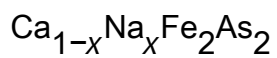


Different resistivity response to spin-density wave and superconductivity at 20 K in



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FAST TRACK COMMUNICATION

Different resistivity response to spin-density wave and superconductivity at 20 K in $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$

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Abstract

We report intrinsic transport and magnetic properties and their anisotropy in high-quality single-crystal CaFe_2As_2 . The resistivity anisotropy (ρ_c/ρ_{ab}) is ~ 50 , less than the 150 of BaFe_2As_2 , which arises from the strong coupling along the c -axis due to an apparent contraction of about 0.13 nm compared to BaFe_2As_2 . In sharp contrast to the case of parent compounds ROFeAs ($R = \text{rare earth}$) and MFe_2As_2 ($M = \text{Ba and Sr}$), spin-density-wave (SDW) ordering (or structural transition) leads to a steep increase of resistivity in CaFe_2As_2 . Such a different resistivity response to SDW ordering is helpful to understand the role played by SDW ordering in Fe-based high- T_c superconductors. The susceptibility behavior is very similar to that observed in single-crystal BaFe_2As_2 . A linear temperature-dependent susceptibility occurs above the SDW transition of about 165 K. Partial substitution of Na for Ca suppresses the SDW ordering (anomaly in resistivity) and induces superconductivity at ~ 20 K.

(Some figures in this article are in colour only in the electronic version)

The discovery of superconductivity at 26 K in $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ ($x = 0.05\text{--}0.12$) [1], and T_c surpassing 40 K, beyond the McMillan limitation of 39 K predicted by BCS theory in $\text{RFeAsO}_{1-x}\text{F}_x$ by replacing La with other trivalent R with smaller ionic radii [2–4], have generated much interest for extensive study of such iron-based superconductors. This is the second family of high- T_c superconductors after the high- T_c cuprates. Such Fe-based superconductors share some similarities with cuprates. They adopt a layered structure with Fe layers sandwiched by two As layers; each Fe is coordinated by an As tetrahedron. Similar to the cuprates, the Fe–As layer is thought to be responsible for superconductivity, and the R–O layer is a carrier reservoir layer to provide electron carriers. The electron carriers induce transfer to the Fe–As layer to realize superconductivity. Electronic properties are

dominated by the Fe–As triple layers, which mostly contribute to the electronic state around the Fermi level.

Recently, the ternary iron arsenide BaFe_2As_2 has been found to show superconductivity at 38 K by hole doping with partial substitution of potassium for barium [5]. This material adopts ThCr_2Si_2 -type structure. There exists a single FeAs layer in the unit cell in the ROFeAs system, while there are two FeAs layers in a unit cell in BaFe_2As_2 . These parent compounds share common features: an anomaly appears in the resistivity and such an anomaly is associated with a structure transition and spin-density-wave (SDW) ordering. The parent material LaOFeAs shows an anomaly in resistivity at 150 K which is associated with the structural transition at ~ 150 K and an SDW transition is observed at ~ 134 K [1, 6]. An anomaly in resistivity occurs at ~ 140 K in BaFe_2As_2 and the susceptibility shows an antiferromagnetic SDW ordering

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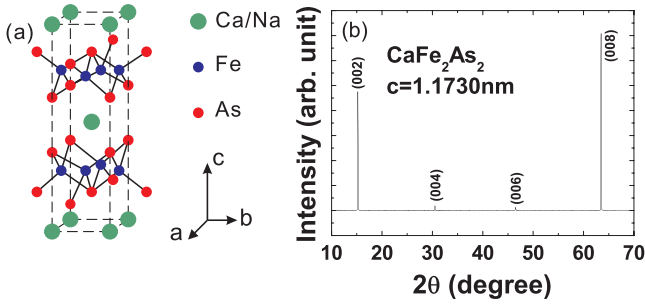


Figure 1. (a) Crystal structure of CaFe_2As_2 . (b) Single crystal x-ray diffraction pattern of CaFe_2As_2 ; only $(00l)$ diffraction peaks show up, suggesting that the c -axis is perpendicular to the plane of the plate.

at almost the same temperature [7]. Neutron scattering further indicates that the antiferromagnetic SDW ordering and structural transition happen at the same temperature, coinciding with the anomaly in resistivity [8]. In all systems of RFeAs ($R = \text{rare earth}$), BaFe_2As_2 and SrFe_2As_2 , SDW ordering (or structural transition) leads to a steep decrease of resistivity [1, 9, 10, 7, 11, 12]. The structural and SDW instabilities are suppressed, the anomaly in resistivity disappears and superconductivity is induced with electron and hole doping in $\text{RFeAsO}_{1-x}\text{F}_x$ [1, 9, 10] and $\text{M}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($M = \text{Ba, Sr}$) [5, 11, 12] systems. Here we report the anisotropy in resistivity and susceptibility in single-crystal CaFe_2As_2 . The resistivity anisotropy is ~ 50 , less than the 150 of BaFe_2As_2 [7]; this is consistent with an apparent contraction in the lattice c -axis relative to BaFe_2As_2 . It is striking that the resistivity increases when SDW ordering occurs in CaFe_2As_2 , in sharp contrast to SDW ordering leading to a steep decrease in resistivity in all other parent compounds RFeAsO and MFe_2As_2 ($M = \text{Ba and Sr}$). Substitution of Na for Ca leads to suppression of the SDW ordering and structural transition, and induces superconductivity at ~ 20 K.

High-quality single crystals of CaFe_2As_2 were grown by the self-flux method, which is similar to that described in our earlier paper about growth of BaFe_2As_2 single crystals with FeAs as flux [7]. Many shiny plate-like CaFe_2As_2 crystals were obtained. Typical dimensions are about $1 \times 1 \times 0.05 \text{ mm}^3$. Polycrystalline samples of $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ were synthesized by the solid state reaction method using CaAs , NaAs and Fe_2As as starting materials. CaAs , NaAs and Fe_2As were presynthesized by heating Ca , Na lumps, Fe and As powder in an evacuated quartz tube at different temperatures for 4 h, respectively. The raw materials were accurately weighed according to the stoichiometric ratio of $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$, then the weighed powders were thoroughly ground and pressed into pellets. The pellets were wrapped with Ta foil and sealed in evacuated quartz tubes. The sealed tubes were heated to 1203 K and annealed for 15 h.

The crystal structure of $\text{Ca}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ is shown in figure 1(a), which is the same as BaFe_2As_2 with the tetragonal ThCr_2Si_2 -type structure [13]. The layers of edge-sharing Fe_4As_4 tetrahedra are separated by Ca atom layers. Figure 1(b) shows the single-crystal x-ray diffraction pattern of CaFe_2As_2 . Only $(00l)$ diffraction peaks are observed; this suggests that

Table 1. Crystallographic data of CaFe_2As_2 . For comparison, the data of BaFe_2As_2 are also listed; the data are from [15].

Temperature = 297 K	CaFe_2As_2	BaFe_2As_2
Space group	$I4/mmm$	$I4/mmm$
a (nm)	0.387 2(9)	0.396 25(1)
b (nm)	0.387 2(9)	0.396 25(1)
c (nm)	1.173 0(2)	1.301 68(3)
V (nm^3)	0.175 94(5)	0.204 38(1)
Atomic parameters		
Ca (Ba)	2a (0, 0, 0)	2a (0, 0, 0)
Fe	4d ($\frac{1}{2}$, 0, $\frac{1}{4}$)	4d ($\frac{1}{2}$, 0, $\frac{1}{4}$)
As	4e (0, 0, z)	4e (0, 0, z)
	$z = 0.3665(9)$	$z = 0.3545(1)$
Average bond lengths (nm)		
Ca (Ba)–As	0.315 4(0)	0.337 9(6)
Fe–As	0.237 0(9)	0.239 7(6)
Fe–Fe	0.273 8(7)	0.279 9(6)
Average bond angles (deg.)		
As–Fe–As ₁	109.5(2)	111.3(6)
As–Fe–As ₂	109.4(6)	108.5(6)

the crystallographic c -axis is perpendicular to the plane of the plate-like single crystal. Table 1 shows the crystallographic data of single-crystal CaFe_2As_2 at room temperature. X-ray diffraction measurement on the intensity data was performed at 297 K (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) using a Gemini S Ultra (Oxford diffraction). All the structures were solved by Patterson methods and refined by full-matrix least-squares methods with SHELX-97 [14]. For comparison, the data of BaFe_2As_2 reported by Rotter *et al* [15] are also listed in table 1. Both CaFe_2As_2 and BaFe_2As_2 have the same space group. The lattice parameters of CaFe_2As_2 are much smaller than those of BaFe_2As_2 . Comparing the average bond lengths of CaFe_2As_2 with BaFe_2As_2 , it is found that the length of the Ca–As bond is much smaller than the Ba–As bond. This indicates that the interaction between the Ca layer and FeAs layer is much stronger than that between the Ba layer and FeAs layer.

The temperature dependence of the susceptibility measured under a magnetic field of $H = 5 \text{ T}$ applied within the ab -plane and along the c -axis, respectively, is shown in figure 2. It should be pointed out that an anisotropy between $H \parallel ab$ -plane and along the c -axis is observed, but these data are not corrected by a demagnetization factor. Susceptibility decreases monotonically for the magnetic field applied within the ab -plane and along the c -axis, and shows a linear temperature dependence above a characteristic temperature of $\sim 165 \text{ K}$. At 165 K, the susceptibility shows a rapid decrease, which is ascribed to occurrence of an antiferromagnetic spin-density wave. Below 165 K, the susceptibility decreases more strongly than a T -linear dependence. At low temperatures, a Curie–Weiss-like behavior in susceptibility is observed. These behaviors are very similar to the susceptibility behavior reported in single crystal BaFe_2As_2 [7]. The magnitude of the susceptibility is almost the same as that of BaFe_2As_2 . The susceptibility behavior observed in both BaFe_2As_2 and CaFe_2As_2

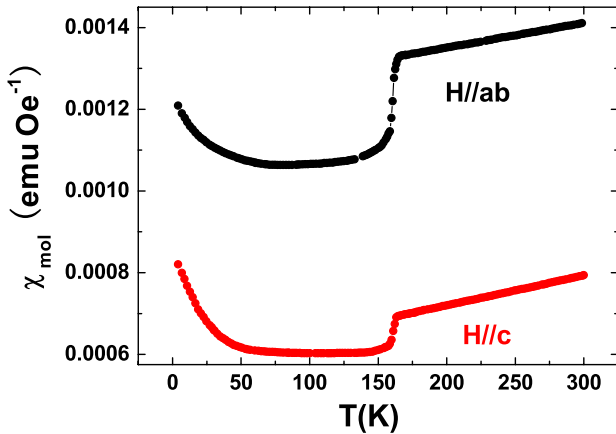


Figure 2. Temperature dependence of susceptibility measured under $H = 5$ T applied within the ab -plane and along the c -axis, respectively, for single crystal CaFe_2As_2 .

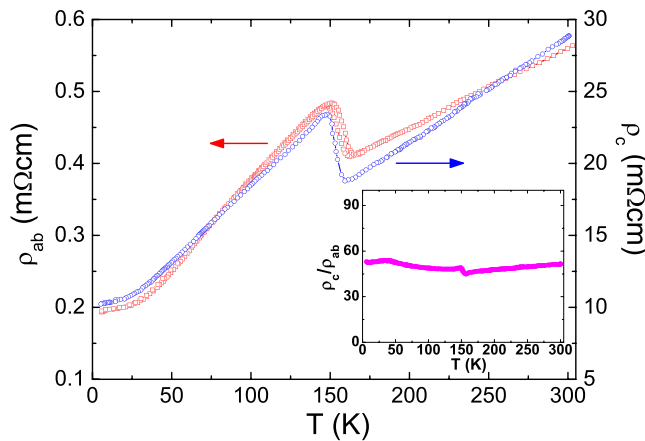


Figure 3. Temperature dependence of in-plane and out-of-plane resistivity ($\rho_{ab}(T)$ (squares) and $\rho_c(T)$ (circles)) for single crystal CaFe_2As_2 . A hysteresis in $\rho_{ab}(T)$ is observed with cooling and heating measurements. The inset shows the temperature dependence of the anisotropy of resistivity (ρ_c/ρ_{ab}). The anisotropy ρ_c/ρ_{ab} is independent of temperature, indicating that the transports in the ab -plane and along the c -axis direction share the same scattering mechanism.

is very similar to that of antiferromagnetic SDW pure Cr [17], in which a temperature-linear dependence persists to the occurrence temperature of the SDW.

Figure 3 shows the temperature dependence of the in-plane and out-of-plane resistivity. Both in-plane and out-of-plane resistivity show similar temperature dependent behavior. In-plane and out-of-plane resistivities show almost a linear temperature dependence above ~ 165 K, and a steep increase at 165 K, then change to metallic behavior. As shown in figure 3, a hysteresis around 165 K is observed with cooling and heating measurements, suggesting a first-order transition at 165 K. This transition temperature coincides with the SDW transition observed in susceptibility as shown in figure 2. This indicates that the SDW ordering leads to a steep increase in resistivity. Such a resistivity response to the SDW transition is in sharp contrast to that for all other

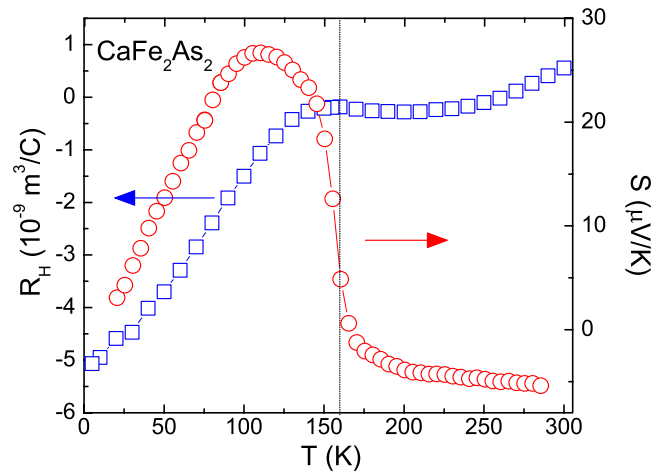


Figure 4. The temperature dependence of the Hall coefficient and thermoelectric power (TEP) of single crystal CaFe_2As_2 .

parent compounds ROFeAs ($R = \text{rare earth}$), BaFe_2As_2 and SrFe_2As_2 [1, 9, 10, 7, 11, 12], in which SDW ordering (or structural transition) leads to a steep decrease of resistivity. Such a different resistivity response to SDW ordering is helpful to understand the role played by the SDW ordering in Fe-based high- T_c superconductors. The inset shows the anisotropy of resistivity (ρ_c/ρ_{ab}). The resistivity anisotropy, ρ_c/ρ_{ab} , is about 50. The anisotropy in CaFe_2As_2 is less than the 150 of BaFe_2As_2 . This could arise from the fact that the interaction between the Ca layer and FeAs layer is much stronger than that between the Ba layer and FeAs layer. Such strong coupling along the c -axis leads to an apparent contraction of about 0.13 nm in the lattice c -axis; the c -axis lattice parameter decreases from ~ 1.302 nm in BaFe_2As_2 to ~ 1.173 nm in CaFe_2As_2 . The almost temperature independent ρ_c/ρ_{ab} suggests that in-plane and out-of-plane transports share the same scattering mechanism.

Temperature dependences of Hall coefficient and thermoelectric power (TEP) for single crystal CaFe_2As_2 are shown in figure 4. The TEP of CaFe_2As_2 is negative in the high temperature range, changes sign at about 165 K and shows a complicated temperature dependence. TEP slightly increases with decreasing temperature to about 170 K, and then a big jump increase is observed due to the SDW transition or structural transition. Below 145 K, TEP slowly increases with decreasing temperature to about 110 K, then decreases monotonically. A similar big jump around 140 K was observed in BaFe_2As_2 , but the negative sign is opposite to that of CaFe_2As_2 [16]. The Hall coefficient of CaFe_2As_2 is negative and changes to positive above 260 K. The temperature dependence of the Hall coefficient is almost independent of temperature between 260 and 160 K. Below $T_s = 160$ K, a pronounced decrease in Hall coefficient is observed, which coincides with the T_s of the SDW transition or structural transition observed in susceptibility and resistivity. The magnitude of the Hall coefficient of CaFe_2As_2 at 5 K is about two orders smaller than that of the parent compound of LaOFeAs with a single FeAs layer. This indicates a higher carrier density in two-layer compounds. The opposite

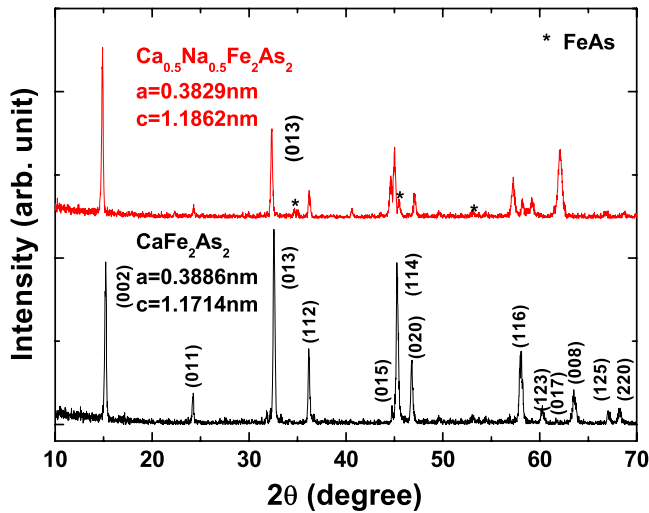


Figure 5. X-ray powder diffraction patterns at room temperature for the polycrystalline samples: CaFe_2As_2 and $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$, respectively.

signs of the Hall coefficient and thermoelectric power are different from the parent compound LaOFeAs , in which the signs of the Hall coefficient and thermoelectric power are both negative. Similar results are also reported in the EuFe_2As_2 compound [18]. These results indicate a multi-band scenario in parent compounds with two FeAs layers in an unit cell.

X-ray powder diffraction patterns are shown in figure 5 for the polycrystalline samples: CaFe_2As_2 and $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$. Nearly all diffraction peaks in the patterns of CaFe_2As_2 and $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$ can be indexed by the tetragonal ThCr_2Si_2 -type structure, indicating that the samples are almost single phase. The lattice parameters are $a = 0.3886$ nm and $c = 1.1714$ nm for the CaFe_2As_2 sample and $a = 0.3829$ nm and $c = 1.1862$ nm for the $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$ sample, respectively. This indicates that Na doping leads to an apparent decrease in lattice a -axis and an increase in lattice c -axis. This result is similar to $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [5].

Figure 6 shows the temperature dependence of the resistivity for polycrystalline samples: CaFe_2As_2 and $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$. The polycrystalline parent compound shows similar behavior to that of the corresponding single crystal. A linear temperature dependent resistivity is observed above the anomaly temperature. The anomaly for increase in resistivity for the polycrystalline sample is much weaker than that observed in the single crystal. Compared to the single crystal, the transition temperature in the polycrystalline sample is about 10 K higher. As shown in figure 6, no anomaly in resistivity is observed and a superconducting transition at ~ 20 K shows up in the sodium-doped sample $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$. This suggests that partial substitution of Na for Ca induces hole-type carriers into the system, leads to the suppression of structural and SDW instabilities and induces superconductivity in $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$. Such behavior is consistent with that reported in the electron-doped $\text{RFeAsO}_{1-x}\text{F}_x$ ($\text{R} = \text{rare earth}$) system [1, 9, 4, 10] and the hole-doped $\text{M}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($\text{M} = \text{Ba and Sr}$) system [5, 16, 11, 12].

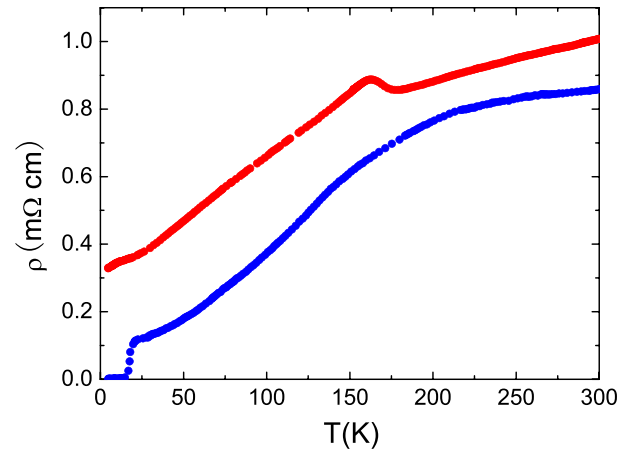


Figure 6. Temperature dependence of resistivity for polycrystalline samples: CaFe_2As_2 and $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$, respectively. The anomaly is completely suppressed and a superconductivity at about 20 K is observed in the Na-doped sample.

In summary, we have systematically studied the anisotropy of resistivity and susceptibility in a high-quality single crystal of parent compound CaFe_2As_2 . The resistivity anisotropy (ρ_c/ρ_{ab}) is about 50, small relative to BaFe_2As_2 due to stronger coupling between the Ca layer and FeAs layer than that between the Ba layer and FeAs layer. An apparent contraction along the c -axis of about 0.13 nm is observed. The susceptibility behavior is very similar to that of antiferromagnetic SDW pure chromium and BaFe_2As_2 . In sharp contrast to the case of other parent compounds ROFeAs ($\text{R} = \text{rare earth}$) and MFe_2As_2 ($\text{M} = \text{Ba and Sr}$), SDW ordering (or structural transition) leads to a steep increase of resistivity. Such different resistivity response to SDW ordering is helpful to understand the role played by SDW ordering in Fe-based high- T_c superconductors. Partial substitution of Na for Ca induces hole-type carriers into the system, leads to the suppression of structural and SDW instabilities, and induces superconductivity at ~ 20 K in $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Fe}_2\text{As}_2$.

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