Electrical resistivity of FeAs, FeAs$_2$ and Fe$_2$As at homogeneous high pressures

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Abstract. Electrical resistivity of binary compounds containing iron and arsenic, FeAs, FeAs$_2$ and Fe$_2$As, is measured at homogeneous high pressures up to 15 GPa. The obtained results indicate the absence of pressure-induced superconductivity for these compounds in the specified pressure range. A new ground state possibly emerges in FeAs above 3 GPa.

1. Introduction
Since the discovery of iron pnictide high-$T_c$ superconductors [1], many iron- and arsenic-containing superconductors have been developed. They belong to the group of superconductors with the second highest critical temperature, for which the pressure studies led to the discovery of a new phenomenon called pressure-induced superconductivity.

Earlier, we investigated some 1111-type (LnFeAsO$_{1+y}$, Ln = La, Ce, Pr, Nd...) [2] and 122-type compounds (AEFe$_2$As$_2$, AE = Ba, Sr, Ca) [3], and observed that tiny amounts of superconducting impurities exhibit large resistive anomalies. In some cases, a drop in resistivity was mistakenly identified as a bulk superconducting transition. In a similar way, several studies reported “pressure-induced superconductivity” for some materials even without reaching zero resistivity[4,5]. In order to avoid such confusions, special efforts were made to investigate bulk superconductivity by using dense homogeneous high pressure samples of superior quality for our studies. Thus, the resistivity at high pressures for binary compounds FeAs, FeAs$_2$, and Fe$_2$As, which are often obtained for iron pnictide superconductors during sample preparation, are studied in this work for the first time.

Pressure-induced superconductivity studies were recently reported for monopnictides of the 3d transition metals, CrAs and MnP [6-8]. These compounds and FeAs have the same crystal structure (MnP type) and exhibit a helimagnetic ground state at atmospheric pressure [9]. In addition, pressure-induced superconductivity can potentially affect the transport properties of FeAs at high pressures.

2. Experimental
High quality FeAs, FeAs$_2$, and Fe$_2$As polycrystalline samples were used in this study. They were synthesized by a high pressure method (HP) using a cubic type multi-anvil apparatus at pressure $P \sim 2$ GPa and temperature $T \sim 1200$ K. The HP synthesis produced very dense and homogeneous samples, which is important for electrical resistivity measurements at high pressures. In order to observe the helimagnetic transition of FeAs in detail, a single crystal FeAs sample was prepared by a solid-state reaction method.
Electrical resistivity measurements at high pressures were performed in a cubic-type setup for low temperatures [10]. As mentioned above, tiny impurity amounts or crystallographic randomness in a sample can lead to misinterpretation of pressure-induced phenomena. In order to avoid this outcome, high pressure has to be isotropically supplied to the sample, which makes the cubic system the best apparatus for this study.

3. Results

3.1. FeAs

Figure 1 shows the temperature dependence of the electrical resistivity at high pressures for the FeAs polycrystalline sample. The general trend reveals a decrease in resistivity with pressure; which, however, does not go down significantly even at the high pressures. This indicates no increase in randomness of the crystal even at the highest pressure value of 15 GPa. A small anomaly was detected at around 65 K and 1 GPa (Figure 1), which can be possibly related to the helimagnetic transition in FeAs observed in an earlier study at around 77 K [9]. However, at higher pressures this anomaly becomes virtually undetectable.

Another experiment was done with the FeAs single crystal. The results are shown in Figure 2(a). At 1 GPa, a resistive anomaly at $T_N = 69$ K is clearly seen. The temperature corresponding to this anomaly shifts when more pressure is applied. In order to determine $T_N$, the resistivity must be differentiated with respect to temperature as shown in Figure 2(b). Below 3 GPa, $T_N$ decreases with pressure; this trend becomes reversed at higher pressure values. At 3 GPa, the differential curve becomes broad and appears to be split into two separate peaks; however, it contains no characteristic differences from the resistivity curves below or above 3 GPa. At the highest pressure of 11 GPa, it is difficult to even determine $T_N$ from the figure. By plotting $T_N$ (defined by the maximum of the differential curve) versus pressure it is possible to construct a pressure phase diagram for FeAs (Figure 3). Contrary to our expectations, no pressure-induced superconductivity was observed in the experimental temperature range ($T > 4$K) at given pressures. A possible phase boundary appears to exist at around 3 GPa; however, no more details about this can be provided at this time. Structural
studies or a neutron diffraction experiment at high pressures would help to determine the ground state of FeAs above 3 GPa.

**Figure 2(a).** Temperature dependence of the electrical resistivity of the FeAs single crystal at different pressures.

**Figure 2(b).** Temperature derivative of the electrical resistivity of the FeAs single crystal. The peak broadens at 3 GPa and shifts to the right at higher pressures.

**Figure 3.** A proposed phase diagram for FeAs defined by the resistivity measurements. The detail on the right remains undefined.
3.2. FeAs$_2$
FeAs$_2$ was reported to be a diamagnetic semiconductor with a band gap of 0.22 eV at room temperature [11]. Its resistivity at high pressures as a function of temperature is shown in Figure 4. Following the general trend of resistivity decrease, it becomes metallic at high pressures. Note that the residual resistivity at the highest pressure of 13 GPa is very small, almost one-tenth of that at atmospheric pressure; nevertheless, FeAs$_2$ remains semiconductive below 130 K. There is still a possibility for pressure-induced superconductivity at pressures higher than 13 GPa.

![Figure 4. Electrical resistivity of FeAs$_2$ as a function of temperature at different pressures. The resistivity exhibits a metallic behavior at 13 GPa and starts to increase at around 130 K.](image)

3.3. Fe$_2$As
Fe$_2$As has a Cu$_2$Sb-type crystal structure. Its unit cell contains two Fe sites and one As site. LiFeAs, which is a typical 111-type iron-pnictide superconductor, has the same crystal structure. An antiferromagnetic transition occurs in Fe$_2$As at around $T_N = 353$ K [12]. Unfortunately, our high pressure apparatus was not capable of heating samples to such a temperature because of the plastic materials near the anvils; therefore, no $T_N$ values could be confirmed for Fe$_2$As at any pressure in this study.

Figure 5 shows the temperature dependence of the electrical resistivity for the polycrystalline Fe$_2$As. At 1 GPa, a poorly resolved anomaly appears between 50 and 70 K, which becomes more unclear at higher pressures (thus making it impossible to determine its critical temperature). Zocco et al. measured the electrical resistivity of Fe$_2$As at high pressures to calculate the heat capacity of Fe$_2$As at ambient pressure [13]. In contrast to the results presented in this work, no anomaly was detected around 50 ~ 70 K.
Figure 5(a). Electrical resistivity of the polycrystalline Fe$_2$As as a function of temperature at different pressures. Out of the three binary polycrystalline compounds considered in this work, it displays the smallest resistivity.

Figure 5(b). Temperature derivative of the resistivity in Fe$_2$As at different pressures. The anomaly, observed at around 50 K and 1 GPa, disappears at higher pressures.

4. Summary
Electrical resistivity of three binary compounds, FeAs, FeAs$_2$, and Fe$_2$As, were measured at homogeneous high pressures. The obtained results reveal a non-superconducting behavior for each of the studied compounds regardless of the pressure, thus eliminating a possibility of pressure-induced superconductivity for these materials (often detected as impurities in iron pnictide compounds). A pressure phase diagram for FeAs was successfully constructed from the obtained data. The $T_N$ values initially decrease with pressure in the low pressure range; however, $T_N$ starts increasing again above the critical pressure of 3 GPa. It appears that a ground state emerges in FeAs at this point. To characterize this new state, further structural studies or neutron diffraction measurements are required.

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