Physical properties of the layered pnictide oxides $Na_2Ti_2P_2O$ (P=As,Sb)

R. H. Liu, D. Tan, Y. A. Song, Q. J. Li, Y. J. Yan, J. J. Ying, Y. L. Xie, X. F. Wang, and X. H. Chen*
Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
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The compounds $Na_2Ti_2P_2O$ (P=As,Sb) with anti-K_2NiF_4 structure were characterized by magnetic susceptibility, magnetoresistance, Hall coefficient (R_H), heat capacity, and thermoelectric power (TEP). These compounds exhibit an anomalous transition in resistivity and susceptibility at $T_S \sim 320$ K for $Na_2Ti_2As_2O$ and $T_S \sim 115$ K for $Na_2Ti_2Sb_2O$. The Hall coefficient of $Na_2Ti_2Sb_2O$ shows a pronounced rise below T_S, indicating a decrease in carrier density. The sign of TEP changes from positive to negative and magnetoresistance pronounced increase at T_S for $Na_2Ti_2Sb_2O$. Heat capacity shows an anomalous peak at $T_S \sim 110$ K, a typical behavior for spin-density-wave (SDW)/charge-density-wave instability or a structure distortion. These behaviors of $Na_2Ti_2Sb_2O$ are quite similar to that of FeAs-based high-T_C parent compound RFeAsO and AFe_2As_2 with a SDW instability. $Na_2Ti_2Sb_2O$ could be considered as a possible parent compound for superconductivity.

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The recent discovery of high-T_C superconductivity in iron-based oxypnictide systems has stimulated extensive studies on layered transition-metal suboxides, such as pnictide oxides and oxychalcogenides. Several types of iron-based superconductors are discovered such as ZrCuSiAs-type RFeAsO (Refs. 1–6) or AFeAsF (R=rare earth elements; A=alkali earth metals), $ThCr_2Si_2$-type AFe_2As_2,[7–10] MFeAs (M=Li and Na) (Ref. 11) and related oxyphosphide and chalcogenide layered compounds.[12] These layered structure parent compounds share the common features of spin-density-wave (SDW) -type antiferromagnetic (AFM) order and a structure transition. It can be characterized by strong anomalies in resistivity, Hall coefficient, magnetic susceptibility, and specific heat. The SDW and structure transition are suppressed and the superconductivity is induced by doping or pressure. Hence, these is a strong evidence that the occurrence of superconductivity in these compounds is relevant with the AFM-type SDW ordering.

Layered d-metal pnictide oxides $Na_2Ti_2P_2O$ (P=As and Sb) discussed by Adam *et al.*[13] in early 1990s. These compounds have a layered structure resembling the high-T_C superconductor, $La_{2-x}Ba_xCuO_4(K_2NiF_4)$ [Fig. 1(b)].[14] However, $Na_2Ti_2P_2O$ is anti-K_2NiF_4 type and edge-shared $Ti_{4/2}P_2O_{4/4}$ layers interspersed by double layers of Na^+ [Fig. 1(a)]. In the $Ti_{4/2}P_2O_{4/4}$ unit [Fig. 1(c)], Ti^{3+} is located between two O^{2-} forming a square planar layer $Ti_{4/2}O$, and two P^{3-} are located above and below the center of the $Ti_{4/2}O_{4/4}$ square unit, which is an anticonfiguration to the $CuO_{4/2}$ layer observed in high-T_C cuprates. The magnetic susceptibility and electrical resistivity of $Na_2Ti_2P_2O$ have been reported by Tadashi *et al.* $Na_2Ti_2Sb_2O$ exhibits a sharp drop in the magnetic susceptibility and a strong abnormal peak in the electrical resistivity at $T_C \sim 115$ K. The As analogue shows also a drop in the magnetic susceptibility at $T_C \sim 320$ K.[15–18] These behaviors are very similar to high-T_C iron-based oxypnictide parent compounds, such as $CaFe_2As_2$.[9] Neutron-diffraction experiment has approved a structural transition from tetragonal to orthorhombic and SDW order in AFe_2As_2 coincident with the anomaly of magnetic susceptibility and electrical resistivity.[19,20] In addition, neutron-diffraction study on $Na_2Ti_2Sb_2O$ indicates that this compound has a structural distortion in the $[Ti_2Sb_2O]^{2-}$ layer at $T_C \sim 115$ K.[16] However, no superlattice reflections due to magnetic ordering or symmetry breaking were observed in neutron experiments. Thus, the anomaly is not likely to arise from simple antiferromagnetic ordering or a spin-Peierls transition.[16,17] The theoretical calculations indicate that a square box Fermi surface with strong nesting leads to a charge-density-wave (CDW)/SDW instability in $Na_2Ti_2P_2O$.[21] However, the experiments and theoretical calculations can not make sure whether it is CDW or SDW in $Na_2Ti_2P_2O$ due to a lack of observed magnetic order.[16,21]

In this paper, we measure systematically magnetic susceptibility, magnetoresistance (MR), Hall coefficient (R_H), specific heat, and thermoelectric power (TEP). These physical properties are similar to that of FeAs-based high-T_C parent compound RFeAsO and AFe_2As_2 with a SDW instability and other CDW/SDW (Refs. 22–24) materials. The compounds $Na_2Ti_2P_2O$ could be considered as a possible superconductor parent compound.

Polycrystalline samples of $Na_2Ti_2P_2O$ (P=As and Sb) were synthesized by solid-state reaction method using NaP (powder), TiO_2 (2N, powder), and Ti (3N, powder) as starting materials. NaP was presynthesized by heating the mixture of Na (2N) lumps and As (6N) powder or Sb (3N) powder at 200 °C for 24 h. The raw materials were accurately weighed according to the stoichiometric ratio of $Na_2Ti_2P_2O$ (P=As and Sb), then thoroughly grounded and pressed into pellets. The pellets were wrapped with Ta foil and sealed in quartz tube under about 1/4 atm Ar gas atmosphere. The sealed tubes were sintered at 800 °C for 50 h. The sample preparation process except for annealing was carried out in glove box in which highly pure argon atmosphere was filled.

Phase identification was carried out by x-ray diffraction with MXPAHF 18 kW rotating target x-ray diffractometer (Japan). Magnetic-susceptibility measurement was performed by a superconducting quantum interference device magnetometer [Quantum Design Magnetic Property Measurement System (MPMS)-XL7s]. MR Hall coefficient (R_H), specific heat, and TEP were measured by using Quantum Design Physical Property Measurement System (PPMS) under fields up to 14 T.

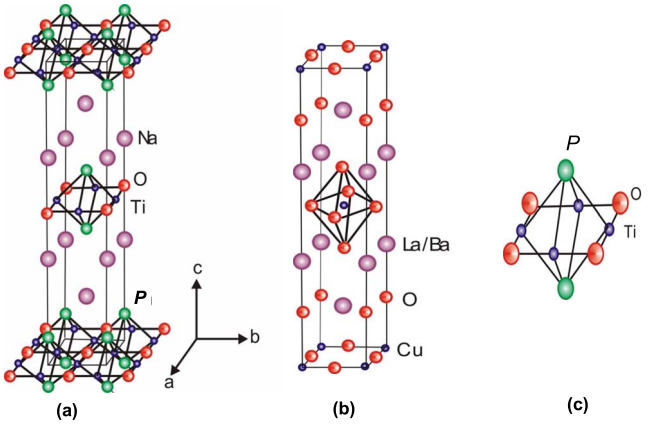

FIG. 1. (Color online) (a) Crystal structure of $Na_2Ti_2P_2O$ (P=As and Sb) with anti-K_2NiF_4 type showing alternation of $[Ti_{4/2}P_2O_{4/4}]^{2-}$ layers and double layers of Na^+, (b) crystal structure of $La_{2-x}Ba_xCuO_4$ with K_2NiF_4 type, (c) $[Ti_{4/2}P_2O_{4/4}]^{2-}$ unit consisting of Ti-O square plane capped with two P^{3-}, and the $Ti_{4/2}O_{4/4}$ square unit is an anticonfiguration to the $CuO_{4/2}$ layer observed in high-T_C cuprates.

Figure 2 shows x-ray powder-diffraction patterns for the samples $Na_2Ti_2P_2O$ (P=As and Sb). All main peaks can be indexed by a tetragonal structure ($I4/mmm$) with a =0.4079(4) nm and c=1.526(2) nm for the sample $Na_2Ti_2As_2O$; a=0.4153(5) nm and c=1.657(3) nm for the sample $Na_2Ti_2Sb_2O$. The lattice constants ***a*** and ***c*** for the samples are in good agreement with those in the literature.[15–18] A little of impurity TiSb and Ti_3O_5 is observed in the x-ray diffraction pattern of $Na_2Ti_2Sb_2O$.

Figure 3 shows temperature dependence of resistivity for the samples $Na_2Ti_2P_2O$ (P=As and Sb). The resistivity of $Na_2Ti_2Sb_2O$ exhibits an anomaly at about 115 K, corresponding to the temperature of the magnetic-susceptibility anomaly. These behaviors are similar to that observed in high-T_C iron-based oxypnictide parent compound $CaFe_2As_2$.[9] In $CaFe_2As_2$, the abnormal behavior in electrical resistivity is associated with the structure transition and

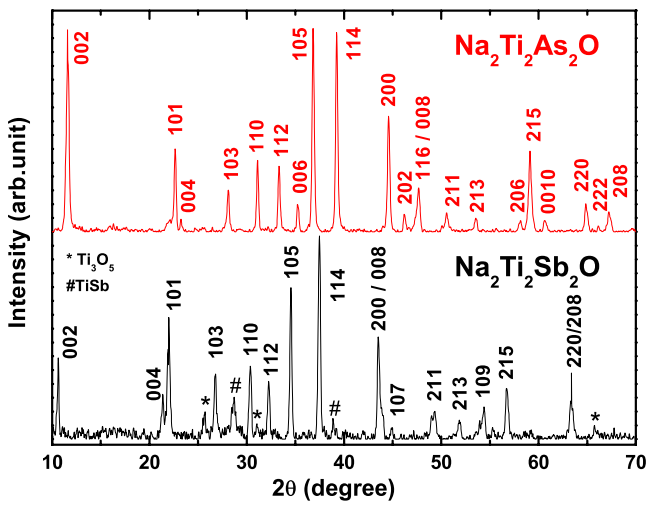

FIG. 2. (Color online) X-ray powder-diffraction patterns at room temperature for the $Na_2Ti_2P_2O$ (P=As and Sb) samples.

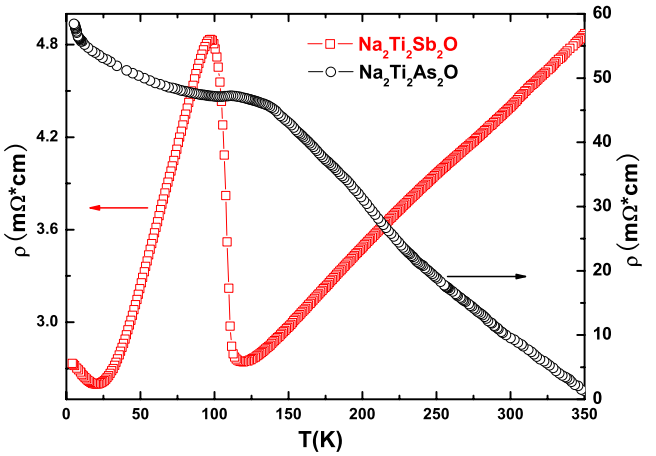

FIG. 3. (Color online) Temperature dependence of resistivity for the $Na_2Ti_2P_2O$(P=As and Sb) samples.

SDW order.[20] While no remarkable anomaly is observed in resistivity for the sample $Na_2Ti_2As_2O$ at the temperature of ~320 K where the magnetic susceptibility shows an anomaly, a kink is observed at about 135 K in resistivity.

The magnetic susceptibility measured under 5 T is shown for the samples $Na_2Ti_2P_2O$ (P=As and Sb) in Fig. 4. $Na_2Ti_2Sb_2O$ exhibits a sharp drop in susceptibility around 115 K which corresponds to the temperature of the anomaly observed in resistivity. In contrast, the sharp drop in magnetic susceptibility is observed around 320 K where no anomaly shows up in the resistivity in $Na_2Ti_2As_2O$. These abnormal behaviors in electrical resistivity and susceptibility are in good agreement with what reported by Tadashi *et al.*[15–18]

In order to further understand the behavior of the anomaly observed in resistivity and susceptibility, Hall coefficient (R_H) and TEP are systematically measured. Figure 5 shows the temperature dependence of Hall coefficient (R_H) and TEP for the sample $Na_2Ti_2Sb_2O$. In order to obtain a good and uniform Hall voltage signal, the samples were cut into rect-

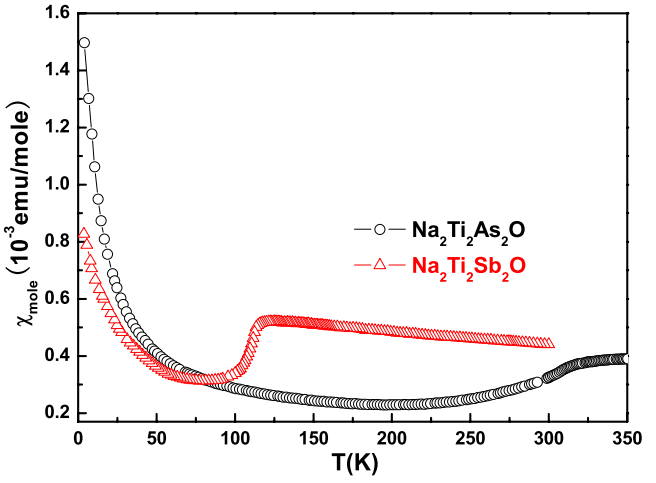

FIG. 4. (Color online) Temperature dependence of susceptibility measured under 5 T for $Na_2Ti_2P_2O$ (P=As and Sb) in the temperature range of 4–300 K.

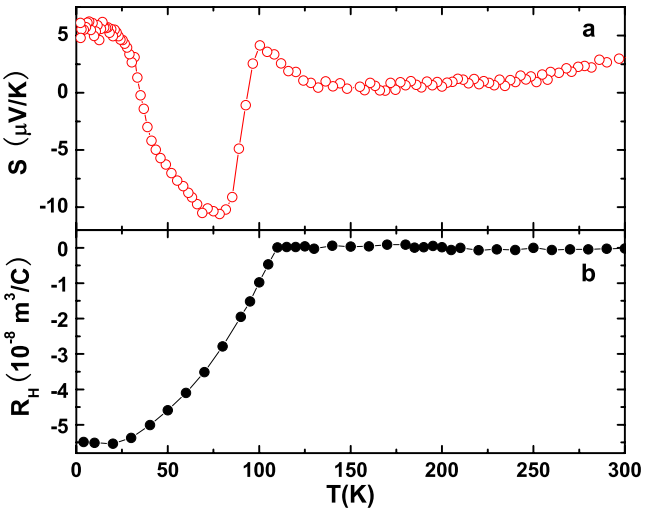

FIG. 5. (Color online) Temperature dependence of thermoelectric power (up panel) and Hall coefficient (down panel) for the samples $Na_2Ti_2Sb_2O$.

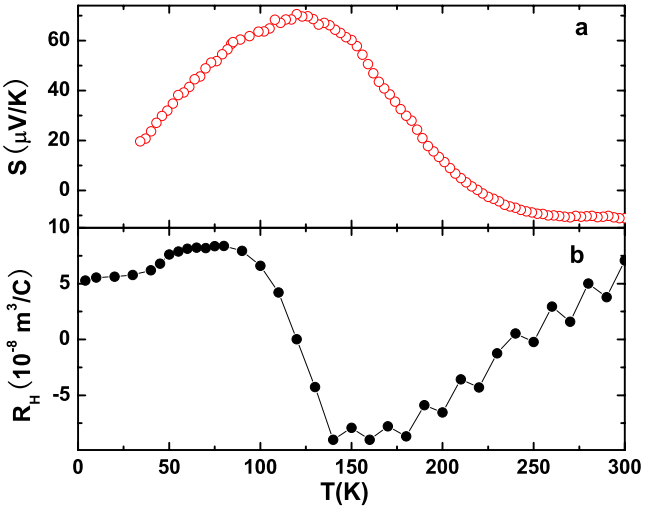

FIG. 6. (Color online) Temperature dependence of thermoelectric power (up panel) and Hall coefficient (down panel) for the samples $Na_2Ti_2As_2O$.

angle shapes with a thickness of ~300 μm. The longitudinal and Hall voltages were measured by using the standard dc six-probe method. The Hall voltage is found to be linear with the magnetic field. The Hall coefficient is negative and very small, and shows a weak temperature dependence above 115 K, indicating that the dominant carrier is electron. As shown in Fig. 5(b), the Hall coefficient shows a pronounced rise below ~115 K which coincides with the temperature of the abnormal peaks observed in resistivity and susceptibility as shown in Figs. 3 and 4. It indicates a drop in carrier concentration at T_S due to the occurrence of possible SDW ordering. Such behavior has been widely observed in heavy-fermion system with strong antiferromagnetic (or SDW) fluctuations[25] and in iron-based oxypnictide parent compounds.[5] Temperature-dependent TEP measurements were performed with a Quantum Design PPMS. TEP is positive above 110 K. TEP sharply drops and its sign changes to negative at the occurrence temperature of the SDW ordering at which the abnormal peak is observed in resistivity and the abnormal drop shows up in R_H. It further indicates a pronounced change in carrier concentration at T_S. The behavior is similar to that of FeAs-based La(1111) (Ref. 26) and Ba(122) (Refs. 8 and 9) system in which the magnitude of TEP shows a distinct change at T_{SDW}. It should be mentioned that the Hall coefficient and TEP show contrasting sign above 110 K, indicating a multiple-bands behavior in $Na_2Ti_2Sb_2O$.

For the sample $Na_2Ti_2As_2O$, the Hall coefficient (R_H) monotonically decreases and changes the sign from positive to negative with decreasing temperature to about 135 K, and rapidly increases below 135 K at which a kink shows up in resistivity. Below 100 K R_H is positive and shows a weak temperature dependence. Figure 6(a) shows temperature dependence of TEP for $Na_2Ti_2As_2O$. TEP is negative above 200 K and increases with decreasing temperature. A broad peak appears around 125 K. The complicated behavior observed in R_H and TEP could arise from SDW/CDW instability and a complicated box Fermi surface.[21] For $Na_2Ti_2Sb_2O$, the resistance, R_H and TEP show an abnormal change just like what observed in the FeAs-based parent compounds at T_{SDW} with the sharp drop of susceptibility. However, the resistance, R_H and TEP of $Na_2Ti_2As_2O$ do not show a visible change at $T_{SDW/CDW}$ with the drop of susceptibility. The CDW/SDW instability is known to be suppressed as the dimensionality of the system increases. Since the c lattice parameter of the As analogue (c=1.526 nm) is smaller than the Sb analogue (c=1.657 nm), the As analogue has stronger interlayer interaction and more three-dimensional character than the Sb analogue. Therefore, the more pronounced CDW/SDW amplitude in Sb analogue may be due to its lower dimensionality.[17]

The properties of electronic scattering has been investigated by MR. Temperature dependence of resistivity under different fields and the isothermal MR $[\Delta\rho/\rho_0=[\rho(H)-\rho_0]/\rho_0$, where $\rho(H)$ and ρ_0 represents the longitudinal resistivity at a magnetic field H and at zero field] at different temperatures for the sample $Na_2Ti_2Sb_2O$ are shown in Figs. 7(a) and 7(b). A linear temperature dependence of the resistivity and a very small positive MR is observed from the SDW/CDW temperature (T_S) ~ 120–350 K. The behavior is similar to Fe-based *R*OFeAs (Refs. 5 and 27) and $CaFe_2As_2$ (Ref. 9) parent compounds. Between 120 and 100 K, the resistivity increases sharply, being consistent with the opening of a gap. Additionally, a hysteresis is observed during a cooling and warming cycle with a cooling/warming rate of 30 K/h in Fig. 7(c). The pronounced anomaly in resistivity is considered to be associated with a structural distortion and CDW/SDW instability, and the structural distortion in the material is a kind of first-order transition. At about T_S ~ 110 K, there is a distinct negative MR and reaches to −2% at 14 T. The negative MR can be ascribed to possible strong spin fluctuations at about T_S and the suppression of the spin fluctuations caused by an external magnetic field. Below the temperature (T_S) due to a structural distortion and CDW/SDW instability, MR monotonically increases with decreasing temperature and reaches to 40% at 14 T below 30

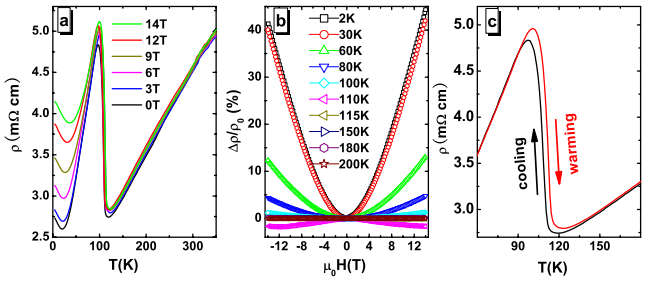

FIG. 7. (Color online) Magnetotransport for the samples $Na_2Ti_2Sb_2O$. (a) Temperature dependence of resistivity at different fields, (b) isothermal magnetoresistance at different temperatures, and (c) the resistivity as a function of temperature was measured in the cooling and warming cycle.

K. Such behavior also has been observed in the Fe-based high-T_c parent compounds *R*OFeAs and AFe_2As_2 and it maybe originate from the enhanced spin scattering while AFM-type SDW order is suppressed in external magnetic field.[27,28] The origin for the anomaly observed in resistivity and susceptibility at T_S should arise from the SDW/CDW instability accompanied with a structural distortion just like the case of iron-based high-T_c parent compound.

In order to check the behavior of the anomaly observed in resistivity and susceptibility, as known in FeAs-based oxypnictide with SDW instability[7,9] and other CDW/SDW materials,[22–24] the heat capacity is measured between 2 and 170 K by a relaxation-time method in a PPMS. A pronounced anomaly peak is clearly observed in $C_p(T)$ at ~110 K as shown in Fig. 8. It definitely indicates occurrence of phase transition at about 110 K and the phase transition could arise from a SDW/CDW instability or a structure distortion. In the low-temperature region the specific heat can be fitted by $C_p = \gamma T + \beta T^3$. The Debye temperature can be estimated from the equation $\beta = (12\pi^4 N k_B)/(5\Theta_D^3)$, where N is the number of atoms per formula unit. From the plot of Cp/T vs. T^2 data between 2 and 16 K, we can estimate a Sommerfeld coefficient $\gamma = 28$ mJ K^{-2} mol^{-1}, $\beta = 1.49$ mJ K^{-4} mol^{-1} and $\Theta_D = 209$ K for $Na_2Ti_2Sb_2O$.

In summary, the samples $Na_2Ti_2P_2O$ (P=As and Sb) with an anti-K_2NiF_4 type were systematically studied by resistivity, susceptibility, Hall coefficient R_H, TEP, MR, and heat capacity. The linear temperature dependence of resistivity

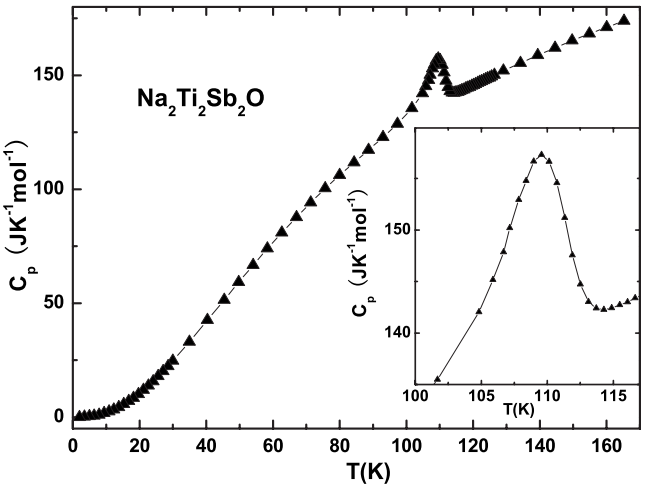

FIG. 8. Temperature dependence of specific heat for the sample $Na_2Ti_2Sb_2O$. Inset: the C_p vs T curve around T_s.

from 120 to 350 K and an anomaly in resistivity at T_S ~115 K have been observed, coinciding with a sharp drop in susceptibility for the sample $Na_2Ti_2Sb_2O$. These behaviors are similar to what observed in Fe-based $CaFe_2As_2$ compound with a SDW instability at 200 K.[9] Additionally, Hall coefficient (R_H) and TEP show a pronounced rise at T_S ~115 K, indicating a drop in carrier concentration at T_S due to the occurrence of SDW/CDW ordering. The heat-capacity measurement shows a pronounced anomaly peak of $C_p(T)$ at ~110 K due to a SDW/CDW instability or a structure distortion. Furthermore, muon-spin rotation (μSR) experiments should be performed on these compounds for detecting the small moment static order. Angle-resolved photoemission spectroscopy (ARPES) experiment indicates AFe_2As_2 has a strongly nested boxlike Fermi surface, resulting in the SDW instability.[29] Thus, a Fermi topology map by the ARPES result can be used to confirm the existence of the SDW or CDW state in these compounds as that of Fe-based high-T_C parent materials.[17]

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*Corresponding author; chenxh@ustc.edu.cn

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