Effect of pressure cycling on Iron: Signatures of an electronic instability and unconventional superconductivity

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High pressure electrical resistivity and x-ray diffraction experiments have been performed on Fe single crystals. The crystallographic investigation provides direct evidence that in the martensitic \textit{b}cc \textit{→} \textit{h}cp transition at 14 GPa the \{110\}_\textit{bcc} become the \{002\}_\textit{hcp} directions. During a pressure cycle, resistivity shows a broad hysteresis of 6.5 GPa, whereas superconductivity, observed between 13 and 31 GPa, remains unaffected. Upon increasing pressure an electronic instability, probably a quantum critical point, is observed at around 19 GPa and, close to this pressure, the superconducting \textit{T}_c and the isothermal resistivity (0 < \textit{T} < 300 K) attain maximum values. In the superconducting pressure domain, the exponent \textit{n} = 5/3 of the temperature power law of resistivity and its prefactor, which mimics \textit{T}_c, indicate that ferromagnetic fluctuations may provide the glue for the Cooper pairs, yielding unconventional superconductivity.

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I. INTRODUCTION

The advent of superconductivity in the hexagonal phase of iron between 13 and 31 GPa, described by Shimizu et al. in 2001, was a surprise for the scientific community. Despite the interest in this discovery, little experimental work has been done so far. Given the difficulties in obtaining good quality crystals and the requirement of high pressure, the detailed study of the nature of superconductivity remains a thrilling challenge.

Low pressure \textit{α}-Fe has a body center cubic (bcc) structure and undergoes a martensitic transition to hexagonal (hcp) \textit{ε}-Fe for pressures higher than 12 GPa. According to Ref 9 and 10, the \textit{ε}-Fe phase is non-magnetic. Besides, it has been reported that under pressure Fe loses its ferromagnetic character due to the widening of the d band (i.e. a reduction in the density of states), and then transforms into the hcp \textit{ε}-Fe phase, emphasizing the driving role of magnetism. The superconducting state emerges in this hexagonal phase above 13 GPa and reaches a maximum \textit{T}_c of 2.2 K around 20 GPa before disappearing at 31 GPa.

The origin of Cooper pairing, whether it is mediated by phonons or by magnetic fluctuations still needs to be unveiled. Although there has been no direct proof yet, the possibility of electron-phonon (\textit{el-ph}) coupling is highly unlikely. The rapid disappearance of superconductivity (SC) at 31 GPa compared to the slower change of elastic properties (i.e. the \textit{el-ph} coupling), and the presence of magnetic fluctuations do not support this conjecture. Theoretical studies by Jarlborg et al. have also questioned the \textit{el-ph} coupling mechanism. Density functional theory calculations have predicted the existence of the ordered antiferromagnetic (incommensurate spin density wave) state in a small pressure region. Recently, evidence for weak magnetism, presumably antiferromagnetic fluctuations, at pressures greater than 20 GPa has been provided by x-ray emission spectroscopy.

The low temperature resistivity of \textit{ε}-Fe has an unusual temperature dependence \rho(\textit{T}) \sim \textit{AT}^{5/3} up to at least 10\textit{T}_c, with a large value of coefficient \textit{A}, which exhibits a similar pressure dependence as the one of the superconducting \textit{T}_c, SC is highly sensitive to crystal disorder and the upper critical field \textit{H}_c2 (∼ 0.7 T) is enhanced compared to the low superconducting \textit{T}_c value. These observations point towards an unconventional nature of SC, mediated by spin fluctuations, possibly of ferromagnetic nature.

In this paper, we report high pressure x-ray diffraction and electric transport measurements on good quality Fe single crystals. In order to address the question of the role of pressure conditions (hydrostaticity) on the \textit{α} \textit{→} \textit{ε} transition of Fe, which was reported to be very sensitive to the pressure medium, the present resistivity investigation was performed in a different pressure medium (pyrophyllite) and is compared to previous studies. Furthermore, pressure cycling (increasing and decreasing) has been implemented to check the effect on the transport properties near the superconducting and magnetic/martensitic transitions. A broad hysteresis is observed on pressure cycling in the room temperature resistivity \rho_{RT} (in agreement with x-ray diffraction) as well as in low temperature transport parameters. Amazingly the superconducting \textit{T}_c does not show a similar effect on pressure cycling. This qualitative discrepancy is consistent with the existence of a threshold residual resistivity for the occurrence of the superconducting state, which is a hallmark of unconventional SC. The transport parameters are analyzed in the light of weakly ferromagnetic compound like \textit{ZrZn}_2 or the triplet superconduc-
tor Sr₂RuO₄₁₈.

II. EXPERIMENTS

The single crystal diffraction study at high pressure was performed on I15, the Extreme Condition Beamline at Diamond Light Source, UK. A monochromatic beam (E = 33.94 keV) was focused onto a thin (24 µm) single crystal (whisker) placed in a diamond anvil cell (DAC). The faces of the whisker were the {100}bcc, and the largest sample surface (50×34 µm²) was perpendicular to the incident wave vector. An area detector was inclined by 5° with respect to the incoming wave vector was used to collect the single crystal images (exposure time of 1 second) while scanning the φ axis. Daphne oil 7373 was used as a pressure medium and the pressure was measured by the ruby fluorescence technique.

Resistivity measurements were performed on a Fe whisker with a residual resistivity ratio RRR ∼ 250. Our previous transport measurements were initially made using steatite and subsequently Daphne oil as pressure transmitting media. From the width of the superconducting transition of the Pb manometer the pressure gradients (∆p/p) in both media were estimated to be about 5% and 3%, respectively. In the literature, the width (w) of the α ↔ ε transition of Fe was reported to be very sensitive to the pressure medium, ranging from w ∼ 0 in helium to more than 10 GPa in a medium of very poor hydrostaticity, like aluminium oxide. In spite of many efforts, we could not succeed to increase sufficiently the maximum pressure of our helium DAC for resistivity measurements. Therefore we decided to try the opposite way and deliberately chose to measure in pyrophyllite, a pressure medium with a relatively low hydrostaticity. This modification was found to be quite compatible with our standard technique where samples and the Pb manometer are inserted in between two soft solid disks. Furthermore with the replacement of steatite by pyrophyllite the pressure cell remained stable while releasing the load, allowing us to cycle the pressure. In pyrophyllite, we obtained ∆p/p ≈ 0.08. Pressure was changed at room temperature and the resistivity of Fe was normalized to ρ = 10.0 µΩcm at ambient conditions. Given that the sintered diamond anvils of the Bridgman pressure cell are slightly magnetic, special care was taken to obtain the correct superconducting transition temperature of Pb and thus the corresponding pressure inside the cell. An external low field coil was used to compensate any remanent magnetic field of the anvil cell.

III. RESULTS

A. X-ray diffraction

Figure 1a and 1b are single crystal diffraction patterns of iron just below and almost above its martensitic transition around 14 GPa. Each pattern is the sum of 40 raw images corresponding to a φ scan of 20° in the steps of 0.5°. With increasing pressure there is a clear change in diffraction pattern and the single crystal spots tend to become powder arcs. After two pressure cycles (5 - 20 GPa) the patterns are almost completely dominated by powder rings (not shown). The images shown in figure 1 correspond to the first pressurization.

As expected in the bcc phase (Fig. 1a) there are four 110 and two 200 diffraction spots. The most interesting point in Fig. 1b is that each 110bcc reflection changes in a 002hcp reflection. In addition, each 002hcp reflection is followed by one 100hcp and one 101hcp reflection, and additionally eight 101hcp reflections appear (Fig. 1b). Thus the bcc whisker transforms into four hcp domains related by the four-fold rotation along [100]bcc axis. To our knowledge this is the first direct evidence of this well admitted microscopic path of the martensitic transformation. Fig. 1c shows the Bragg angles of the diffraction spots or powder rings vs. pressure.

FIG. 1. (Color online) a) and b): Single crystal diffraction patterns of iron just below and almost above its martensitic α → ε transition around 14 GPa. c): Bragg angles of the diffraction spots or powder rings vs. pressure.
FIG. 2. (Color online) The pressure dependencies of \( \rho_{RT}(T = 290\, \text{K}) \) and of the low temperature parameters \( \rho_0 \), \( A \), and \( n \) show broad hysteresis while increasing (open circles) and decreasing (filled circles) pressure. Open squares and star symbols correspond to the measurements performed in steatite and triangles to those performed in Daphne oil.

The pressure dependence of the total transition width \( w \sim 1.5 - 2.0\, \text{GPa} \) in agreement with the literature. The pressure dependence of the 110\(_{hcv}\) reflection shows a smooth variation with \( p \) and becomes the 002\(_{hcp}\) reflection. The 102 and 103 reflections of the hcp phase are very weak and undetectable beyond 17.4 or 17.9 GPa, respectively. For decreasing pressure the hcp phase is observed down to pressures much lower than 14 GPa, and the hcp\(\rightarrow\)hcp transition occurs around 7 GPa with a similar width as for increasing \( p \). Accordingly our results confirm the large pressure hysteresis of 7 GPa observed in previous studies. For the second pressure cycle we obtained the same values for the transition pressure and width.

B. Resistivity

Following our previous studies on Fe in Daphne oil and steatite media we performed electrical resistivity measurements from room temperature down to 50 mK and up to 21 GPa using pyrophyllite as pressure medium. The normal state as well as the superconducting properties in pyrophyllite were found to be almost identical to those measured in other media. The resistivity of \( \alpha\)-Fe is weakly pressure dependent. As a function of temperature, \( \rho(T) \) exhibits the typical properties of a long-range ferromagnetic metal with large Curie temperature and then varies superlinearly due to the addition of the el-ph and electron-magnon scattering terms. In comparison, \( \rho(T) \) of \( \varepsilon\)-Fe is strongly enhanced and more pressure dependent. The residual resistivity \( \rho_0 \) is increased by one order of magnitude and \( \rho(T) = \rho_0 + AT^n \) with \( n \approx 5/3 \) up to about 30 K, and an enhanced value of \( A \). At higher temperatures \( \rho(T) \) evolves towards a nearly linear temperature dependence. We do not show these \( \rho(T) \) data here in order to avoid repetition. However we have combined the results from previous measurements with the new data to bring forth a consistent picture of the transport properties of Fe.

Figure 2 shows the pressure variation of the room temperature resistivity \( \rho_{RT} \), as well as the low temperature parameters \( \rho_0 \), \( A \), and \( n \) up to 30.5 GPa. Upon increasing \( p \), our recent measurements \((0 \leq p \leq 21\, \text{GPa}) \) match quite well with the data obtained in steatite \((21 \leq p \leq 30.5\, \text{GPa})\) as well as with previous data. The important point is that the pressure cell remained quite stable when using the pyrophyllite medium and thus enabled us to cycle the pressure. There are two main new results. First, the resistivity as parameterized by \( \rho_{RT} \), \( \rho_0 \), \( A \), and \( n \) shows a broad hysteresis of roughly 6.5 GPa around the martensitic transition, in agreement with the x-ray diffraction data. Second, with decreasing \( p \), the hysteresis starts at about 19 GPa which is the pressure of the maximum of the superconducting transition temperature \( T_c \).

Concerning \( \rho_{RT}(p) \), enhanced magnetic scattering when transiting from ferromagnetic \( \alpha\)-Fe to non-magnetic \( \varepsilon\)-Fe leads to the increase in resistivity. The width of the transition \( w \sim 3\, \text{GPa} \), as observed in steatite is slightly broader in pyrophyllite and narrower in Daphne oil. With decreasing pressure, the \( \varepsilon\)-Fe phase persists with a continuous rise in resistivity down to roughly 10 GPa, before collapsing to \( \alpha\)-Fe. Similar to \( \rho_{RT} \), \( \rho_0 \) also shows a broad hysteresis and recovers low values for \( p < 3\, \text{GPa} \). The \( \rho_{RT} \) can be influenced by the change in the el-ph coupling, thus the hysteresis seen in \( \rho_0 \) is a better signature of an intrinsic hysteresis at the magnetic (martensitic) transition. This result is the first indication of a hysteresis in the low temperature properties of iron.

The \( A \)-coefficient follows a similar trend as that of \( \rho_{RT}(p) \) and \( \rho_0(p) \), showing a large increase at the transition and then slowly decreasing in the \( \varepsilon\)-Fe phase. The increase in \( A(p) \) can be associated with the enhanced spin fluctuations upon the transition to the \( \varepsilon\)-Fe phase. Its large value evidences a strongly correlated phase and supposedly the maximum observed at 19 GPa signals the location of a quantum critical point (QCP). The extended \( \varepsilon\)-Fe phase upon decreasing pressure leads to the increase in the \( A \) value down to \(~12\, \text{GPa}\). The exponent \( n \) also shows a hysteresis with pressure cycling, going from \( n \sim 2.1 \), characteristic of a long-range ferromagnet like \( \alpha\)-Fe, to the more exotic value \( n \approx 1.67 \approx 5/3 \) in the \( \varepsilon\)-Fe phase. The \( n = 5/3 \) exponent indicates the ferromagnetic nature of the spin fluctuations. The variation in \( n(p) \) near the low pressure regime could be related to the ferromagnetic domain wall scattering.

The top panel of Fig. 3 exhibits the pressure dependence of the onset of the superconducting transition \( T_c^{\text{onset}} \), where \( \rho(T) \) drops by 1% of its lowest normal state value just before transiting. With increasing pressure \( T_c^{\text{onset}} \) is first detected at 13 GPa, reaching a maximum value of 2.3 K at 19 GPa, in good agreement with
previous reports. However, $T_c(p)$ does not show a large hysteresis while decreasing pressure and it is even lower around 15 GPa in comparison to the increasing pressure data. Although the $\varepsilon$-Fe phase exists prominently down to $\sim 10$ GPa with a notably large $A-$coefficient, $T_c(p)$ decreases sharply and vanishes at the same pressure at which it had initially appeared. This behavior is unexpected and at first sight it seems to contradict the view that SC evolves concomitantly with the expected and at first sight it seems to contradict the view which it had initially appeared. This behavior is unexplained by previous measurements done in steatite and Daphne oil. Furthermore, it might be due to an artefact of the el-ph term. The slopes of the fits are the $A-$coefficients shown in Fig. 3. The absence of a hysteresis in $T_c(p)$ due to the increase of $\rho_0$ beyond 1.5 $\mu\Omega$cm is consistent with the notion of unconventional SC in $\varepsilon$-Fe.

The temperature dependent part of the resistivity is plotted in Fig. 4 against $T^{5/3}$ for increasing pressures between 15.3 and 29.2 GPa. Excellent fits (dashed lines) are obtained up to a temperature $T^*$, where data start to deviate upwards due to the rapid rise of the el-ph resistivity term. The slopes of the fits are the $A-$coefficients shown in Fig. 2. In fact, the $T^{5/3}$ law is accurately followed already from temperatures just above $T_c$ (see different plots in Ref. [3] and [4]) and then extends over more than an order of magnitude up to $T^*$. It is also noteworthy that the $T^{5/3}$ law is observed for pressures that cover almost the entire superconducting domain, $13 < p < 31$ GPa. Moreover, as shown in the inset of Fig. 4, $T^*$ finds its maximum around 21 GPa, i.e. close to the maxima of $T_c$, $A$ and $\rho_0$. Usually, one expects $T^* \propto A^{-1/2}$ for a normal Fermi liquid ($n = 2$), while in this case the higher $A$, the higher $T^*$. Such a correlation, also observed in heavy fermions or Fabre salts can be considered as an indication of a QCP in $\varepsilon$-Fe in the vicinity of 20 GPa. In addition it seems unlikely that the $T^*(p)$ maximum might be due to an artefact of the el-ph term given that its pressure dependence is expected to be monotonic (see the discussion section).

Figure 5 shows the pressure dependence of the superconducting $T_c$, estimated from three different criteria corresponding to the resistivity drop of 1%, 10%, and 100%. To draw a comprehensive $T_c - p$ phase diagram for Fe, the recent data obtained in pyrophyllite are completed by previous measurements done in steatite and Daphne oil. Using the 1% drop criterion ($T^{1\%}_c$), our results confirm the bell-shape of $T_c(p)$, originally discovered by Shimizu et al. The pressure domain and the maximum $T_c \approx 2.3$ K are similar. For good samples (RRR $\sim 200$ at $p = 0$) of different origins, all our results agree without exception. Moreover, the $T_c^{1\%}$ values observed in Daphne oil, steatite and pyrophyllite are in good agreement with each other. A slight difference seems that the $\rho(T)$ drop is somewhat more rapid in the best medium which is Daphne oil. The superconducting transition is very broad in temperature and most often partial for all these media. Considering a more restrictive criterion like $T_c^{10\%}$, the superconducting region shrinks in $T$ and $p$, whereas the complete (> 99%) $\rho(T)$ transitions are limited to a narrow pressure domain between
cause the very broad superconducting transition comes
the pressure medium with the highest hydrostaticity be-
ilar results would be obtained in solid helium (i.e. in
above 12 GPa is intrinsic in nature. Presumably, sim-
temperature in Daphne oil pressure medium give a width
of resistivity from its normal state value, respectively.

19 and 23 GPa with maximum $T_c^{100\%}$ of only 0.5 K. In
fact, the $T_c(p)$—curve exhibits a small asymmetry and
its maximum in $p$ depends slightly on the resistivity cri-
teria (dashed line in Fig. 5). Both $T_c^{100\%}(p)$ and $T^*(p)$
have maxima around 21 GPa. The detection of complete
resistive transitions strongly depends on the measuring
method or on the applied magnetic field, suggesting the
existence of superconducting islands with weak links. SC
starts to be suppressed for current densities $j$ as low as
1 A/cm$^2$ or in magnetic fields of a few Gauss. Conversely
with the $T_c^{1\%}$ criterion, SC is much more robust. No de-
crease of $T_c^{\text{onset}}$ was detected for $j = 10^3$ A/cm$^2$ and a
relatively high upper critical field $H_{c2}(T \to 0) \approx 0.7$ T was
observed for such a low $T_c$ metal. Let us add that small
Meissner signals have been reported, but we did not find
any bulk signature of SC by ac-calorimetry. The inde-
dence of results from the pressure conditions strongly
suggests that the $T_c^{1\%}(p)$ curve and in particular its rise
above 12 GPa is intrinsic in nature. Presumably, sim-
ilar results would be obtained in solid helium (i.e. in
the pressure medium with the highest hydrostaticity) be-
cause the very broad superconducting transition comes
mainly from the sample limitation and is not an experi-
mental artefact.

IV. DISCUSSION

The x-ray diffraction measurements performed at room
temperature in Daphne oil pressure medium give a width
$w \sim 1.5 - 2$ GPa for the $\alpha \leftrightarrow \varepsilon$ transition of Fe. The
order of the structural transition is not yet established
since it is a displacive transformation. In comparison,
the transport measurements which probably reflect prin-
cipally the magnetic collapse indicate a larger width. For
any $T \leq 300$ K, the resistivity (see Fig. 2) dramatically
increases in the pressure interval 12.5 - 15.5 GPa. Most
likely only a small part of this increase is due to the
change of the el-ph coupling, as inferred from investiga-
tion of metastable non-magnetic $\gamma$-Fe. The width of the
transition $w \approx 3$ GPa agrees with the value $w \sim 2.4$ GPa
observed by x-ray magnetic circular dichroism. Moreover,
we find that $w$ is nearly the same in Daphne oil, steatite
or pyrophyllite media, i.e. weakly dependent on the
pressure conditions, in disagreement with Taylor et al.
who reported different $w$ for different pressure media.
Our observations are consistent with a width $w$ consid-
erably larger than the respective $\Delta p$ inside the pressure
cell (in the range $3\% < \Delta p/p < 8\%$), and indicate that
$w$ is intrinsic to the $\alpha \leftrightarrow \varepsilon$ structural and magnetic
transition. Thus the growth of anomalous scattering up to
a hypothetical QCP located around 19 GPa is a genuine
property of $\varepsilon$-Fe.

Interestingly, the room temperature resistivity $\rho_{RT}(p)$
has a cusp at 13 GPa in steatite as shown by studies with
small pressure increments, and an even bigger cusp (30% jump)
in Daphne oil. This sharp anomaly marks the start of the
breakdown of the long-range ferromagnetic order which
slightly precedes the structural transition by about
0.5 GPa. Moreover, as the emergence of SC coincides
with the cusp in $\rho_{RT}(p)$, the coexistence of SC with fer-
romagnetic clusters seems clear at least up to 15 GPa. At
that pressure the exponent $n$ of the temperature power
law of resistivity is already locked to $n = 5/3$, reflecting
the presence of ferromagnetic spin fluctuations. Aside
from that it is instructive to compare the behavior of Fe
with Pb (our manometer), which undergoes a martensitic
$fcc \rightarrow hcp$ transformation between 13 and 16 GPa. In
this pressure window, $\rho_{RT}$ increases smoothly by around
20% without any cusp. At low temperature the super-
conducting resistive transition at $T_c$ remains narrow and
$T_c(p)$ does not deviate from its slow decrease with in-
creasing $p$. Apparently the phonon modes responsible
for the conventional SC in Pb are not affected by the
structural transition.

The most interesting result of the pressure cycling is
that the increasing and decreasing $p$ data merge only at
$p_{\text{max}} \approx 19$ GPa, suggesting that the $\alpha \leftrightarrow \varepsilon$ magnetic
transition has a tail and that non-magnetic $\varepsilon$-Fe is re-
alyzed only for $p \geq p_{\text{max}}$. This is true for the four quan-
tities shown in Fig. 2, but not for $T_c$ presumably due
to a sharp pair breaking effect. For instance consider-
ing the $A$—coefficient, above 12.5 GPa where the tran-
sition starts, the difference between the decreasing and
increasing $A(p)$ values can be viewed as directly linked
to the amount $\eta$ of magnetic clusters, remnant of the
ferromagnetic $\alpha$-Fe. The scenario is that these magneti-
cally unstable clusters induce ferromagnetic fluctuations
which grow up to a QCP marked by the vanishing of $\eta$ at
$p_{\text{max}}$. As a result at the QCP the resistivity is maximum
and in particular the coefficient $A$ as well as the super-
conducting $T_c$. Furthermore the $n = 5/3$ temperature
power law of resistivity extends up to a maximum $T^*$
at almost the same $p$. It is noteworthy that, at a pressure
close to $p_{\text{max}}$, a cusp has been reported in the weak magnetic signal detected by x-ray emission spectroscopy\cite{1}. However, such a feature could also be related to other types of electronic instabilities like an electronic topological transition. With decreasing $p$, the strength of the interaction between the electrons and spin fluctuations is maximum at about 13 GPa where $A$ takes its maximum, indicating that the electronic instability has the same hysteresis as the structural transition. This electronic instability appears to be a precursor sign of the long range ferromagnetic order which becomes stable around 7 GPa below the instability. The decrease of $A$ at lower $p$ would be due to the progressive growth of ferromagnetically stable clusters on approaching the bcc phase. Up to now it is not clear why the total width of the magnetic transition including its tail corresponds to the observed broad hysteresis of 7 GPa, but our observation supports the driving role of magnetism in the $\alpha \leftrightarrow \varepsilon$ transition of Fe. With increasing $p$, the value of the $A$ coefficient appears to track $T_c$, implying that the same ferromagnetic fluctuations responsible for the non-Fermi liquid behavior in resistivity may also be responsible for the superconducting pairing interaction. Moreover, reaching 31 GPa, the $A$ coefficient seems to fall below a certain minimum threshold value, necessary for SC. However, this point is less clear for the emergence of $T_c$ around 13 GPa, simply because the $A(p)$ and $T_c(p)$ variations are too rapid and likely to be smeared by the $p$ gradient.

The absence of hysteresis in $T_c(p)$ (Fig. 3) suggests the existence of a certain $\rho_0$-value, beyond which SC is suppressed. Indeed a strong enhancement of $\rho_0$ is observed in the hcp phase, mimicking the one seen in $A(p)$. As to its origin, pressure cycling may induce some microstructural changes leading to a slow decline of the single crystallinity, as can be inferred from the x-ray diffraction data. However, these changes are not very significant, at least in affecting $\rho_0$, since it finally recovers to low values at low pressure. As an alternative explanation, we suggest that the effect of lattice disorder on $\rho_0$ gets substantially amplified by spin fluctuations in this particular pressure region, hence leading to the observed enhancement in $\rho_0$. Coming back to an eventual threshold value of $\rho_0$ for SC, such a phenomenon is also found for example in $\text{Sr}_2\text{RuO}_4$ for which non-magnetic impurities kill the superconducting state when the carrier mean free path $l \propto \rho_0^{-1}$ falls below the superconducting coherence-length $\xi$. Mackenzie et al. have shown that the generalized theoretical model for non-magnetic impurities in an unconventional superconductor (which is based on the pair breaking Abrikosov-Gorkov theory for magnetic impurities in BCS superconductors), fits very well with the dependence of $T_c(\rho_0)$. A threshold of $\rho_0 = 1.1 \, \mu\Omega\text{cm}$ was established for $\text{Sr}_2\text{RuO}_4$ samples of different chemical purities. For Fe, when the impurity level is below 100 ppm the crucial parameter is not the chemical purity but the metallurgical state of the sample.\cite{2}

The threshold $\rho_0 = 1.5 \mu\Omega\text{cm}$ was estimated by controlling the intrinsic sample disorder, either by rolling (cold work induces dislocation defects) or by annealing. The electronic mean free path $l \propto \rho_0^{-1}$ has a threshold value around 10 nm for SC. According to the critical field data, the coherence length $\xi$ appears to be close to $l$, i.e. the clean limit is required which supports an unconventional nature for the pairing mechanism. For $\text{Sr}_2\text{RuO}_4$ a narrow transition is observed at $T_c$ when $\rho_0$ is much lower than the threshold value. This condition is never satisfied in Fe and thus only broad transitions are observed. Moreover, when $T_c$ decreases, the criterion $\xi < l$ introduces further limitations because $T_c \propto \xi^{-1}$. Obtaining narrow resistive transitions would be essential in order to progress in the study of SC of Fe. However, there is little hope for that as the $\rho_0$ enhancement when entering the $\varepsilon$-Fe is in a large part intrinsic, i.e. only a small decrease is observed with improving sample quality. Also, the in-situ annealing of the sample seems impossible. Iron samples with a sufficiently low $\rho_0$ should exhibit bulk SC in the pressure domain $13 < p < 31$ GPa with a maximum $T_c$ value higher than 2.5 K.

The power law $\rho(T) \propto A T^{5/3}$ has been reported for some weakly ferromagnetic metals including $\text{Zr}_2\text{Ni}_{17}$, $\text{Ni}_3\text{Al}_{22}$ and $\text{Pd}_2\text{Ni}_{1-x}$. In the case of the alloy $\text{Pd}_x\text{Ni}_{1-x}$, a ferromagnetic quantum critical point clearly occurs for $x = 0.025$ where $n = 5/3$ is minimum while $A = 2n \Omega \text{cm}/K^{5/3}$ is maximum, culminating at a value a bit larger than that of Fe at $p_{\text{max}} \approx 19$ GPa. For $\text{Zr}_2\text{Ni}_2$ the picture is less standard: surprisingly $A = 9n \Omega \text{cm}/K^{5/3}$ and $n \sim 5/3$ are almost $p$-independent up to pressures close to $p_c = 2$ GPa, where the ferromagnetism is suppressed completely and the exponent drops to $n \sim 3/2$. Moreover, there is a change of slope at the Curie temperature in the $T^{5/3}$ plot of the resistivity. These anomalies have been considered to be compatible with the marginal Fermi liquid state expected in weakly ferromagnetic metals. In the case of Fe the situation is still different as $n$ is fixed on a broad $p$-range outside the ferromagnetic phase while $A(p)$ varies strongly.

The subtraction of a phonon term $\rho_{pb}$ to the total resistivity (data from Ref.\cite{1}) suggests that the $T^{5/3}$ temperature dependence might hold up to $T \sim 200$ K, i.e. a temperature much higher than $T^*$ as defined in Fig. 4. However, extension of such an analysis to pressures below the superconducting $T_c(p)$ maximum leads to an unlikely pressure dependence of $\rho_{pb}$. Furthermore, the data treatment assumes a strict validity of Matthiessen’s rule considering that $AT^{5/3}$ is only about 30% of $\rho_0$ and that the pressure in our case is sufficiently temperature independent, which seems not to be the case. Indeed, the deviation from linearity of the resistivity $\rho(T)$ of Pb points to a slight increase of pressure above 80 K (by about 5% up to 300 K) and $p$ can be considered as constant only below 50 K. Therefore the simple $T^{5/3}$ plot of Fig. 4 is the most reliable analysis, showing the occurrence of the $T^*(p)$ maximum. Nevertheless, the resistivity term ascribed to spin fluctuations persists up to 300
K with an unknown $T$ dependence that is not far from $T^{5/3}$. It is also noteworthy that we did not observe any anomaly which could mark a Curie temperature similar to ZrZn$_2$. Accordingly, resistivity measurements above 300 K are desirable in order to evaluate the spin fluctuation temperature $T_{SF}$ which sets the overall scale for spin mediated SC. For Fe a huge $T_{SF}$ seems not to be excluded, explaining qualitatively the relatively high superconducting $T_c$ value.

V. CONCLUSIONS

X-ray diffraction and electric transport measurements have been carried out under high pressure on high quality Fe single crystals. The x-ray data yield the first direct experimental evidence of the microscopic path of the martensitic $\alpha \leftrightarrow \varepsilon$ transformation. Combining this study with previous ones, only a very weak dependence on the pressure conditions is revealed. As a main outcome, it is now evident that the superconducting pocket observed at the border of ferromagnetic bcc-Fe is intrinsic to the hcp-Fe phase. As to its origin, new insight comes from the unprecedented pressure cycling of electric transport, and its analysis in terms of $\rho(T) = \rho_0 + AT^n$. Indeed, maxima in $A(p)$ and $\rho_0(p)$ are observed (as well as $n \approx 5/3$) slightly above the structural transformation (i.e. within the hcp phase), with a similar hysteresis in pressure. These features likely signal a region of strong ferromagnetic fluctuations, which may as well be responsible for superconductivity, since $T_c(p)$ culminates in the same pressure range. As a synoptic scenario, we suggest that the magnetic transition has a tail (of a yet unknown nature) ending at a QCP or another type of electronic instability, precisely where the ferromagnetic spin fluctuations are maximum. Given the proximity to long-range ferromagnetic order, it may act as its precursor sign. The striking absence of hysteresis in $T_c(p)$ may be explained by the high sensitivity of $T_c$ on $\rho_0$ and the electronic mean free path, which additionally points to an unconventional nature of the superconducting state. Further experimental and theoretical progress is still necessary to understand in detail the microscopic interplay between the $\alpha \leftrightarrow \varepsilon$ structural and magnetic transitions in elementary Fe, in particular in order to unveil the nature of the electronic instability inside the hcp phase. Concerning superconductivity, experimental improvements (such as narrow resistive transitions) seem however compromised by the intrinsic rise of $\rho_0$ and still represent an enormous challenge.

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