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 bcc → hcp transition at 14 GPa the $\{110\}_{\rm bcc}$ become the $\{002\}_{\rm hcp}$ 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 T_c and the isothermal resistivity ($0 < T < 300$ K) attain maximum values. In the superconducting pressure domain, the exponent $n = 5/3$ of the temperature power law of resistivity and its prefactor, which mimics 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.[1] Despite the interest in this discovery, little experimental work has been done so far.[2–5] 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 α-Fe has a body-centered-cubic (bcc) structure and undergoes a martensitic transition to hexagonal (hcp) ε-Fe for pressures higher than 12 GPa.[6–8] According to Refs. 9 and 10, the ε-Fe phase is nonmagnetic.[9,10] 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 ε-Fe phase, emphasizing the driving role of magnetism.[11,12] The superconducting state emerges in this hexagonal phase above 13 GPa and reaches a maximum T_c of 2.2 K around 20 GPa before disappearing at 31 GPa.[1–4]

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 (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 el-ph coupling), and the presence of magnetic fluctuations do not support this conjecture.[13] Theoretical studies by Jarlborg *et al.* have also questioned the el-ph coupling mechanism.[14] Density functional theory calculations have predicted the existence of the ordered antiferromagnetic (incommensurate spin density wave) state in a small pressure region.[15] Recently, evidence for weak magnetism, presumably antiferromagnetic fluctuations, at pressures greater than 20 GPa has been provided by x-ray emission spectroscopy.[16]

The low temperature resistivity of ε-Fe has an unusual temperature dependence $\rho(T) \sim AT^{5/3}$ up to at least $10T_c$, with a large value of coefficient A, which exhibits a similar pressure dependence as the one of the superconducting T_c.[3,4] SC is highly sensitive to crystal disorder and the upper critical field H_{c2} ($\sim$0.7 T) is enhanced compared to the low superconducting T_c value.[3] 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 $\alpha \to \varepsilon$ transition of Fe, which was reported to be very sensitive to the pressure medium,[9] 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 $\rho_{\rm RT}$ (in agreement with x-ray diffraction) as well as in low temperature transport parameters. Amazingly, the superconducting 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 a weakly ferromagnetic compound such as $ZrZn_2$ (Ref. 17) or the triplet superconductor Sr_2RuO_4.[18]

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 ($50 \times 34\ \mu m^2$) was perpendicular to the incident wave vector. An area detector[19] inclined by 5° with respect to the incoming wave vector was used to collect the single crystal images (exposure time of 1 s) 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[3,4] and subsequently Daphne oil[5] as pressure transmitting media. From the width of the superconducting transition of the Pb manometer the pressure gradients ($\Delta p/p$) in both media were estimated to be about 5% and 3%, respectively. In the literature, the width (w) of the $\alpha \leftrightarrow \varepsilon$ transition of Fe was reported to be very sensitive to the pressure medium, ranging from $w \sim 0$ in helium to more than 10 GPa in a medium of very poor hydrostaticity, such as aluminum oxide. In spite of many efforts, we could not succeed to increase sufficiently the maximum pressure of our helium DAC for resistivity measurements.[20,21] 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.[22] 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 $\Delta p/p \sim 8\%$. Pressure was changed at room temperature and the resistivity of Fe was normalized to $\rho = 10.0\ \mu\Omega$ cm at ambient conditions.[23] 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

Figures 1(a) and 1(b) are single crystal diffraction patterns of iron just below and almost above its martensitic $\alpha \rightarrow \varepsilon$ transition around 14 GPa. Each pattern is the sum of 40 raw images corresponding to a ϕ scan of 20° in steps of 0.5°. With increasing pressure there is a clear change in the 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 Fig. 1 correspond to the first pressurization.

As expected in the bcc phase [Fig. 1(a)] there are four 110 and two 200 diffraction spots. The most interesting point in Fig. 1(b) is that each 110_{bcc} reflection changes into a 002_{hcp} reflection. In addition, each 002_{hcp} reflection is followed by one 100_{hcp} and one 101_{hcp} reflection, and additionally eight 101_{hcp} reflections appear [Fig. 1(b)]. Thus the bcc whisker transforms

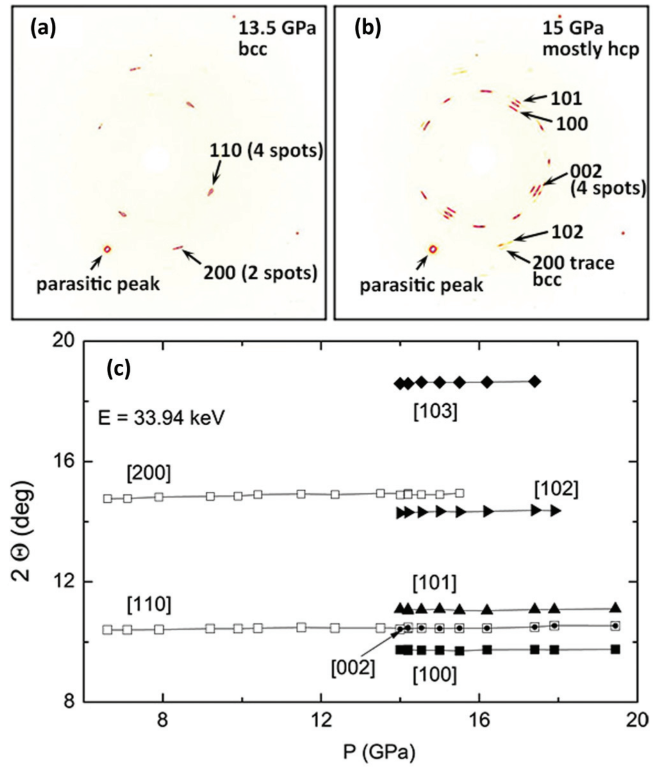

FIG. 1. (Color online) (a), (b) Single crystal diffraction patterns of iron just below and almost above its martensitic $\alpha \rightarrow \varepsilon$ transition around 14 GPa. (c) Bragg angles of the diffraction spots or powder rings vs pressure.

into four hcp domains related by the fourfold rotation along the $[100]_{bcc}$ axis, which directly evidences this well admitted microscopic path of the martensitic transformation.[8] Figure 1(c) shows the Bragg angles of the diffraction spots or powder rings versus p, indicating that the bcc $\rightarrow$ hcp transition starts a bit below 14 GPa. From the spot intensities, it appears that qualitatively a large fraction of the iron sample transforms in a narrow pressure interval (<1 GPa), in agreement with the first order character of the structural transition.[24] However, there are weak traces of the 200_{bcc} reflection up to 15.5 GPa and this allows us to roughly estimate the total transition width $w \sim$ 1.5–2.0 GPa, in agreement with the literature.[12,16] The pressure dependence of the 110_{bcc} 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 $\rightarrow$ bcc 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.[9] 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,[3,4] we performed electrical resistivity measurements from room temperature down to 50 mK and up to 21 GPa using pyrophyllite as the 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 α-Fe is weakly pressure dependent. As a function of temperature, $\rho(T)$ exhibits the typical properties of a long-range ferromagnetic metal with a 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 ε-Fe is strongly enhanced and more pressure dependent. The residual resistivity ρ_0 is increased by one order of magnitude and $\rho(T) = \rho_0 + AT^n$ with $n \simeq 5/3$ 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 these results with those from previous measurements to bring forth a consistent picture of the transport properties of Fe.

Figure 2 shows the pressure variation of the room temperature resistivity ρ_{RT}, as well as the low temperature parameters ρ_0, A, and n up to 30.5 GPa. Upon increasing p, our recent measurements ($0 \leqslant p \leqslant 21$ GPa) match quite well with the data obtained in steatite ($21 \leqslant p \leqslant 30.5$ GPa),[4] as well as with previous data.[2,3,5] 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 key features. First, the resistivity as parametrized by ρ_{RT}, ρ_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, corresponding to the maximum superconducting transition temperature T_c.

Concerning $\rho_{RT}(p)$, enhanced magnetic scattering when transiting from ferromagnetic α-Fe to nonmagnetic ε-Fe leads to an increase in resistivity. The width of the transition $w \sim 3$ GPa, as observed in steatite, is slightly broader in pyrophyllite and narrower in Daphne oil. With decreasing pressure, the ε-Fe phase persists with a continuous rise in resistivity down to roughly 10 GPa, before collapsing to α-Fe.

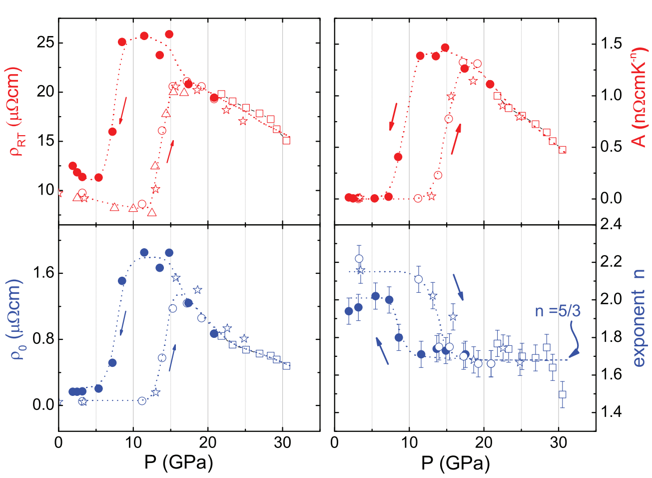

FIG. 2. (Color online) The pressure dependencies of ρ_{RT} ($T =$ 290 K) and of the low temperature parameters ρ_0, A, and n show broad hysteresis while increasing (open circles) and decreasing (solid circles) pressure. Open squares and star symbols correspond to the measurements performed in steatite (Refs. 3 and 4) and triangles to those performed in Daphne oil (Ref. 5).

Similar to $\rho_{RT}(p)$, $\rho_0(p)$ also shows a broad hysteresis and recovers low values for $p < 3$ GPa. Since $\rho_{RT}(p)$ can be affected by a change in the el-ph coupling, the hysteresis seen in $\rho_0(p)$ at the magnetic (martensitic) transition can be considered as a more intrinsic signature, pointing to 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 ε-Fe phase. The increase in $A(p)$ can be associated with the enhanced spin fluctuations upon the transition to the ε-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 ε-Fe phase upon decreasing pressure leads to the increase in the A value down to $\sim$12 GPa. The exponent n also shows a hysteresis with pressure cycling, going from $n \sim 2.1$, characteristic of a long-range ferromagnet such as α-Fe, to the more exotic value $n \approx 1.67 \simeq 5/3$ in the ε-Fe phase. The $n = 5/3$ exponent indicates the ferromagnetic nature of the spin fluctuations.[25] 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^{onset}, where $\rho(T)$ drops by 1% of its lowest normal state value just before transiting. With increasing pressure T_c^{onset} is first detected at 13 GPa, reaching a maximum value of 2.3 K at 19 GPa, in good agreement with previous reports.[1–4] However, $T_c(p)$ does not

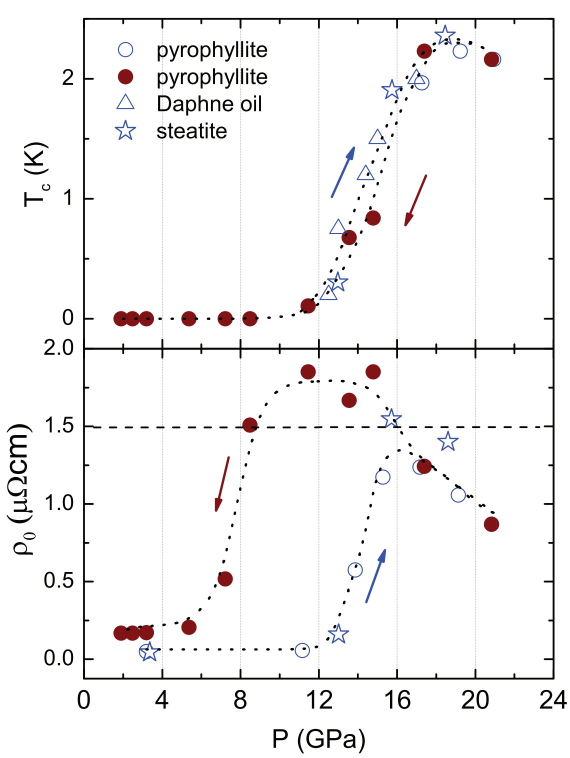

FIG. 3. (Color online) The pressure dependence of the superconducting transition temperature T_c^{onset} for increasing (open symbols) and decreasing pressure (solid circles) does not exhibit hysteresis. In combination with the $\rho_0(p)$ data (lower panel), this can be related to a strong suppression of superconductivity in the ε-Fe phase beyond a certain threshold ρ_0 value.

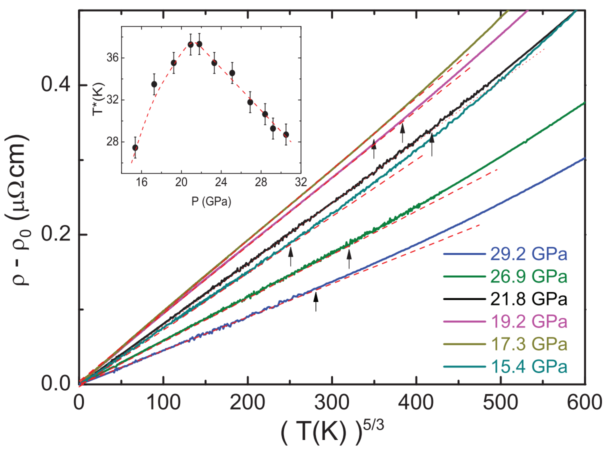

FIG. 4. (Color online) Temperature dependent part of resistivity (ρ-ρ_0) plotted as a function of $T^{5/3}$ for selected pressures between 15.3 and 29.2 GPa. Dashed lines correspond to the $AT^{5/3}$ fit. The inset shows the pressure dependence of the temperature T^* up to which the $T^{5/3}$ dependence is observed.

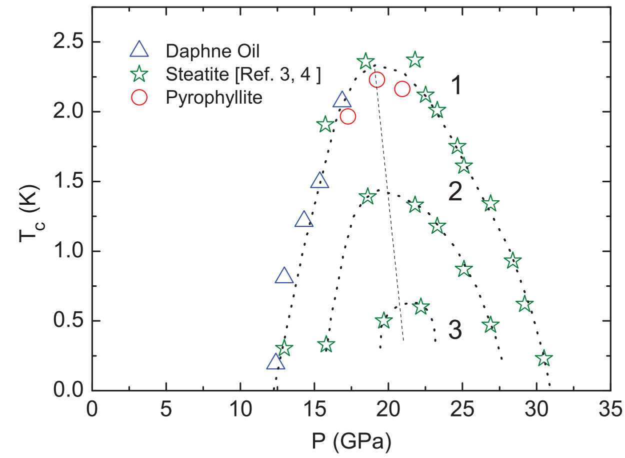

FIG. 5. (Color online) Superconducting T_c vs pressure phase diagram for Fe, measured in different pressure media. Dotted curves marked as 1, 2, and 3 correspond to the transition temperature T_c taken from the 1%, 10%, and 100% drop of resistivity from its normal state value, respectively.

show a large hysteresis while decreasing pressure and it is even lower around 15 GPa, in comparison to the increasing pressure data. Although the ε-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 A coefficient, suspected to reflect the strength of the superconducting coupling in a spin fluctuation scenario.[3,4] Nevertheless, such an argument neglects the pair breaking effect due to the increase of ρ_0 beyond 1.5 $\mu\Omega$ cm while decreasing pressure, as shown in the lower panel of Fig. 3.[3,21] The absence of a hysteresis in $T_c(p)$ due to the increase of ρ_0 beyond 1.5 $\mu\Omega$ cm is consistent with the notion of unconventional SC in ε-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 Refs. 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 ρ_0. Usually, one expects $T^* \propto A^{-1/2}$ for a normal Fermi liquid ($n = 2$), while in this case the higher the A coefficient, the higher is T^*. Such a correlation, also observed in heavy fermions or Fabre salts, can be considered as an indication of a QCP in ε-Fe in the vicinity of 20 GPa.[26,27] In addition, it seems unlikely that the $T^*(p)$ maximum might be due to an artifact of the el-ph term given that its pressure dependence is expected to be monotone (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[3,4] and Daphne oil.[5] Using the 1% drop criterion ($T_c^{1\%}$), our results confirm the bell shape of $T_c(p)$, originally discovered by Shimizu *et al.*[1] The pressure domain and the maximum $T_c \approx 2.3$ K are similar. For good samples (RRR ~ 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.[5] The superconducting transition is very broad in temperature and most often partial for all these media. Considering a more restrictive criterion such as $T_c^{10\%}$, the superconducting region shrinks in T and p, whereas the complete (>99%) $\rho(T)$ transitions are limited to a narrow pressure domain between 19 and 23 GPa with a 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 criteria (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 current 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 decrease of T_c^{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,[1] but we did not find any bulk signature of SC by ac calorimetry. The independence 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, similar results would be obtained in solid helium (i.e., in the pressure medium with the highest hydrostaticity) because the very broad superconducting transition comes mainly from the sample limitation and is not an experimental 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.[28] In comparison, the transport measurements, which probably reflect principally the magnetic collapse, indicate a larger width. For any $T \leqslant 300$ 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,[3] as inferred from investigation of metastable nonmagnetic γ-Fe.[29] 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.[12] 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.*,[9] who reported different w for different pressure media. Our observations are consistent with a width w considerably larger than the respective Δp 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 ε-Fe.

Interestingly, the room temperature resistivity $\rho_{\mathrm{RT}}(p)$ has a cusp at 13 GPa in steatite, as shown by studies with small pressure increments,[2] 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.[12] Moreover, as the emergence of SC coincides with the cusp in $\rho_{\mathrm{RT}}(p)$, the coexistence of SC with ferromagnetic 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 $\to$ hcp transformation between 13 and 16 GPa.[30] In this pressure window, ρ_{RT} increases smoothly by around 20% without any cusp. At low temperature the superconducting resistive transition at T_c remains narrow and $T_c(p)$ does not deviate from its slow decrease with increasing 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 $p_{\max} \approx 19$ GPa, suggesting that the $\alpha \to \varepsilon$ magnetic transition has a tail and that nonmagnetic ε-Fe is realized only for $p \geqslant p_{\max}$. This is true for the four quantities shown in Fig. 2, but not for T_c, presumably due to a sharp pair breaking effect. For instance, considering the A coefficient, above 12.5 GPa where the transition starts, the difference between the decreasing and increasing $A(p)$ values can be viewed as directly linked to the amount η of magnetic clusters, remnant of the ferromagnetic α-Fe. The scenario is that these magnetically unstable clusters induce ferromagnetic fluctuations which grow up to a QCP marked by the vanishing of η at $p_{\max}$. As a result, at the QCP the resistivity is maximum and in particular the coefficient A as well as the superconducting 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 $p_{\max}$, a cusp has been reported in the weak magnetic signal detected by x-ray emission spectroscopy.[16] However, such a feature could also be related to other types of electronic instabilities such as an electronic topological transition.[31] 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 ρ_0 value, beyond which SC is suppressed. Indeed, a strong enhancement of ρ_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 ρ_0, since it finally recovers to low values at low pressure. As an alternative explanation, we suggest that the effect of lattice disorder on ρ_0 gets substantially amplified by spin fluctuations in this particular pressure region, hence leading to the observed enhancement in ρ_0. Coming back to an eventual threshold value of ρ_0 for SC, such a phenomenon is also found, for example, in in the pressure-induced superconductor $CePd_2Si_2$.[32] Actually, the best documented case is the spin triplet superconductor Sr_2RuO_4 for which nonmagnetic impurities kill the superconducting state when the carrier mean free path $l \propto \rho_0^{-1}$ falls below the superconducting coherence length ξ. Mackenzie *et al.* have shown that the generalized theoretical model for nonmagnetic 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 $T_c(\rho_0)$.[18] A threshold of $\rho_0 = 1.1\mu\Omega$ cm was established for Sr_2RuO_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.[3] The threshold $\rho_0 = 1.5\ \mu\Omega$ 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 ξ appears to be close to l, i.e., the clean limit is required which supports an unconventional nature for the pairing mechanism. For Sr_2RuO_4 a narrow transition is observed at T_c when ρ_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 ρ_0 enhancement when entering the ε-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 ρ_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 $\rho(T) \propto AT^{5/3}$ has been reported for some weakly ferromagnetic metals including $ZrZn_2$,[17] Ni_3Al,[33] and Pd_xNi_{1-x}.[34] In the case of the alloy Pd_xNi_{1-x}, a ferromagnetic quantum critical point clearly occurs for $x = 0.025$, where $n = 5/3$ is minimum while $A = 2\ \mathrm{n\Omega\,cm/K^{5/3}}$ is maximum, culminating at a value a bit larger than that of Fe at $p_{\max} \approx 19$ GPa. For $ZrZn_2$ the picture is less standard: Surprisingly, $A = 9\ \mathrm{n\Omega\,cm/K^{5/3}}$ 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 ρ_{ph} to the total resistivity (data from Ref. 4) 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 ρ_{ph}. Furthermore, the data treatment assumes a strict validity of Matthiessen's rule considering that $AT^{*5/3}$ is only about 30% of ρ_0 and that the pressure in our cell 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 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, insight comes from the 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 ρ_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 ρ_0 and still represent an enormous challenge.

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