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Absence of superconductivity in single-phase $CaFe_2As_2$ under hydrostatic pressure

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Recent high-pressure studies found that structural/magnetic phase transitions are very pressure sensitive in $CaFe_2As_2$ and that superconductivity can be achieved under modest pressure, although details of the sharpness and temperature of transitions vary between liquid medium and gas medium measurements. To better understand this issue, we performed high-pressure susceptibility and transport studies on $CaFe_2As_2$, using helium as the pressure medium. The signatures of the transitions to the low-temperature orthorhombic and collapsed tetragonal phases remained exceptionally sharp, and no signature of bulk superconductivity was found under our hydrostatic conditions. Our results suggest that superconductivity in $CaFe_2As_2$ is associated with a low-temperature, multicrystallographic-phase sample that is the result of nonhydrostatic conditions associated with the combination of a first-order structural phase transition and frozen liquid media.

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The recent discovery of superconductivity in doped iron arsenide compounds[1–3] and the later improvement of the superconducting transition temperature T_c in both the pnictide oxides such as ROFeAs (1111) (Refs. 4–7) and the $ThCr_2Si_2$-structure compounds such as $(Ba,K)Fe_2As_2$ (122) (Ref. 3) have caused extensive experimental and theoretical studies in this class of materials with layered FeAs planes. Similar to the high-T_c cuprates, the parent compounds exhibit structural transitions from a high-temperature tetragonal phase to a low-temperature orthorhombic phase, and the orthorhombic phase is usually antiferromagnetically (AF) ordered.[8,9] Upon doping, both the orthorhombic structure and the AF phase are suppressed and superconductivity is induced.

Several unique properties have been found in the iron arsenide superconductors. For example, these materials are semimetals and therefore metallic even without doping, in contrast to the cuprates. Superconductivity has been reported under hydrostatic pressure in the parent compounds $CaFe_2As_2$,[10–12] $SrFe_2As_2$,[13–15] and $BaFe_2As_2$.[14] In particular, for $CaFe_2As_2$, T_c as high as 10 K has been found in a moderate 0.4 GPa pressure,[10–12] while for $SrFe_2As_2$ and $BaFe_2As_2$, superconductivity is achieved at about 28 K at $P=3.2$ and 4.5 GPa, respectively.[14]

In $CaFe_2As_2$ in ambient pressure, a structural phase transition (from tetragonal to orthorhombic) is seen at $T_{S1}=170$ K,[16] accompanied by the appearance of magnetic order;[9] this transition is seen as a sharp upward anomaly in resistivity. Applied pressure causes a reduction in T_{S1}. In a conventional liquid medium clamp pressure cell, the signature in resistivity becomes a broad upturn rather than the sharp discontinuous change seen in ambient pressure.[10,12] Above 0.5 GPa, a collapsed tetragonal structure is identified below a separate structural transition temperature (T_{S2}).[10,17] The collapsed tetragonal phase has the same crystal symmetry as the high-temperature one but with a ~10% reduction in the c axis parameter and a 2% expansion of the in-plane lattice parameters.[17] The transition to the collapsed phase is also seen in resistivity measurements,[10] where a broad downward change in slope has been observed. The temperature T_{S2} increases with further increases in pressure.[10,17] The transition of $CaFe_2As_2$ from the high-temperature tetragonal phase to either of the low-temperature phases seems very sensitive to different pressure conditions. Transport studies using a conventional clamp cell see wide transitions,[10,12] whereas neutron scattering using helium as the pressure medium suggests that the orthorhombic and collapsed tetragonal phases emerge sharply at low temperatures.[17] The maximum superconducting T_c is achieved at about 10 K around an inferred phase boundary $P\approx 0.5$ GPa (Refs. 10 and 12) between the two low-temperature structures. This near vertical boundary was explicitly detected in isothermal pressure sweeps.[17,18] Recently Lee *et al.*[12] postulated the existence of a third phase in the region of the phase boundary and associated superconductivity with that border phase.

In order to clarify the phase diagram and the nature of the various phase transitions we have studied the high-pressure dc susceptibility and resistivity of $CaFe_2As_2$ using a helium gas pressure system. Compared with clamp pressure cells, helium has a low freezing point, which only increases to about 50 K at $P=0.7$ GPa. $CaFe_2As_2$ single crystals were grown by the Sn-flux method,[16] and afterward surface Sn was removed by etching with HCl. For the transport measurements, samples were loaded in a pressure cell with either a standard four-probe or a Van der Pauw configuration. The pressure cell was cooled in a helium storage dewar, and the pressure was applied *in situ* by an external helium compressor. For the magnetization measurements using a Quantum Design magnetic property measurement system (MPMS), the sample was loaded in a separate cell which was connected to the same helium compressor. The maximum pressure was about 0.7 GPa for both pressure cells, and we employed a cooling rate of about 1 K/min through the structural transitions. To ensure that the applied pressure in the compressor was transmitted to the pressure cells, we always set the pressure with the system temperature above 70 K, thus avoiding the possibility of helium freezing in the capillary.

Figure 1(a) shows the resistivity of a $CaFe_2As_2$ single crystal under different pressures. All measurements were reproducible from sample to sample. At ambient pressure, the

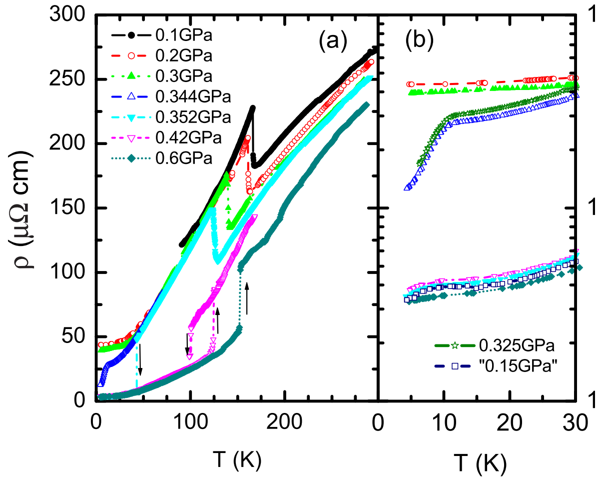

FIG. 1. (Color online) (a) The resistivity of a $CaFe_2As_2$ single crystal at different pressures. For pressures above 0.35 GPa, the cooling or the warming directions are indicated by an arrow next to the plots. (b) The low-temperature resistivity of the same $CaFe_2As_2$ crystal. The 0.15 GPa data are taken after decreasing pressure from 0.4 to 0.15 GPa at $T=50$ K.

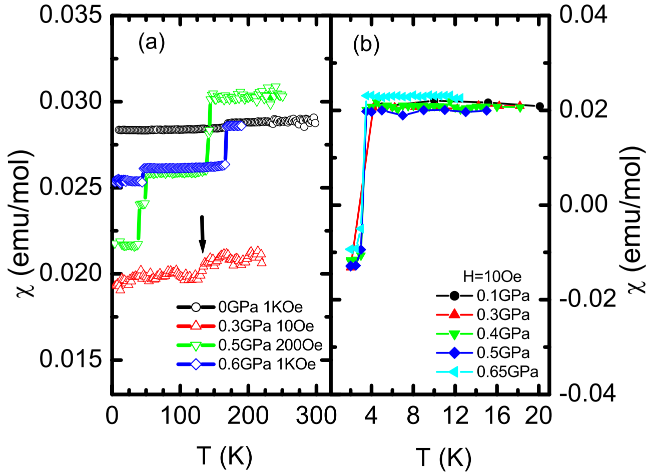

FIG. 2. (Color online) (a) The zero-field-cooled dc susceptibility of $CaFe_2As_2$ single crystals under pressure measured in the MPMS. The magnetic field is aligned along the crystalline *a* (or *b*) axis. (b) The low-temperature dc susceptibility with an applied magnetic field of 10 Oe.

sample shows a sharp increase in resistivity at $T_{S1} \approx 170$ K, corresponding to a first-order structural transition from the tetragonal phase to the orthorhombic/AF phase.[9,16] The residual resistance ratio (RRR) of our sample is about 5–6, which is similar to the other reports of etched samples.[10,12,16] The resistivity decreases gradually with pressure at room temperature. As pressure increases to 0.344 GPa, T_{S1} decreases to 120 K, and a sharp first-order phase transition is still clearly seen. This is very different from previous measurements in liquid media clamp cells where the resistivity changes gradually with pressure and becomes smooth with temperature at high pressures.[10,12] Above 0.4 GPa, the transition to the orthorhombic phase, with its sharp upward anomaly in resistivity, disappears completely.

For $P \geq 0.4$ GPa, a second phase transition occurs at about $T_{S2}=100$ K with a sudden drop of resistance as seen in Fig. 1(a), which is known to be from the high-temperature tetragonal structure to the low-temperature collapsed tetragonal structure.[17] T_{S2} increases with increasing pressure, in agreement with the neutron[17] and transport[10,12] results. Our data show the following features of the second phase. (i) *Low resistivity*: From the high-temperature tetragonal phase to the collapsed tetragonal phase, the resistivity drops by a factor of two or more at the transition for all pressures. As seen in Fig. 1(b), the residual resistivity of the collapsed phase is about 3.5 $\mu\Omega$ cm. As originally reported[10] the RRR is about 70, which barely changes with pressure once saturated. (ii) *Sharp transitions*: At all pressures, the resistance drops steeply through the transition with a transition width less than 1 K. This is a striking difference from the liquid medium measurements.[10,12] (iii) *Large thermal hysteresis*: As shown in Fig. 1(a), the onset temperature of the structural transition changes by 20 K during the cooling and warming up processes at $P=0.42$ GPa, which form a hysteresis loop. This is similar to hysteresis reported in Refs. 10 and 12. (iv) *Hysteresis with pressure*: The collapsed tetragonal phase also shows a strong hysteresis with pressure. As shown in Fig. 1(b), by decreasing the pressure from 0.4 to 0.15 GPa at 50 K, the collapsed tetragonal phase is still trapped as indicated by the low resistivity value. The orthorhombic phase is only recovered below 0.1 GPa. This is consistent with neutron-scattering measurements taken in He cells.[17,18]

The phase boundary between the orthorhombic phase and the collapsed tetragonal phase is found at $P \approx 0.35$ GPa. We did fine tuning of the pressure in steps of 0.01 GPa close to 0.35 GPa, and saw a direct transition between the orthorhombic phase and the collapsed tetragonal phase upon cooling at 0.354 GPa. As shown in Fig. 1(a), the sample first goes to the orthorhombic phase with a sharp increase in resistivity at $T_{S1} \approx 110$ K. On further cooling, there is a direct transition from the orthorhombic phase to the collapsed tetragonal phase with a dramatic decrease in resistivity at $T_{S2} \approx 45$ K.

Our magnetization data are consistent with the transport results. In Fig. 2(a), the zero-field-cooled (ZFC) dc susceptibility of $CaFe_2As_2$ is shown for various pressures. At ambient pressure, a drop of susceptibility is clearly seen at the structural transition temperature $T_{S1} \approx 170$ K. The transition temperature drops to 125 K at $P \approx 0.3$ GPa. Further increase in pressure causes another sharp drop of susceptibility at $T \approx 140$ K with $P \approx 0.5$ GPa, and $T \approx 150$ K with $P \approx 0.6$ GPa, which is consistent with the structural transition T_{S2} seen in resistivity. Below T_{S2}, another drop of susceptibility is seen at $T \approx 50$ K for $P=0.5–0.6$ GPa. However, this temperature corresponds to the helium solidification temperature at these pressures, which suggests that the collapsed tetragonal phase is very sensitive to even the small changes in the pressure environment when the helium freezes and does not represent an additional phase transition. The susceptibility below 20 K is shown in Fig. 2(b). For all pressures, we did not see any diamagnetism down to 4 K. Below 4 K, there is a diamagnetic signal at all pressures as shown in Fig. 2(b). We ascribe this diamagnetism to superconductivity of very small amounts of unetched tin flux, noting that the

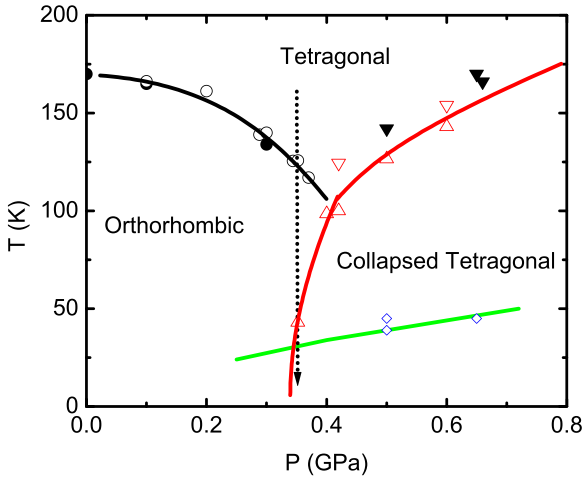

FIG. 3. (Color online) The (pressure, temperature) phase diagram of $CaFe_2As_2$ constructed from the transport and susceptibility measurements. The solid circles and the solid inverted triangles correspond to T_{S1} and T_{S2}, respectively, measured by susceptibility during warm-up after ZFC. The hollow circles and the hollow inverted triangles correspond to T_{S1} and T_{S2}, respectively, measured by transport during warm-up. The hollow triangles correspond to T_{S2} measured by transport during cooling down. The dashed line indicates two structural transitions upon cooling at $P=0.352$ GPa. The hollow diamonds correspond to the temperature of the second jump in the susceptibility, and the green (lowest) line near the diamonds is the helium solidification temperature for reference.

superconducting volume corresponds to only about 0.5% of the total sample volume.

In Fig. 3 we have constructed a (P,T) phase diagram from our transport and susceptibility measurements. The transition temperature measured during warm-up is consistent for both techniques. For the higher-pressure structural transition, the transition temperature first rises quickly with pressure from $P\approx 0.35$ to 0.4 GPa and then increases by about 20 K/kbar above 0.4 GPa; there is about 20 K of hysteresis in the T_{S2} transition.

Our results are quite different from the transport data using the clamp cells in a few aspects. First, we found a clear phase boundary at $P\approx 0.35$ GPa where the orthorhombic phase changes to the collapsed tetragonal phase with temperature or pressure abruptly. Second, the signatures of the higher-pressure structural transition, which is of the first-order type, are now extremely sharp as well as hysteretic with pressure and temperature. Finally and most importantly, we did not see bulk superconductivity at any pressure up to 0.65 GPa.

A major difference between the helium pressure cell and the liquid media pressure cells is that helium's solidification temperature is much lower and that even when frozen, helium cannot support much shear stress. As shown in Fig. 3, the helium solidification temperature increases to about 50 K at $P\approx 0.6$ GPa and is much lower than both structural transition temperatures. At a temperature below the helium solidification temperature, as shown in Fig. 2(a), a sharp drop of susceptibility is clearly seen. In contrast, the solidification temperature of other pressure mediums, for example FC-77, is usually much higher than 100 K at $P\approx 0.35$ GPa. Therefore it is likely that the pressure is nonhydrostatic through the structural transitions around the phase boundary $P\approx 0.35$ GPa.

In $CaFe_2As_2$ the lattice parameters change dramatically at the transition to the collapsed tetragonal phase,[17] and so pressure homogeneity will be an issue if the sample is embedded in a solid pressure medium at the transition temperature. For example at $P\approx 0.4$ GPa, the structural transition causes a decrease in the c axis lattice parameter by $\sim 10\%$ and an increase in the a axis parameter by $\sim 2\%$. For the worst case, i.e., assuming that the frozen pressure medium is unable to make plastic adjustment with the volume change in the sample, then the sample clearly must phase separate, most likely into a mixture of the known tetragonal, orthorhombic, and collapsed tetragonal phases. Such a *constant volume* assumption upon cooling, rather than a constant pressure one, seems consistent with the muon-spin-rotation (μSR) studies using nephane as the pressure medium, where a 50% volume fraction of the magnetic phase is seen at $P\approx 0.5$ GPa (Ref. 19) as well as recent neutron results.[18] In an organic system $(TMTSF)_2PF_6$, phase separation is also reported at the phase boundary of spin-density wave (SDW) and superconductivity, caused by a constant volume cooling under pressure.[20]

Nonhydrostatic conditions may cause the formation of domains with different properties (possibly including superconductivity). In a nonhydrostatic condition, large domain walls may be generated between highly phase-separated regions. Since the low-temperature orthorhombic and tetragonal phases have a large lattice mismatch, intermediate phases with different lattice parameters could be generated in the domain walls. In particular, if an orthorhombic structure with smaller lattice parameters is formed in the domain walls, a virtual high-pressure effect is realized on the orthorhombic phase. This constant volume scenario also suggests that the volume ratio in the phase separation region and the pressure range of superconductivity can be different if pressure media with different melting temperatures are used. It is also possible that superconductivity is caused by a uniaxial component of the pressure. Uniaxial stress can also cause a constant volume situation since the uniaxial pressure is not dynamically maintained through the transition temperature either. Therefore, it may be hard to distinguish this from the constant volume scenario.

The constant volume scenario does not conflict with the diamagnetic signal from high-pressure ac susceptibility on $CaFe_2As_2$ in a clamp cell.[12] If superconductivity is generated in the domain walls to form a thick wall honeycomblike superconductor, it will be hard to distinguish from bulk superconductivity by transport or susceptibility measurements.

In summary, we have studied the high-pressure susceptibility and the transport properties of $CaFe_2As_2$, using helium as the pressure medium. Our data have identified two first-order phase transitions separated at $P\approx 0.35$ GPa. In contrast to other high-pressure studies using liquid media clamp cells, we did not see any superconductivity. Therefore, our data indicate that the phase separation and superconductivity in the previous studies are most likely caused by a nonhydrostatic component of pressure. Our results invite caution with respect to the nature of high-pressure superconductivity in all three parent compounds, $CaFe_2As_2$, $SrFe_2As_2$, and $BaFe_2As_2$. We note that the proposed third phase under pressure[12] is not seen in our work. Further study is necessary to identify the actual phase properties of the superconducting region. Local probes, such as NMR or μSR, should be useful to perform the studies under nonhydrostatic conditions and verify our scenario.

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