is observed for $H \parallel b$ at the same temperature. For an FM ordering transition, the applied magnetic field enhances the FM correlations of spins as well as the transition temperature, and a negative magnetoresistance is expected due to the reduction of spin scattering. However, for an AF transition, the transition temperature decreases with magnetic field since the AF correlations are suppressed in an applied field, and a positive magnetoresistance is expected due to the enhancement of spin scattering in the AF state. The resistivity results indicate that the magnetic ordering is FM-like for $H \parallel b$ and AF-like for $H \perp b$, consistent with the susceptibility measurement given above. Note that $\rho_b(T)$ behaves remarkably different from the previous report by Todorov *et al.*,[17] where $\rho_b(T)$ shows metallic behavior from 5 K to 300 K with none phase transition.

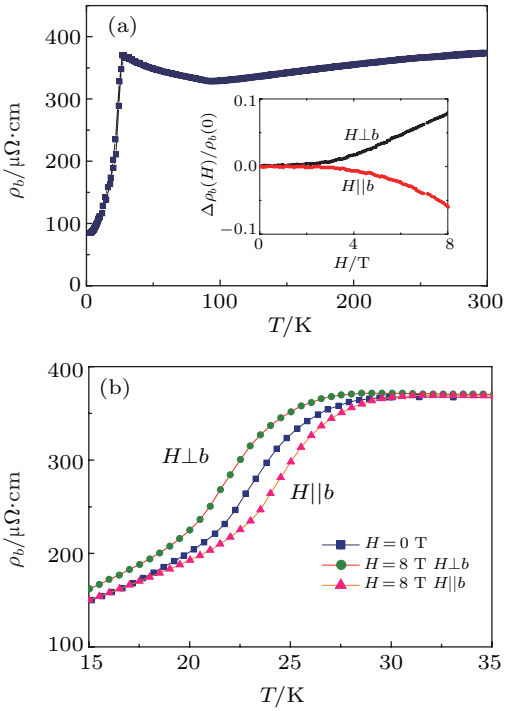


Fig. 3. (colour online) (a) Temperature dependence of b-axis resistivity ρ_b for $CaFe_4As_3$. Two transitions at $\sim$ 90 K and $\sim$ 27 K are clearly seen. The inset shows the field dependence of magnetoresistance $\Delta\rho_b(H)/\rho_b(0)$ [where $\Delta\rho_b(H) = \rho_b(H) - \rho_b(0)$] at 25 K for for $H \parallel b$ and $H \perp b$, respectively. (b) ρ_b between 10 and 40 K in zero field (square), 8 T for $H \parallel b$ (triangle) and 8 T for $H \perp b$ (circle), respectively. All the measurements were done with lowering the temperature.

The above experiments suggest that there is a magnetic transition from an AF state to a canted antiferromagnetic state below 27 K. The canted antiferromagnetism is normally induced by applied fields in many anisotropic AF ordered materials, such as $Ca_2CoSi_2O_7$[21] and $Na_{0.85}CoO_2$.[22,23] The magnetic field can polarize the spins along the easy-axis but still leave AF correlations at other directions. It can also exist in some materials via a magnetic phase transition from a paramagnetic state by lowing temperature. For example, Gd_5Sn_3,[24] $MnPS_3$[25] and Ca_2RuO_4.[26] However, to our knowledge, we have not

found any other materials showing canted antiferromagnetic transition from an AF state by lowering the temperature.

In $CaFe_4As_3$, there are 4 non-equivalent iron sites[17]. There is a possibility that not all the iron spins were AF ordered below 90 K. The unordered iron spins could become canted AF ordered below 27 K. If it were the case, the low temperature magnetic transition would be in fact be a transition from a paramagnetic state to a canted AF state, and it should be a second-order transition instead of a first-order one. However, our thermal hysteresis and specific heat measurements rule out this possibility. Figure 4 shows susceptibility in a field of 1 T and resistivity results in zero field measured by increasing T and decreasing T, respectively. Clearly, a large thermal hysteresis of about 2 K is observed around 25 K for both susceptibility and resistivity measurements. This is strong evidence that the lower temperature magnetic transition is of a first-order transition. In addition, it is found that a subtle structural distortion is accompanied by the magnetic transition,[17] consistent with our results.

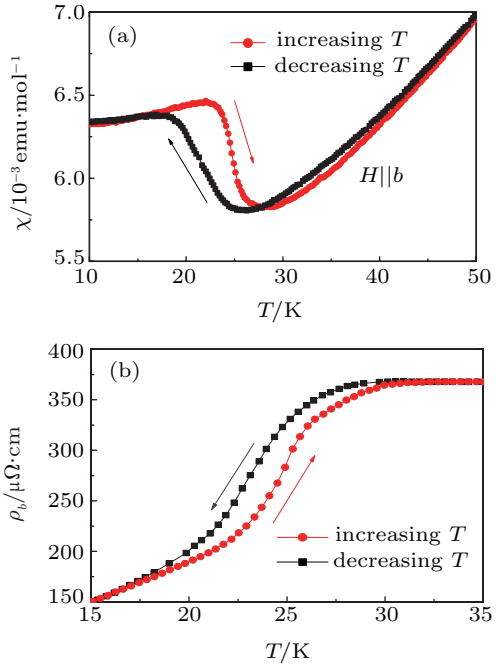


Fig. 4. (colour online) (a) $\rho_b(T)$ measured with decreasing T (square), and increasing T (circle), respectively. (b) $\chi(T)$ measured with decreasing T (square), and increasing T (circle), respectively. Thermal hysteresis is clearly seen around 25 K in both the resistivity and susceptibility curves.

Figure 5(a) shows the specific heat C versus T from 0.5 K to 120 K. Apparently, a peak is observed at $\sim$ 90 K and confirms the bulk antiferromagnetism below this temperature. Surprisingly, similar to that reported by Todorov *et al.*,[17] no anomaly is observed in specific heat around 27 K even in a careful measurement with temperature spacing less than 0.2 K (see Fig. 5(b)). For a transition from a paramagnetic state to a magnetic ordered state, there is a large change in magnetic entropy, so a specific heat anomaly should be observed around the transition temperature. This is indeed the case for 90 K transition. The absence of anomaly around 27 K is possible, because there is no magnetic entropy change between the AF and canted AF magnetic states, or the specific heat anomaly of such a first-order transition is too narrow to be detectable.

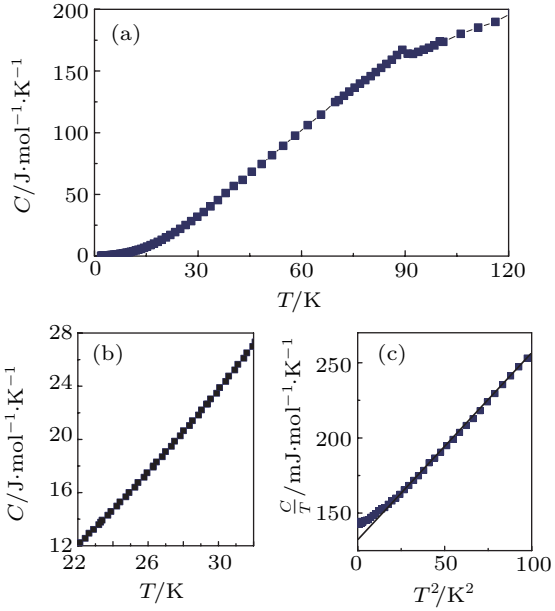


Fig. 5. (colour online) (a) Specific heat C versus temperature T in the range of from 0.5 K to 120 K. (b) C versus temperature T around 27 K in an enlarged scale. (c) C/T versus T^2 from 0.5 K to 10 K.

Figure 5(c) shows T^2 dependence of C/T in zero field below 10 K. Above 4 K, C/T is linear with T^2, indicating that the specific heat can be well described by $C = \gamma T + \beta T^3$. From the fitting, the electronic coefficient γ is found to be $\sim$ 134 mJ/mol·K^2, slightly less than that obtained by Todorov *et al.*,[17] but slightly higher than that obtained by Zhao *et al.*[18] The value of γ is much larger than the other Iron-Arsenic-based compounds, for example, for LaOFeAS, γ is 3.7 mJ/mol·K^2 (Ref. [13]) and for $SrFe_2As_2$ γ is 7 mJ/mol·K^2 (Ref. [27]). In a Fermi liquid system, γ is proportional to density of states at Fermi level as well as effective mass of electrons. The extreme large value of γ indicates a large mass-enhancement in $CaFe_4As_3$, revealing a heavy fermion behavior. Typically, the

heavy fermion systems are found mostly in Ce or U-based f-electron alloys. However, there are very few d-electron systems showing heavy fermion behavior. Among them, LiV_2O_4 ($\gamma \approx 420$ mJ/mol·K^2)[28] and $Ca_{1.5}Sr_{0.5}RuO_4$ ($\gamma \approx 255$ mJ/mol·K^2)[29] are two typical transition-metal-oxides showing heavy fermion behavior. The large value of γ in LiV_2O_4 originates from either a Kondo effect[28] or the geometrically frustrated spins.[29] The origin of the large mass enhancement in $CaFe_4As_3$ needs to be further investigated. Below 4 K, C/T deviates from linear T^2 dependence. C/T reaches ~ 143 mJ/mol·K^2 at 0.5 K.

With the above experimental results, we can compare the magnetism of $CaFe_4As_3$ with that of parent of layered iron pnictide superconductors. In the parent of layered iron pnictide superconductors like *Re*OFeAs (*Re*=rare earth) or AFe_2As_2 (*A*=Ca, Sr, Ba), a collinear AF type SDW ordering is found below $\sim$ 150 K for LaFeAsO and 140 K for $BaFe_2As_2$. An energy gap opens below the transition temperature and partial of density of state (DOS) at fermi surface are removed as revealed by specific heat and optical measurements.[13,27,30] In $CaFe_4As_3$, although the antiferromagnetism is observed below 90 K, the specific heat results show that there is a large enhancement of mass as well as DOS at low temperatures. No gap opening feature is observed. The results indicate that the magnetic orderings in $CaFe_4As_3$ have a different origin from that in LaFeAsO or $BaFe_2As_2$. In $CaFe_4As_3$, there are four non-equivalent iron sites and Fe–Fe distances are between 2.5 Å and 2.8 Å in *ac* plane, much less than that in LaOFeAs or $BaFe_2As_2$, where the Fe–Fe distances are $\sim$ 3.9 Å. The direct coupling between Fe spins in $CaFe_4As_3$ is relatively strong and should dominate the magnetism. We believe the multiple Fe sites and Fe–Fe interactions lead to the complex magnetic properties in $CaFe_4As_3$.

In conclusion, we have presented an extensive investigation of the physical properties of high quality single crystal $CaFe_4As_3$. We found two magnetic transitions at 90 K and 27 K, respectively. The high temperature transition is an AF ordering transition. However, the low temperature transition shows complex magnetic properties. It shows a ferromagnetic-like transition when a field is applied along the *b*-axis, while antiferromagnetism-like transition when a field is applied perpendicular to the *b*-axis. These results show that the low temperature transition at 27 K is first-order transition from an AF state to a canted AF state. We believe that the direct interaction between Fe spins plays a dominate role in understanding the complex magnetic properties. In addition, the low temperature electron specific heat coefficient reaches as high as 143 mJ/mol·K^2, showing a heavy fermion behavior.

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