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Pressure cycle of superconducting $Cs_{0.8}Fe_2Se_2$: A transport study

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ABSTRACT

We report measurements of the temperature and pressure dependence of the electrical resistivity (ρ) of single-crystalline iron-based chalcogenide $Cs_{0.8}Fe_2Se_2$. In this material, superconductivity with a transition temperature (T_c) $\sim$ 30 K develops from a normal state with extremely large resistivity. At ambient pressure, a large "hump" in the resistivity is observed around 200 K. Under pressure, the resistivity decreases by two orders of magnitude, concomitant with a sudden T_c suppression around $p_c \sim 8$ GPa. Even at 9 GPa a metallic resistivity state is not recovered, and the $\rho(T)$ "hump" is still detected. A comparison of the data measured upon increasing and decreasing the external pressure leads us to suggest that the superconductivity is not related to this hump.

1. Introduction

From a structural point of view, FeSe is the simplest material among the new Fe-based pnictide and chalcogenide "high-temperature" superconductors [1,2]. It is a tetragonal compound in which layers formed by edge-sharing $FeSe_4$ tetrahedra are stacked along the c-axis of the crystal. It possesses several outstanding characteristics, among them a large pressure effect on the superconducting temperature that increases from $T_c(p = 0) \approx 13$ K to $T_c \approx 37$ K at 4 GPa [3]. This steep rise in $T_c(p)$ is thought to be due in part to a reduction in the distance h between the Se anion and the Fe plane (known as the "anion height"), which approaches the optimum height for superconductivity, $h^* \approx 1.38$ Å [4].

Recently, a new family of Fe-based superconductors with $T_c \sim 30$ K and the general formula $A_xFe_{2-y}Se_2$ has been identified. Element A is either the alkaline K [5], Rb [6] or Cs [7], or also Tl in the +1 valence state [8]. These compounds crystallize in the well-known $ThCr_2Si_2$-type tetragonal structure (space group $I4/mmm$), obtained by the intercalation of A in superconducting FeSe. Introducing the element A expands the tetragonal c-axis but reduces the anion height, which approaches the optimum value h^* [7]. Muon-spin spectroscopy, resistivity, magnetization, and differential scanning calorimetry investigations performed on the system A = Cs (hereafter Cs-122) have shown a microscopic coexistence between the superconductivity and a magnetic phase with very high $T_N = 478$ K [9]. A similar behavior has subsequently been reported in the system A = K, based on a neutron study [10]. In addition, resistivity measurements on $K_{0.8}Fe_{1.7}Se_2$ up to 11 GPa [11] seem to indicate that T_c cannot be further optimized by applying high pressures and suggest a relationship between the resistivity hump around 200 K and the occurrence of superconductivity. Our present results question this relation, in line with recent reports studying this interdependence in a large variety of samples at ambient pressure [12–14].

2. Experimental details

Single crystals of nominal composition $Cs_{0.8}(FeSe_{0.98})_2$ were grown using the Bridgman technique [7]. Detailed crystallographic analysis revealed the presence of only one single phase [15], and the magnetization data [9] are compatible with 100% superconducting volume fraction (on crystals of the same batch as the present one). Two samples were carefully cleaved from a larger crystal. High-pressure four-probe resistivity measurements along the basal (ab) plane were performed on sample $S1$, a $1020 \times 170 \times 30$ μm^3 cuboid. The sample, together with a strip of Pb, which served as a pressure gauge, was mounted in a Bridgman-type high-pressure cell [16] using steatite as transmitting medium.

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Electrical contacts were obtained by pressing annealed 10 μm gold wires directly onto the sample. We have observed a progressive reduction of the wire–sample contact resistance, from around 1 kΩ at 1.2 GPa to ∼10 Ω at 9 GPa. All measurements were performed with currents ranging from 1 to 10 μA ($0.02 \leq j \leq 0.2$ A cm^{-2}), although larger currents do not have a measurable effect on the superconducting transition (the reported critical current density in $K_{0.86}Fe_{1.84}Se_2$ is of the order of 10^3 A cm^{-2} [14]).

In order to test the relation between the superconductivity and the normal-state transport of Cs-122, we have studied the temperature dependence of the electrical resistivity with both increasing and decreasing pressure.

A $2.0 \times 0.72 \times 0.36$ mm^3 cuboid, sample $S2$, was measured at zero pressure. Electrical contacts were obtained by gluing gold wires with the DuPont conductor paste 4929N.

3. Results

In Fig. 1(a), we present the temperature dependence of the electrical resistivity of sample $S1$ at selected *increasing* pressures ($p\uparrow$). At the lowest pressure, $p \approx 1.2$ GPa, $\rho(T)$ displays a similar T-dependence as sample $S2$ at $p = 0$, which is typical of other $A_xFe_2Se_2$ compounds reported in the literature [5,14,17,6,9,18]. The resistivity first increases towards lower temperatures, it displays a "hump" at $T_{\max} \sim 200$ K, and the superconducting transition occurs at $T_c^{50\%} \approx 28$ K. Between the onset of superconductivity, $T_c^{\text{onset}} \approx 30$ K, and roughly 90 K, the resistivity can be described as $\rho(T) = \rho_0 + \alpha T^2$, with $\rho_0 = 0.38\ \Omega$ cm and $\alpha = 51\ \mu\Omega$ cm/K^2 (at 1.2 GPa); see the fits in Fig. 1(a). Between 0 and 4.8 GPa, the resistivity coefficient decreases roughly as $\alpha(p) \sim 120e^{-p/1.2}\ \mu\Omega$ cm/K^2. For $p > 5$ GPa, this T^2 behavior is observed in a very narrow temperature range.

As the pressure increases, we observe a dramatic drop in the magnitude of the electrical resistivity. Despite the large reduction of $\rho(T)$, no metallic behavior is observed even at $p \approx 9$ GPa, and the hump remains at roughly the same temperature, $T_{\max} \approx 200$ K, although with a smaller relative amplitude. This can be seen in Fig. 1(b), depicting the resistivity normalized at 295 K, $\rho(T)/\rho(295\text{ K})$. The ratio $\rho(T_{\max})/\rho(295\text{ K})$ decreases from 1.65 at 1.15 GPa to 1.17 at 8.9 GPa. If $T_{\max}$ is associated with some characteristic temperature of this material, its roughly constant value indicates that it is related to a process weakly affected by pressure.

The progressive decrease of $T_c^{\text{onset}}(p)$ can be followed in Fig. 1(b). For comparison, we have included the low-temperature $\rho(T)$ data measured at $p = 0$ in sample $S2$. We see that $T_c(p)$ remains almost unchanged between $p = 0$ and ∼3 GPa, and that it decreases steadily for $p > 4$ GPa. At $p \sim 7.5$ GPa we only detect a partial transition, while at 8.9 GPa $\rho(T)$ increases continuously as $T \to 1.2$ K. The evolution of $T_c^{\text{onset}}(p)$ and $T_c^{50\%}(p)$ is depicted in the phase diagram of Fig. 3(a). We have not detected any anomaly in $\rho(T)$ that may indicate that the magnetic order measured in Cs-122 at $T_N \approx 480$ K [9,15] is being suppressed in this pressure range.

Fig. 2 depicts $\rho(T)$ of Cs-122 measured with *decreasing* pressure ($p\downarrow$). The $\rho(T)$-dependence is notably changed when compared with the data presented in Fig. 1. The hump is no longer evident for $p\downarrow < 6$ GPa, and $\rho(T)$ increases continuously with lower temperatures. For $p\downarrow = 3$ and 4.2 GPa, the resistivity follows $\rho(T) \sim \ln(T_0/T)$ between T_c^{onset} and roughly 80 K; see the fits represented by continuous curves. The inset displays $\rho(T)$–$\alpha \ln(T_0/T)$ for these two pressures. The maximum is still detected around 200 K, but with a very small amplitude. Despite this, we detect a partial superconducting transition with an onset that reaches $T_c^{\text{onset}} \approx 30$ K at 3 GPa, coinciding with the onset temperature observed for $p\uparrow \approx 2.7$ GPa: the superconducting state recovers, while the hump attains only ∼5% of its previous value at a similar pressure. At least phenomenologically, this superconducting state develops in a material with semiconductor-like behavior.

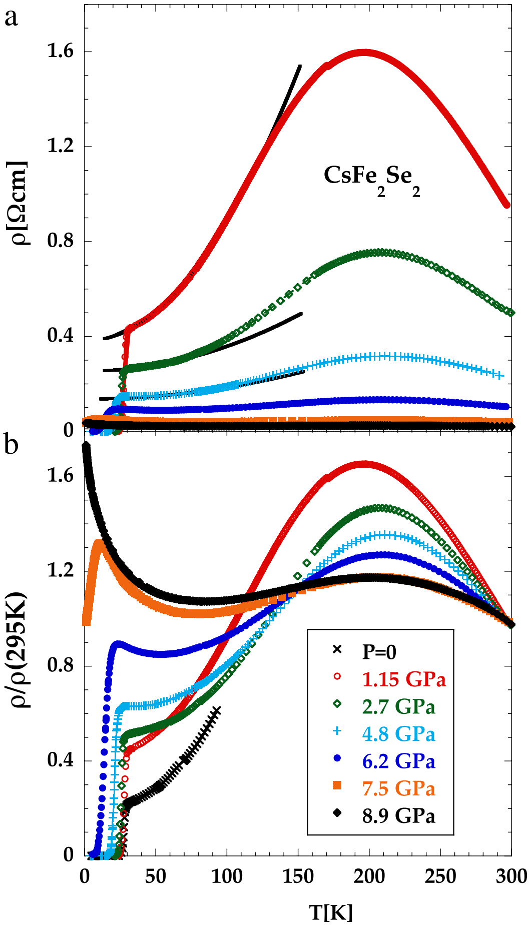

Fig. 1. (color online) Temperature dependence of the electrical resistivity of Cs-122 at different pressures (increasing). (a) Raw data (with T^2-fits as continuous lines). (b) Data normalized to the corresponding room-temperature value. Suppression of T_c and of the high resistivity with increasing pressure can clearly be observed.

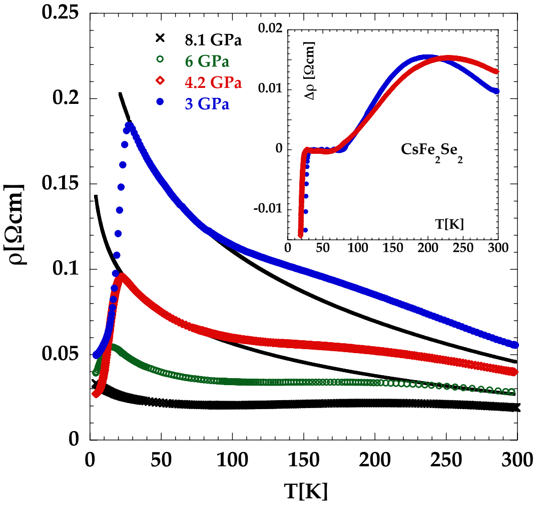

Fig. 2. (color online) Temperature dependence of the electrical resistivity of Cs-122 at different pressures (decreasing). The onset of T_c recovers, while the hump is much less reversible. Solid lines are a fit of the type $\alpha \ln(T_0/T)$, where α and T_0 are the adjusted parameters. The inset depicts the difference of the measured resistivity with these fits, $\rho(T) - \alpha \ln(T_0/T)$, in order to make the small, still existing hump visible.

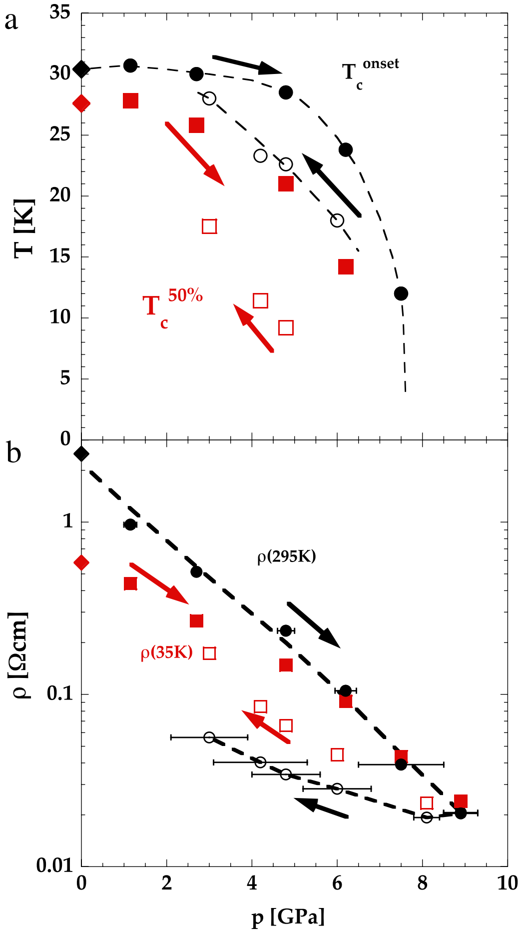

Fig. 3. Pressure dependence of (a) the superconducting transition temperature, as shown by the resistivity (black: onset and red: mid-height, 50%), and of (b) the resistivity at 35 K (red) and 295 K (black). Full symbols indicate increasing pressure, and open symbols decreasing pressure. The indicated error bars mainly reflect the width of the superconducting transition of Pb. Obviously, the onset T_c is almost reversible (with hysteresis), whereas the resistivity does not recover its initially very high magnitude. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Fig. 3(a), we present the p–T phase diagram of Cs-122, comparing the changes in the superconducting ordering temperature with increasing and decreasing pressure. The circular symbols represent the onset of superconductivity, $T_c^{\text{onset}}(p)$, while the rectangular symbols indicate the mid-point of the resistive transition, $T_c^{50\%}(p)$. We first focus on the "*increasing* pressure" experiment, represented in the figure by filled symbols. At low pressures, the transition is relatively narrow, so T_c^{onset} and $T_c^{50\%}(p)$ are close, and our data agree with the results reported in [19]. With increasing p, $T_c^{50\%}(p)$ diminishes, although $T_c^{\text{onset}}(p)$ remains almost constant up to $p \sim 5$ GPa. For $p > 5$ GPa, $T_c^{\text{onset}}(p)$ decreases steeply, and it is no longer detected above 8 GPa. We estimate the critical pressure for superconductivity to be $p_c^{\text{Cs}} \approx 7.6$ GPa. The steep decrease of T_c^{onset} as $p \to p_c^{\text{Cs}}$ contrasts with the progressive suppression of superconductivity in isostructural $K_{0.8}Fe_{1.7}Se_2$ [11], although the critical pressure $p_c^{\text{K}} \approx 9$ GPa is rather similar. Notice that this pressure should correspond to a large volume reduction, of the order of 15% [20].

With *decreasing* pressure (open symbols), T_c^{onset} recovers completely around 3 GPa, although the transition is rather broad, and no zero-resistance state is detected. We interpret this recovery as a reversibility of superconductivity under pressure cycling, despite the apparent pressure hysteresis of roughly 2 GPa. In Fig. 3(b), we represent the $\rho(35\text{ K})$ and $\rho(295\text{ K})$ p-dependence to stress that the resistivity is not reversible at all.

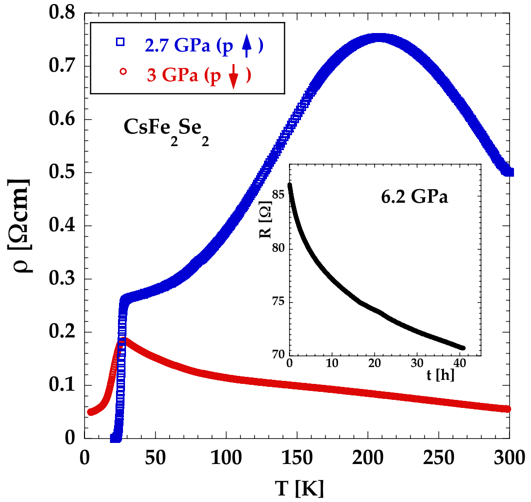

Fig. 4. Temperature dependence of the electrical resistivity of Cs-122 at around 3 GPa, measured when increasing and decreasing pressure. The onset of T_c seems quite robust against pressure cycling, whereas the complete $\rho(T)$ curve is strongly modified. The inset visualizes the time dependence (at room temperature) of the electric resistance of the sample after increasing the pressure from 4.8 to 6.2 GPa: the observed changes are not negligible.

4. Discussion

As already pointed out, superconductivity develops in AFe_2Se_2 compounds out of normal-state resistivities of $\sim 0.2\ \Omega$ cm, which is about three orders of magnitude higher than say in FeSe [1]. For the Cs-122 samples studied here, we estimate $\rho(295\text{ K}) \approx 2.5\ \Omega$ cm at $p = 0$. We verified that this value does not change on exposing the sample to the air for around one hour, the time necessary to cleave it and close the high-pressure cell. To our knowledge, there are no other systems that exhibit such a large T_c combined with such large normal-state resistivities. Even more, Hall effect data in a related compound do not point to a reduced carrier number [5]. On the other hand, it should be noted that the AFe_2Se_2 family is in close proximity to an insulating state [8,13,12]. Further, it is remarkable that the room-temperature resistivity decreases by two orders of magnitude between $p = 0$ and 9 GPa; see Fig. 3(b) (semi-log scale). Nevertheless, even at the highest pressure (9 GPa) we do not observe a metallic behavior of the resistivity.

From our previous studies of organic superconductors in different pressure media [21], there is strong indication that the limited pressure conditions in the steatite medium may induce the resistivity upturn observed at low temperature. The fact that this feature steadily increases in magnitude with the number of pressure steps supports this point of view. So it remains a challenging question to determine whether the high-pressure phase is intrinsically non-metallic. High-pressure experiments under better hydrostatic conditions are highly desirable.

Concerning the resistivity hump, let us first recall that experimentally it is strongly affected by pressure cycling: Fig. 4 compares the resistivity data at around 3 GPa for increasing and decreasing pressure. On the bottom curve ($p\downarrow$), one can only see a trace around 200 K of the resistivity hump and the development of the low-temperature upturn (see also Fig. 2), while the onset temperature of superconductivity recovers and is close to that when increasing the pressure ($p\uparrow$, upper curve). As an explanation, one possible scenario evokes the ordering of iron vacancies in the FeSe layers just above T_N [13,15,8,22,10,23–25], which could be pressure sensitive and not reversible. The inset of Fig. 4 exhibits the time evolution of the sample resistance at room temperature, just after the increase of pressure to 6.2 GPa. A significant relaxation of $\sim$15% in 24 h is observed. We have confirmed that $\rho(T)$ is T-reversible, meaning that this mechanism is not active at low temperatures. The observed relaxation could be related to a mechanism of moving vacancies. Whatever the microscopic origin of the resistivity hump, phenomenologically it is now clearly established from detailed composition studies that the transport properties strongly depend on the Fe (and A) content in the non-stoichiometric $A_xFe_{2-y}Se_2$ compounds [8,13,14,12,26]: in particular, decreasing the Fe deficiency shifts the hump to higher temperatures, whereas the superconducting T_c is hardly affected. Combined with our results obtained after one pressure cycle (full recovery of T_c but only partial recovery of the hump), a close relationship between the resistivity hump and the superconductivity seems unlikely, in contrast to the results reported in [11].

Finally, doping studies in AFe_2Se_2 compounds show that T_c appears rather abruptly around 30 K [8]. The steep decrease of T_c^{onset} in a narrow pressure range just before p_c as well as the $T_c(p)$ hysteresis suggests that the T_c vanishing might not be a continuous phase transition. In any case, the apparent "robustness" of "30 K superconductivity" in the AFe_2Se_2 family should be noted: roughly speaking, superconductivity seems to appear irrespective of A, doping[1] and stoichiometry (within the appropriate parameter range) with a somehow "fixed" transition temperature. Even pressure cycling seems inefficient in significantly affecting T_c (except to make it disappear promptly above 4 GPa for Cs-122).

5. Conclusion

In conclusion, high-pressure measurements on single-crystalline $Cs_{0.8}Fe_2Se_2$ show a suppression of $T_c(p)$, which is almost constant up to 5 GPa and then decreases steeply, not being detected above 8 GPa. The resistivity hump of unknown origin is only very partially recovered with decreasing pressure, while T_c seems to be reversible. This questions the connection between T_c and the resistivity hump, in line with recent publications [12–14] that arrive at a similar conclusion. At the high-pressure side of the superconducting phase, a metallic state is not unambiguously recovered. To test this, experiments in a more hydrostatic pressure medium should be performed.

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[1] Except for Co-doping [27], quenching T_c abruptly (quite opposite to the case of $BaFe_2As_2$).