

Anisotropy in the Electrical Resistivity and Susceptibility of Superconducting BaFe₂As₂ Single Crystals

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We report that sizable single crystals of BaFe₂As₂ have been grown with the self-flux method. Measurements and anisotropy of intrinsic transport and magnetic properties from high-quality single crystal are first presented. The resistivity anisotropy (ρ_c/ρ_{ab}) is as large as 150 and independent of temperature. In contrast to the susceptibility behavior observed in polycrystalline samples, no Curie-Weiss behavior is observed, and a linear- T dependent susceptibility occurs from the spin-density-wave transition temperature, (T_s), to 700 K. This result suggests that strong antiferromagnetic correlations are present well above T_s . A twofold symmetry of susceptibility in the ab plane indicates a stripelike spin structure as observed by neutron scattering. The resistivity minimum is strongly dependent on the magnetic field, suggesting that the upturn of the resistivity at low temperatures should be related to spin fluctuation.

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The discovery of superconductivity in the layered iron arsenic compounds has generated much interest. Pnictide superconductivity was initially studied below 26 K in LaO_{1-x}F_xFeAs ($x = 0.05-0.12$) [1] and T_c surpassing 40 K, beyond the McMillan limitation of 39 K predicted by BCS theory, was obtained in RO_{1-x}F_xFeAs by replacing La with other trivalent R with smaller ionic radii [2-4]. The question naturally arises as to how the iron-based high T_c superconductors (HTSC) compare to cuprates. The Fe-based superconductors share some similarities with cuprates. They both adopt a layered structure. The doping phase diagram of Fe oxypnictide system is remarkably similar to that of the cuprates. For both systems, superconductivity emerges upon doping carriers into an antiferromagnetic parent compound, while the antiferromagnetic order is suppressed by doping [1,2,5]. These similarities are of great significance because the parent compounds in the two families are very different. The parent compounds of the pnictides and the cuprates appear to have different magnetic ground states. The pnictides appear to be itinerant systems with magnetism arising from a nesting-induced spin density wave (SDW), in contrast with the cuprates, which are Mott-Hubbard insulators with antiferromagnetic ground states. On the other hand, the parent compounds of new Fe-based superconductors are bad metals and share a similar electronic structure with five orbitals contributing to a low density of states at the Fermi level [5-11]. This contrasts to the case of cuprates in which parent compounds are Mott-insulators with long-range antiferromagnetic ordering. Therefore, it is very important to study the various behaviors of the parent compound to compare with the cuprates.

In order to understand high- T_c superconductivity, it is important to obtain further insight into the differences and similarities of the pnictide and cuprate HTSCs. A crucial step for study intrinsic, especially anisotropic,

properties is to grow sizable single crystals. Unfortunately, growth of single crystals of these materials has proven very difficult. So far, only single crystals with hundreds of μm are reported in the RFeAsO system [12,13]. Superconductivity at 38 K was realized in Ba_{1-x}K_xFe₂As₂ without oxygen [14]. As pointed out by Ni *et al.*, single crystals of such intermetallic compound systems without oxygen can be grown by the conventional flux method [15]. Growth of single crystals with mm size has been reported with a tin flux, but the single crystal is contaminated with Sn [15]. Here we report growth of sizable single crystals of BaFe₂As₂ with the self-flux method to avoid the contamination by flux. Intrinsic resistivity and susceptibility obtained from high-quality single crystals are first presented, intrinsic susceptibility behavior is in contrast to that observed in polycrystalline samples due to impurities. These intrinsic behaviors will be helpful for understanding the underlying physics of the parent compound.

High-quality BaFe₂As₂ single crystals were grown by the self-flux method. In order to avoid contamination from incorporation of other elements into the crystals, FeAs was used as the flux. FeAs was obtained by reacting the mixture of the element in powdered form in evacuated quartz tubes at 1173 K for 4 h. Then Ba powder and FeAs powder were accurately weighed according to the ratio of Ba:FeAs = 1:4, and thoroughly ground. The mixture was loaded into an alumina crucible and then sealed under vacuum in a quartz tube. The tube was slowly heated to 973 K at a rate of 120 K/h and kept at 973 K for 200 min to allow the reaction of the mixture of Ba and FeAs. Subsequently, the temperature was raised to 1373 K in 100 minutes, the quartz tube was kept at 1373 K for 1600 min, and then the tube was cooled to 1173 K at a rate of 4 K/h. Finally the quartz tube was cooled in the furnace after shutting off the power. The shining platelike BaFe₂As₂ crystals were

mechanically cleaved from the flux and obtained for measurements.

Figure 1(a) shows the picture of a single crystal of BaFe_2As_2 on a 2 mm grid. A typical crystal size is $2 \times 2 \times 0.10 \text{ mm}^3$. As shown in Fig. 1(a), the linear dimension is as large as 5 mm. All of the crystals are prone to exfoliation and easily cleaved. Figure 1(b) shows the single crystal x-ray diffraction pattern. Only (00l) diffraction peaks are observed, suggesting that the crystallographic c axis is perpendicular to the plane of the platelike single crystal. The FWHM in the rocking curve of the (004) reflection is 0.18° . Elemental analysis was performed using energy dispersive x-ray spectroscopy (EDX). The obtained atomic ratio of Ba:Fe:As is roughly 20.82:40.65:38.53 for all grains; no other phases are detected. The atomic ratio is consistent with the composition BaFe_2As_2 within instrumental error.

Figure 2 shows the temperature dependence of in-plane and out-of-plane resistivity measured with PPMS (Quantum Design Inc.). Both in-plane and out-of-plane resistivity show similar temperature dependent behavior. The in-plane and out-of-plane resistivities show metallic behavior above 138 K and a steep decrease at 138 K. This behavior is consistent with that of polycrystalline samples [16,17], but the residual resistivity ratio (RRR) of about 2 in single crystal is less than 4 in polycrystalline sample [17]. It could arise from a metallic impurity contribution

(such as Fe) in the polycrystalline samples. The results observed here for single crystal BaFe_2As_2 are in sharp contrast to those from single crystals BaFe_2As_2 grown by Ni *et al.* [15]. This contrasting behavior could arise from the contamination of Sn from the tin flux in Ref. [15]. It suggests that the use of the self-flux (FeAs) technique is very important to obtain single crystals without contamination. It further indicates that we are able to probe the intrinsic properties of the superconductor in our clean single crystal grown by the self-flux method. The inset shows the resistivity anisotropy (ρ_c/ρ_{ab}). ρ_c/ρ_{ab} is as large as 150, indicating that the system is quasi-two dimensional. The near temperature independence of the ratio ρ_c/ρ_{ab} suggests that in-plane and out-of-plane transports share the same scattering mechanism. It should be addressed that all results discussed here are well reproducible. We measured more than ten crystals to check the results reproducible from crystal to crystal. In order to make sure that out-of-plane resistivity measured is intrinsic, and is not dominated by microcracks between the layers, single crystals used for measurements are characterized by rocking curve and the rocking curve just shows the sharp single peak (no splitting) for all single crystals as shown in Fig. 1(c).

The temperature dependence of the susceptibility (χ), measured with SQUID (Quantum Design Inc.) under the magnetic field (H) of 6.5 T applied in the ab -plane and parallel to the c axis, is shown in Fig. 3(a). It should be pointed out that an anisotropy between $H \parallel ab$ plane and $H \parallel c$ axis is observed. As shown in Fig. 3(a), the susceptibility decreases monotonically with decreasing temperature and shows a linear temperature dependence above 136 K. At 136 K corresponding to the anomaly in resistivity shown in Fig. 2, the susceptibility shows a rapid

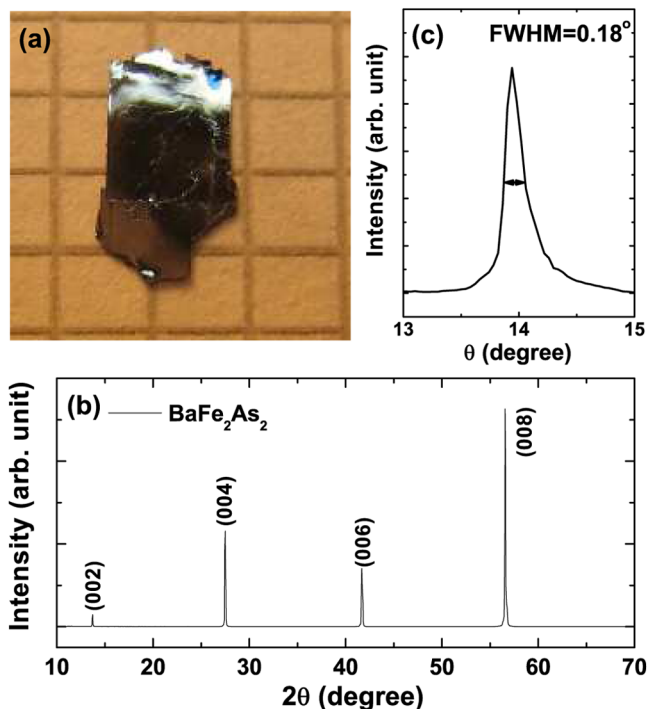


FIG. 1 (color online). (a) Photograph of a single crystal of BaFe_2As_2 on 2 mm grid; (b) single crystal x-ray diffraction pattern of BaFe_2As_2 . Only (00l) diffraction peaks show up, suggesting that the c axis is perpendicular to the plane of the plate; (c) rocking curve of (004) reflection.

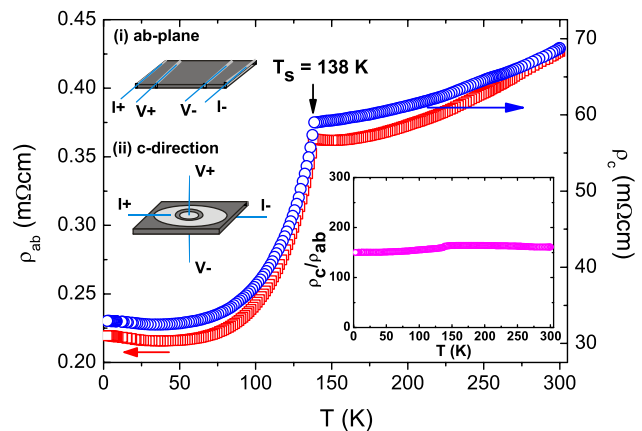


FIG. 2 (color online). Temperature dependence of in-plane and out-of-plane resistivity [$\rho_{ab}(T)$ (squares) and $\rho_c(T)$ (circles)] for single crystal BaFe_2As_2 . The inset shows that the resistivity anisotropy (ρ_c/ρ_{ab}). ρ_c/ρ_{ab} is independent of temperature, indicating that transport in the ab plane and along the c -axis direction share the same scattering mechanism.

decrease which should be ascribed to the occurrence of an antiferromagnetic SDW. Below 136 K the susceptibility decreases more strongly than linear- T dependence. A slight increase in susceptibility is observed at low temperatures. These behaviors are in contrast to that reported in polycrystalline sample LaOFeAs and BaFe₂As₂ [1,16]. In polycrystalline samples, a strong Curie-Weiss tail is always observed at lower temperatures. Such a strong Curie-Weiss tail arises from impurities. Interestingly, the linear- T susceptibility has been widely observed in undoped or highly underdoped La_{2-x}Sr_xCuO₄ [18], in Na_{0.5}CoO₂ [19] and in chromium and its alloys [20]. The linear- T susceptibility occurs before the antiferromagnetic transition for both La_{2-x}Sr_xCuO₄ and Na_{0.5}CoO₂, and above the antiferromagnetic SDW transition for chromium and its alloys, just like in the pnictides. Such linear- T susceptibility indicates a strong antiferromagnetic correlation. Recently, Zhang *et al.* give a theoretical discussion on the linear- T susceptibility [21]. The inset of Fig. 3(a) shows a linear- T susceptibility up to 700 K, similar to the case of highly underdoped La_{2-x}Sr_xCuO₄, in which χ increases linearly with temperature up to higher than 600 K [18]. In addition, the value of the susceptibility at 400 K is about 1×10^{-3} emu/mol for BaFe₂As₂, while it is about 0.17×10^{-3} emu/mol for pure Cr [20]. The susceptibility of BaFe₂As₂ is much larger than those of the 3d electron based superconductors, e.g., about 10^{-4} emu/mol for La_{2-x}Sr_xCuO₄ [22]. The linear- T susceptibility with large magnetization implies the coexistence of local moment and itinerant SDW in the pnictide superconductors. The coexistence of local moment and itinerant electrons has been observed in Na_xCoO₂ [23].

The susceptibility is measured at 4 K under the magnetic field $H = 6.5$ T rotated within the ab plane. As shown in Fig. 3(b), a twofold symmetry in susceptibility is observed, and a jump in susceptibility happens at certain angles. It should be emphasized that the twofold symmetry disappears above 136 K, indicating that the twofold symmetry is likely related to SDW ordering. These results indicate that an easy axis exists in the ab plane and a stripelike spin ordering occurs as observed by neutron scattering [24,25], and the spin prefers to one direction. The jump in susceptibility arises from that spin orientation along the easy axis is strongly pinned, and shows up when the pinning force cannot overcome anisotropy energy. Although the spin prefers one direction and there exists anisotropy energy due to pinning, the anisotropy of susceptibility in the ab plane is small, just 1.14. It should be pointed out that the isothermal M - H curves have been measured under the magnetic field (H) applied along the c axis and within the ab plane from 2 K to 300 K. All results show that M is proportional to H in the whole temperature range from 2 to 300 K for different orientations of H within the ab plane and along the c axis. It suggests that the susceptibilities shown in Fig. 3(a) and 3(b) are independent of H .

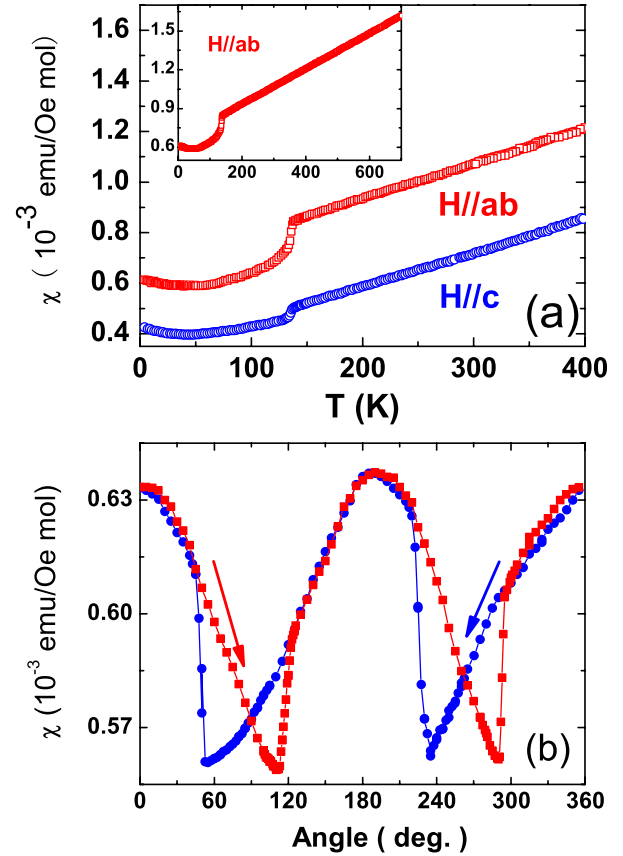


FIG. 3 (color online). Temperature dependence of susceptibility measured under $H = 6.5$ T applied along the ab plane and along the c axis, respectively. The inset shows susceptibility up to 700 K. (b) Susceptibility at 4 K as a function of magnetic field angle ($H = 6.5$ T) within ab plane. A twofold symmetry in susceptibility under rotation in the ab plane indicates a stripelike magnetic structure, as observed by neutron scattering in LaFeAsO [24].

The temperature dependence of both in-plane and out-of-plane resistivity is shown in Fig. 4 under $H = 0$, $H = 6.5$ T within the ab plane, and $H = 6.5$ T along the c axis, respectively. Almost no in-plane and out-of-plane magnetoresistivity is observed above the SDW transition. Below 100 K, apparent in-plane and out-of-plane magnetoresistivity appears. Both in-plane and out-of-plane magnetoresistivity are as large as 10% at 5 K under $H = 6.5$ T along the c axis. The effect of H on in-plane resistivity is much the same with H applied within the ab plane or along the c axis. The inset shows results of ρ_{ab} and ρ_c vs T in the low temperature range. Both zero-field in-plane and out-of-plane resistivity show a minimum at the same temperature of ~ 35 K. Below 35 K, the in-plane and out-of-plane resistivities follow a $\log(1/T)$ behavior and deviate from $\log(1/T)$ behavior below ~ 12 K and saturate at low temperatures. This behavior could arise from the Kondo effect. Applying a magnetic field leads to a shift of the resistivity minimum to higher temperature. The temperature of the

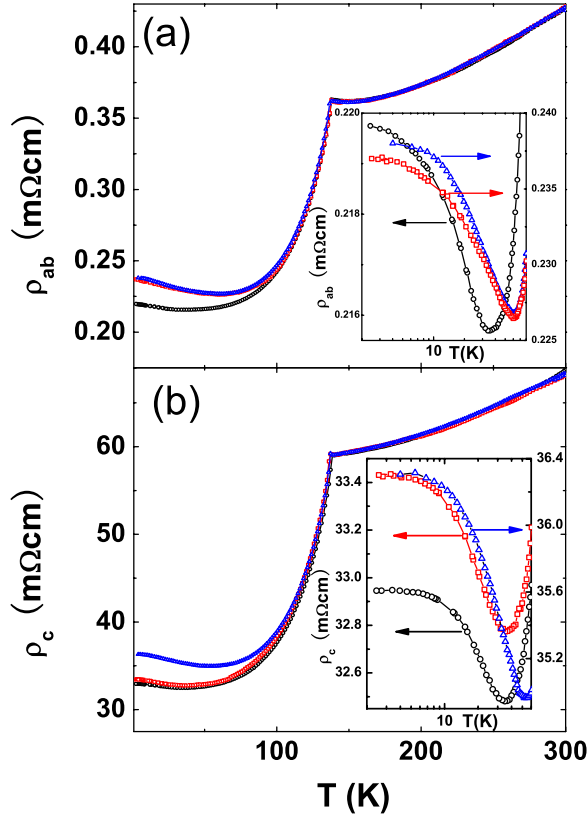


FIG. 4 (color online). Temperature dependence of in-plane and out-of-plane resistivity under magnetic field (H) of 0 and 6.5 T with $H \parallel$ to the ab plane and along the c axis, respectively. Zero-field resistivity (circles); $H \parallel ab$ plane (squares); and $H \parallel c$ -axis direction (triangles). Insets show the plot of low temperature ρ_{ab} and ρ_c vs T in log scale.

resistivity minimum is the same under the applied magnetic field within the ab plane and along the c axis. The temperature of the resistivity minimum shifts to 60 and 53 K for in-plane and out-of-plane applied field of $H = 6.5$ T, respectively. Strong dependence of the resistivity minimum on the applied magnetic field suggests spin fluctuations or the Kondo effect, instead of localization in the pnictides. The Kondo effect, the most likely possible mechanism, arises from magnetic impurity scattering from defects at Fe sites. The spin fluctuations can be enhanced by H as observed in cuprates.

In summary, we systematically study the anisotropy of resistivity and susceptibility in high-quality single crystal BaFe_2As_2 . The results indicate that the system is quasi-two dimensional. A linear temperature dependent susceptibility is observed well above $T_s = 136$ K up to about 700 K,

indicating strong antiferromagnetic correlations well above T_s . Notably, the susceptibility behavior we observe is in contrast to all observations of polycrystalline samples, due to impurity effects. These intrinsic behaviors are helpful to understand the underlying physics of the parent compound. The strongly magnetic field-dependent resistivity minimum is similar to those of underdoped cuprates. These results will help us to compare the pnictides with the cuprates and to understand the high- T_c superconducting mechanism.

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