Hydrostatic and chemical pressure tuning of CeFeAs$_{1-x}$P$_x$O single crystals

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We carried out a combined P-substitution and hydrostatic pressure study on CeFeAs$_{1-x}$P$_x$O single crystals in order to investigate the peculiar relationship of the local moment magnetism of Ce, the ordering of itinerant Fe moments, and their connection with the occurrence of superconductivity. Our results evidence a close relationship between the weakening of Fe magnetism and the change from antiferromagnetic to ferromagnetic ordering of Ce moments at $p^* = 1.95$ GPa in CeFeAs$_{0.78}$P$_{0.22}$O. The absence of superconductivity in CeFeAs$_{0.78}$P$_{0.22}$O and the presence of a narrow and strongly pressure sensitive superconducting phase in CeFeAs$_{0.70}$P$_{0.30}$O and CeFeAs$_{0.65}$P$_{0.35}$O indicate the detrimental effect of the Ce magnetism on superconductivity in P-substituted CeFeAsO.

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The discovery of superconductivity in LaFeAsO$_1$-xF$_x$ and the highest $T_c$'s up to 55 K observed in F-doped SmFeAsO have sparked tremendous interest among the scientific community. In most of the iron-pnictide materials, the application of hydrostatic pressure or chemical substitution introduces superconductivity by suppressing the Fe spin-density wave (SDW) ordering in the non-superconducting parent compound. This induces systematic changes in $T_c$ in pnictide superconductors.

The Fe moments in CeFeAsO order in a commensurate SDW at about 145 K, while the local Ce moments order antiferromagnetically below 3 K. Investigations evidence a sudden change of the Ce ordering in the non-superconducting parent compound at about 145 K, which was found to be in good agreement with the actual composition. 4-probe electrical-resistance measurements in the $ab$-plane were carried out using an LR700 resistance bridge. Temperatures down to 1.8 K and magnetic fields up to 14 T were achieved in a Quantum Design PPMS. Magnetic field was applied in the $ab$-plane parallel to the electrical current. Pressures up to 2.85 GPa were generated in a double-layer piston-cylinder type pressure cell using silicon oil as pressure transmitting medium. The pressure shift of the SC transition at all pressures confirmed the good hydrostatic conditions inside the pressure cell.

The normalized electrical resistance $R(T)/R_{300K}$ of CeFeAs$_{0.78}$P$_{0.22}$O for various pressures up to 2.33 GPa is depicted in Fig.1. At ambient pressure, $R(T)$ exhibits a maximum followed by a pronounced drop attributed to the onset of Fe-SDW ordering at $T_{N}^{Fe} = 93$ K and a further kink at $T_{C}^{Fe} = 3.5$ K due to the AFM ordering of Ce moments, which is in agreement with Ref.14. Compared with CeFeAsO 22% P-substitution already suppresses $T_{N}^{Fe}$ by about 50 K. The feature at $T_{C}^{Fe}$ shifts to lower temperatures on application of hydrostatic pressure up to $p = 1.95$ GPa. On further increasing pressure $T_{C}^{Fe}(p)$ stops almost constant at about 28 K (1.95 GPa $< p < 2.33$ GPa). It is important to note that the maximum in $R(T)$ becomes sharper and more pronounced upon increasing pressure for $p ≤ 1.95$ GPa.
whereas above 1.95 GPa it broadens and starts to fade away.

In the following, we focus on the pressure dependence of the Ce ordering. \( R(T)/R_{15 K} \) for different pressures is shown in Fig. 2a. Up to 1.89 GPa application of pressure shifts the kink indicating \( T_{N}^{C} \) in \( R(T) \) to higher temperatures. Upon further increasing pressure the feature in \( R(T) \) broadens significantly and shifts to lower temperatures in contrast to the behavior at low pressures. While at high pressures the kink at the transition temperature is hardly visible (we used the maximum in the first derivative of \( R(T) \) to determine the transition temperature), the magnetoresistance \( \Delta R(R) \) displays a well defined minimum followed by an increase toward low temperatures due to the Ce ordering (see Fig. 2b). The position of the minimum in \( \Delta R(T) \) is in good agreement with the results from \( R(T) \). Initially, \( T_{N}^{C}(p) \) increases with a rate of about 0.5 K/GPa, which is only about half the value reported for polycrystalline CeFeAsO [18]. We take the abrupt change of the pressure dependence of the ordering temperature and the significantly broadened feature in \( R(T) \) above 1.95 GPa as a hint for a change of the Ce ordering at \( p^* \approx 1.95 \) GPa. Comparing our pressure data with the results of P-substitution in CeFeAs\(_{1-x} \) P\(_{x}\)O lets us to propose that the Ce ordering changes from AFM to FM, which we will substantiate in the following. However, in CeFeAs\(_{0.78} \) P\(_{0.22}\)O under pressure we observe a decrease in FM Ce ordering temperature \( (T_{C}^{C}) \) above 1.95 GPa in contrast to the increase of \( T_{C}^{C} \) observed on chemical pressure by phosphorus substitution. This points at differences between the effect of hydrostatic and chemical pressure on the physical behavior in CeFeAs\(_{1-x} \) P\(_{x}\)O, which we will address later.

Electrical resistance measurements in applied magnetic fields give further information on the magnetic ordering of the Ce moments. Figs. 2c-f depict \( R(T)/R_{15 K} \) of CeFeAs\(_{0.78} \) P\(_{0.22}\)O in different magnetic fields applied parallel to the ab-plane for selected pressures. At \( p = 0.05 \) GPa, a peak-like anomaly in the resistance indicates the AFM ordering of the Ce moments. Upon increasing magnetic field a step-like feature develops and shifts to lower temperatures. The monotonic decrease of \( T_{N}^{C}(B) \) is in agreement with the AFM ordering of the Ce moments in the ab-plane. At 1.28 GPa only a kink in \( R(T) \) remains and marks \( T_{C}^{C} \). However, we still observe the same field dependence of \( T_{C}^{C} \). Also at 1.72 GPa we observe a small kink in \( R(T) \) shifting to lower temperatures upon increasing \( B \). The effect of a small magnetic field \( B \leq 0.5 \) T on \( R(T) \) is tiny until \( p^* \approx 1.95 \) GPa. In contrast, above \( p^* \) a huge effect appears above \( T_{C}^{C} \) already at low fields. It is worth mentioning that the value of the change of the resistance in 0.5 T at 2 K is about one order of magnitude larger above \( p^* \) than below, substantiating that the Ce magnetism below and above \( p^* \) is fundamentally different.

A monotinous decrease of \( T_{N}^{C} \) is observed in magnetic fields for \( p \leq p^* \) as shown in Fig. 2g. The \( T_{N}^{C}(B) \) curves for different pressures do not cross; for any fixed magnetic field, \( T_{N}^{C}(p,B) \) increases upon increasing

FIG. 1. (Color online) Temperature dependence of the electrical resistance of single crystalline CeFeAs\(_{0.78} \) P\(_{0.22}\)O normalized by its value at room temperature under various hydrostatic pressures up to 2.33 GPa.

FIG. 2. (Color online) a) Temperature dependence of \( R(T) \) normalized by its value at 15 K of CeFeAs\(_{0.78} \) P\(_{0.22}\)O for various pressures up to 2.33 GPa (shifted by 0.1). b) Magnetoresistance with magnetic field applied in the ab-plane parallel to the electrical current at different pressures. The arrows in a) and b) mark \( T_{C}^{C} \) and \( T_{N}^{C} \), see text for details. c-f) Temperature dependence of \( R(T)/R_{15 K} \) in different magnetic fields for \( p = 0.05 \) GPa, 1.28 GPa, 1.72 GPa, and 2.33 GPa. Note the different scales for \( R(15 K) \) in c-f). g) Magnetic field dependence of \( T_{C}^{C} \) for various pressures up to 2.33 GPa.
Due to the broadening of the transition anomaly the maximum field up to which we can define $T_N^{\text{Fe}}$ decreases with pressure. Fig. 2 suggests an increase of the ordering temperature with increasing field, but the curves for $B > 0$ do not present a clear kink allowing for a reliable definition of the transition temperature. This gives a further hint at the change of the Ce ordering from AFM to FM (for $p = 1.89$ GPa no field data is available).

The $T – p$ phase diagram in Fig. 3 summarizes the results on CeFeAs$_{0.78}$P$_{0.22}$O. The transition temperatures deduced from electrical resistance and MR are in good agreement (solid and open symbols, respectively). Upon application of pressure $T_N^{\text{Fe}}$ decreases monotonously up to $p^* \approx 1.95$ GPa, upon further increasing pressure $T_N^{\text{Fe}}$ is almost constant before its signature in the resistance starts to disappear. $T_N^{\text{Fe}}(p)$ monotonously increases with increasing pressure up to $p^* = 1.95$ GPa. Above $p^*$ our results indicate a sudden change of the type of the Ce ordering from AFM to FM but, in contrast to P-substitution in CeFeAs$_{1-x}$P$_x$O, $T_N^{\text{Fe}}$ decreases upon further increasing pressure. Up to 2.33 GPa no indication for superconductivity was found. Even though superconductivity might develop at higher pressure, we note that we did not find any indication of superconductivity around $p^*$ where the Ce ordering changes from AFM to FM. In this region superconductivity develops in chemically pressurized CeFeAs$_{1-x}$P$_x$O.

Fig. 3b displays the normalized isothermal resistance $R_T(p) = R_{T=\text{const}}(p)/R_{300K}(p)$ at different temperatures. The isothermal resistance at 20 K just below $T_N^{\text{Fe}}$ can be considered as a measure of the strength of the Fe moment fluctuations. $R_{20K}(p)$ possesses a pronounced maximum around 1.95 GPa, where $T_N^{\text{Fe}}(p)$ starts to saturate. Thus upon increasing pressure the Fe moment fluctuations gradually increase, becoming strongest around 1.95 GPa and decrease again for higher pressures. On lowering temperature the maximum stays at the same pressure. Even more surprising the size of the maximum in $R_T(p)$ remains almost unchanged upon reducing temperature from 20 K to 7.5 K, the latter temperature being far below $T_N^{\text{Fe}}$. This indicates that even at 7.5 K strong fluctuations of the Fe moments are present. Furthermore, at 5 K and even at 2 K, well below the Ce ordering, a clear maximum shows up in $R_T(p)$. The result at 2 K is remarkable since it evidences the presence of iron moment fluctuations down to lowest temperatures. We note that at the same pressure where we observe the maximum in $R_T(p)$ the Ce ordering changes from AFM to FM.

We now turn to the compounds with higher P content. CeFeAs$_{0.70}$P$_{0.30}$O and CeFeAs$_{0.65}$P$_{0.35}$O show FM ordering of the Ce moments ($T_C = 4.1$ K and 4.3 K, respectively) and superconductivity at slightly lower temperatures ($T_c = 3.7$ K and 4.1 K, respectively). In our resistance data we detect only a weak anomaly at the SDW transition at about $T_N^{\text{Fe}} = 38$ K for both concentrations in good agreement with Ref. [14]. The results of the pressure experiments for CeFeAs$_{1-x}$P$_x$O, $x = 0.30$ and 0.35, are similar and summarized in the $T – p$ phase diagram in Fig. 4a. For both compounds $T_N^{\text{Fe}}(p)$ decreases monotonously upon increasing pressure from 38 K at am-

![Figure 3](image_url)

**FIG. 3.** (Color online) a) $T – p$ phase diagram of CeFeAs$_{0.78}$P$_{0.22}$O. Solid and open symbols represent the transition temperatures deduced from $R(T)$ and MR($T$), respectively. b) Pressure dependence of the isothermal resistance normalized by its value at 300 K.

![Figure 4](image_url)

**FIG. 4.** (Color online) a) $T – p$ phase diagram for CeFeAs$_{0.70}$P$_{0.30}$O and CeFeAs$_{0.65}$P$_{0.35}$O. b) $R(T)/R_{300K}$ for selected pressures. c) Temperature dependence of the electrical resistance normalized by its value at 15 K for various pressures up to 2.85 GPa. At 0.29 GPa arrows indicate the anomaly at $T_C$ and the onset of the SC transition at $T_c^{\text{onset}}$. 


bient pressure to below 30 K at 1.72 GPa with an initial rate d ln $T_N^{Fe}/dp = -0.084$ GPa$^{-1}$. Above this pressure we cannot determine $T_N^{Fe}$ from the data anymore.

The observed pressure dependence of $T_N^{Fe}(p)$ is surprisingly considering the previous results on CeFeAs$_{0.75}$P$_{0.25}$O$_{0.5}$. In the comparable pressure regime where Ce orders ferromagnetically in CeFeAs$_{0.75}$P$_{0.25}$O$_{0.5}$ ($p > 1.95$ GPa) $T_N^{Fe}(p)$ is almost constant and much smaller than in CeFeAs$_{0.70}$P$_{0.30}$O and CeFeAs$_{0.65}$P$_{0.35}$O at ambient pressure. This substantiates the different effects of chemical and hydrostatic pressure. At low temperatures increasing pressure effectively separates $T_c(p)$ and $T_{C}^{Ce}(p)$. In CeFeAs$_{0.65}$P$_{0.35}$O we find that upon increasing pressure to $p = 0.29$ GPa, $T_c(p)$ decreases from 3.7 K at ambient pressure to 2.7 K, while the feature at $T_{C}^{Ce} = 4$ K becomes clearly visible and separated from $T_c$. Further increasing pressure above 0.29 GPa does not leave any signature of superconductivity anymore. However, we were able to detect $T_{C}^{Ce}$ up to 1.28 GPa before we loose the anomaly in our data. While superconductivity is present, increasing pressure leads to a minute decrease of the ferromagnetic $T_{C}^{Ce}$, but once superconductivity disappeared, $T_{C}^{Ce}$ starts to increase significantly with increasing pressure in contrast to the smaller P concentration, $x = 0.22$. For both concentrations, $x = 0.30$ and 0.35, $T_c(p)$ is suppressed to zero temperature at an extrapolated pressure around 0.46 GPa. It is noticeable that the FM Ce ordering cannot be traced in electrical resistance data taken in magnetic fields ($B \geq 0.1$ T) parallel to the $ab$ plane (not shown). This is similar to our findings in CeFeAs$_{0.75}$P$_{0.25}$O at pressures above $p^*$. As expected, the SC transition shifts toward lower temperatures with increasing the magnetic field. For $x = 0.35$, the upper critical field $\mu_0 H_{c2}^{ab}(0)$ can be estimated to about 1.25 T for 0.05 GPa and only 0.25 T for 0.29 GPa taking $T_{C}^{magn}(H)$, indicating that the value of $H_{c2}^{ab}(0)$ is more effectively suppressed by pressure than $T_c(p)$.

In the layered iron pnictides, hydrostatic and chemical pressure reduces the ratio of the $c$- and $a$-axis lattice parameters, which is resulting in a strong influence on the antiferromagnetically ordered Fe moment and $T_{C}^{Ce}$ [20, 21]. The chemical pressure by P-substitution in LnFeAsO ($Ln$=Ce, La, Sm) compresses the $c$-axis stronger than the $a$-axis, and furthermore decreases the pnictogen ($Pn$) height [6, 7, 15, 17, 20]. This corresponds to a strong compressing of the FeAs/P layer and therefore one expects a strong increase of the hybridization between Fe and $Pn$ states. Accordingly we observe a strong initial decrease of $T_{C}^{Ce}$ with hydrostatic pressure by $d \ln T_{C}^{Ce}/dp = -0.36$ GPa$^{-1}$ in CeFeAs$_{0.75}$P$_{0.25}$O$_{0.5}$ compared with only $-0.071$ GPa$^{-1}$ in CeFeAsO [18]. In contrast, chemical pressure results in a stretching of the $Ln$O layer [6], while hydrostatic pressure results in a compressing of this layer [17]. This is very likely the reason for the different dependence of $T_N^{Fe}$ and $T_{C}^{Ce}$ under hydrostatic and chemical pressure.

In summary, we carried out a hydrostatic and chemical pressure investigation on CeFeAs$_{1-x}$P$_x$O single crystals. In CeFeAs$_{0.75}$P$_{0.25}$O we found first a fast decrease of $T_N^{Fe}(p)$ and then above $p^* = 1.95$ GPa a leveling of at about 28 K. This behavior seems to exclude a quantum critical point scenario in CeFeAs$_{0.75}$P$_{0.25}$O under pressure. At $p^*$ the Ce ordering changes from AFM to FM. Our analysis of the isothermal resistivity suggests the presence of Fe moment fluctuations down to lowest temperatures. We notice that the magnetic ordering of the Ce changes from AFM to FM ordering at the same pressure where we find the maximum in the isothermal resistance. We do not find superconductivity in the region around $p^*$ in contrast to the results of P-substitution in CeFeAs$_{1-x}$P$_x$O where superconductivity is observed coexisting with ferromagnetism close to the P-concentration where the AFM Ce ordering changes to FM [14]. The reason could lie in the different response of CeFeAs$_{0.75}$P$_{0.25}$O to pressure and to P-substitution as it is evidenced, for example, in the different behavior of $T_{C}^{Ce}$ on pressure and P-substitution. However, we point out that we cannot exclude the appearance of superconductivity at pressure higher than our experimentally accessible range. CeFeAs$_{0.70}$P$_{0.30}$O and CeFeAs$_{0.65}$P$_{0.35}$O are situated right in the narrow P-concentration regime where superconductivity and FM ordering of Ce moments coexist. At ambient pressure we observe a weak Fe-SDW ordering around $T_{C}^{Fe} = 38$ K which is suppressed upon increasing pressure. In both compounds increasing pressure enhances $T_{C}^{Ce}(p)$. The superconductivity is highly sensitive to pressure and $T_c(p)$ is already suppressed to zero temperature around $p \approx 0.46$ GPa. Our study highlights the delicate interplay between iron and cerium magnetism, their sensitivity to structural properties and, not at last, the subtle connection to superconductivity.

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