Unconventional superconductivity and non-Fermi liquid behaviour of ε-iron at high pressure

Unconventional superconductivity and non-Fermi liquid behaviour of ε-iron at high pressure

A T Holmes[1,4]**, D Jaccard**[1]**, G Behr**[2]**, Y Inada**[3] **and Y Onuki**[3]

[1] DPMC, University of Geneva, 24 Quai Ernest-Ansermet, CH1211 Geneva 4, Switzerland
[2] IFW Dresden, PO Box 27 00 16, D-01171 Dresden, Germany
[3] Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

E-mail: alexander.holmes@physics.unige.ch

Abstract
We report further resistive measurements under pressure of samples of iron from multiple sources. The normal state resistivity of ε-iron varied as $\rho_0 + AT^{5/3}$ at low temperature over the entire superconducting pressure domain. The superconductivity could be destroyed by mechanical work, and was restored by annealing, demonstrating sensitivity to the residual resistivity ρ_0. There is a strong correlation between the ρ_0 and A coefficients and the superconducting critical temperature T_c. The critical field B_{c2} corresponding to the maximum T_c was found to be 0.73 T, implying a coherence length of about 20 nm, i.e. slightly shorter than the electronic mean free path. Within the partial resistive transition there was a significant current dependence, with $V(I) = a(I - I_0) + bI^2$, and $a \gg b$, possibly indicating flux-flow resistivity, even in the absence of an externally applied magnetic field.

1. Introduction

Since the discovery of superconductivity in the ε phase of iron under pressure [1], several observations have hinted that the electron pairing has an unconventional origin. Firstly, the restricted pressure range of the superconducting (SC) state is hard to explain by BCS theory [2–5]. The partial resistive transitions observed implied an unusual sensitivity to disorder, a characteristic property of certain unconventional superconductors. Proximity to the ferromagnetic phase suggests that spin fluctuations could be involved in the relevant electronic interactions.

Subsequent experiments confirmed the unusual properties of ε-Fe. An attempt to observe superconductivity in a high purity commercial sample failed (sample No 0, Goodfellow 4 $N+$, with impurities (ppm) Ag < 1, Al < 1, Cu < 1 and Si 1). However, to achieve the dimensions

[4] Author to whom any correspondence should be addressed.

necessary for a pressure experiment, the sample had been rolled down to a thickness of around 3 μm, introducing disorder, which significantly raised its residual resistivity.

Further experiments succeeded in obtaining complete superconducting resistive transitions [6] when special care was taken over the choice of samples and their preparation, to avoid not only chemical impurities but structural disorder due to mechanical work.

Other indications about the nature of the superconductivity come from the normal state resistivity of the ε phase at low temperature. This appeared, at a pressure $P = 22.2$ GPa, to follow a $T^{5/3}$ power law with a strongly enhanced prefactor over a broad range of temperature, a T-dependence expected of a nearly ferromagnetic Fermi liquid (NFFL). The presence of ferromagnetic fluctuations could imply p-wave triplet superconductivity, a scenario suggested in the case of ZrZn$_2$ [7], which has many features in common with iron (partial resistive transitions, non-Fermi liquid power law, sensitivity to disorder). This stands in contrast with band structure calculations [2–5, 8] where antiferromagnetic fluctuations are expected to dominate the ground state, and p-wave superconductivity is not favoured.

The nature of the pressure-driven bcc–hcp α–ε transition complicates the situation. The transition is martensitic [9], and its pressure width (but not its hysteretic behaviour) is highly dependent on the pressure conditions [10]. In the quasi-hydrostatic conditions of the steatite medium used in our experiments, where pressure gradients are up to 5%, this should lead to a transition spread over at least 10 GPa, very similar to the SC pressure range. The superconductivity may therefore be somehow linked with the structural transition itself, rather than being an intrinsic property of the ε phase. In this series of experiments we have not addressed this question, though it may turn out to be a crucial one. Future studies using different pressure media should help to clarify the issue.

2. Experimental methods and sample preparation

The high pressure experiments were carried out using the same Bridgman anvil technique as used for [6]. The aim of these follow-up measurements was to explore further the role of structural disorder in the appearance or otherwise of superconductivity, and to confirm the non-Fermi liquid $T^{5/3}$ behaviour of the normal state resistivity in the ε phase.

We wished to investigate whether superconductivity could be destroyed, and/or recovered or induced, by mechanical work and annealing, respectively. There were four samples in this study; three came from the superconducting batches reported in [6], one from Dresden (No 6) and two from Osaka (Nos 3 and 4). The remaining sample (No 5) (Goodfellow 99.998% Fe, impurities (ppm) Ag < 1, Al < 1, Cu < 1, Mg 1, Mn 1 and Ni < 1) was obtained from the same commercial metallurgical supplier as No 0. No trace of superconductivity had been found in a previous investigation of sample No 0, where the residual resistivity ratio (RRR) was 15. (The RRR is defined by $\rho(298\ \mathrm{K})/\rho(4.2\ \mathrm{K})$ and used as a measure of sample quality.)

The four samples were prepared as follows.

They were rolled down to a thickness appropriate for the pressure experiment ($\sim$15 μm). Initial RRR values of up to 300 were reduced to $\sim$50 by this operation. Three of the samples (Nos 4–6) were subsequently annealed in an induction furnace for 24 h at 1000 °C in a high vacuum ($<10^{-7}$ mbar). After annealing, RRRs in the range 245–310 were recovered in samples from all sources, and grain sizes comparable to the eventual sample length were observed. Sample No 3 was left unannealed.

The samples were then cut using a razor blade to the appropriate width and length. They were arranged in the pressure cell, along with a lead manometer, so that current passed through in series. Four-point resistance measurements could be carried out separately on each sample. A knowledge of each sample's dimensions enabled the absolute resistivity to be calculated with an error of less than 15% over the whole pressure range, neglecting the compressibility.
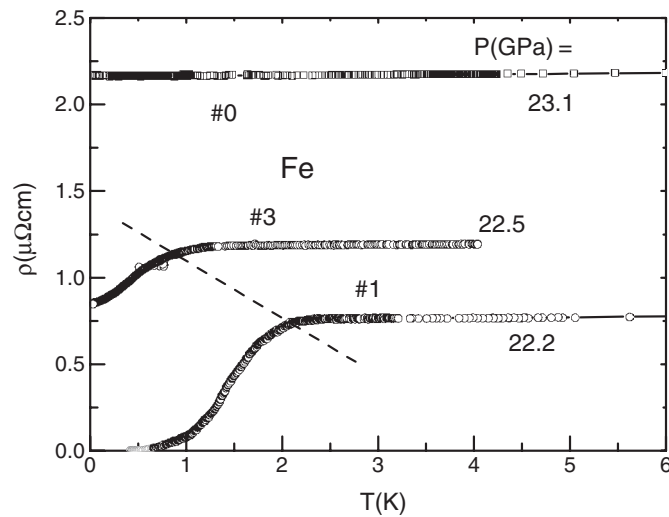
Figure 1. Effect of disorder in different samples on the superconducting transition of iron. The dashed line suggests the T_c variation versus ρ_0.

3. Experimental results and discussion

The effect of disorder on the superconducting state can be seen in figure 1, where the resistivities of three representative samples, Nos 0, 1 and 3, are shown at pressures close to the maximum $T_c(P)$; their residual resistivities were $2.13, 0.77$ and $1.19\,\mu\Omega$ cm respectively. With increasing disorder, measured by ρ_0, the resistive transition becomes only partially complete, then disappears entirely. The remaining samples had resistance drops somewhere between Nos 1 and 3. A transition in No 3, the unannealed sample, was only detectable once the pressure had reached 22 GPa, while the annealed samples started to show signs of superconductivity almost as soon as the structural transition had initiated (as identified in the room temperature resistivity). Rolling and annealing thus have opposite effects, tending to suppress or restore the superconductivity, with associated ρ_0 variation. The metallurgical state, rather than the chemical impurity level appears to be the dominant factor. Sample No 1, however, exhibited the highest T_c (2.5 K). It was not annealed or rolled, but cut to shape with a diamond saw, implying that the annealing process may introduce some contamination which can affect T_c. These results suggest that if ρ_0 can be lowered further, T_c values larger than 2.5 K could be obtained.

Figure 2 shows the relation $\rho = \rho_0 + AT^{5/3}$ in sample No 6 at several pressures, extending up to nearly 35 K, with the upward deviation at higher temperature ascribed to electron–phonon scattering. Similar temperature dependence was seen in the other samples. If the exponent was allowed to vary, a fit of $\rho = \rho_0 + \tilde{A}T^n$ gave n between 1.66 and 1.75 over the entire superconducting pressure range. There is an evident change with pressure of the residual resistivity ρ_0, along with the temperature coefficient A.

The inset of figure 2 shows that the $T^{5/3}$ law remains valid down to very low temperature when the superconductivity is suppressed by a magnetic field of 1 T. The normal state resistance varied with magnetic field B as $(\rho - \rho_0) \propto B^{3/2}$ up to 8 T at 4.2 K and 700 mK.

Figure 3 shows the resistivity at room temperature and 4.2 K in a superconducting (No 6) and a non-superconducting sample (No 0) as the pressure is increased. The α–ε transition is clearly visible at both temperatures, with a substantial increase in ρ. However, the martensitic
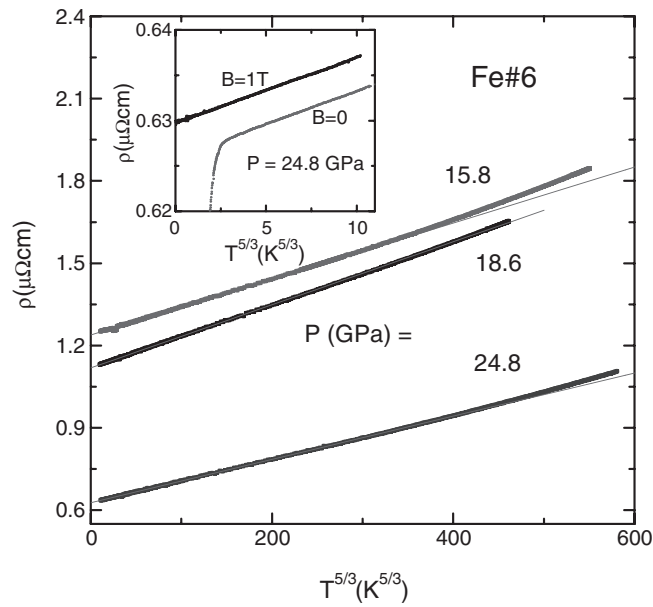
Figure 2. The resistivity of ε-Fe on a $T^{5/3}$ scale at selected pressures. Inset: in a magnetic field $B = 1$ T, the $T^{5/3}$ dependence persists below T_c.
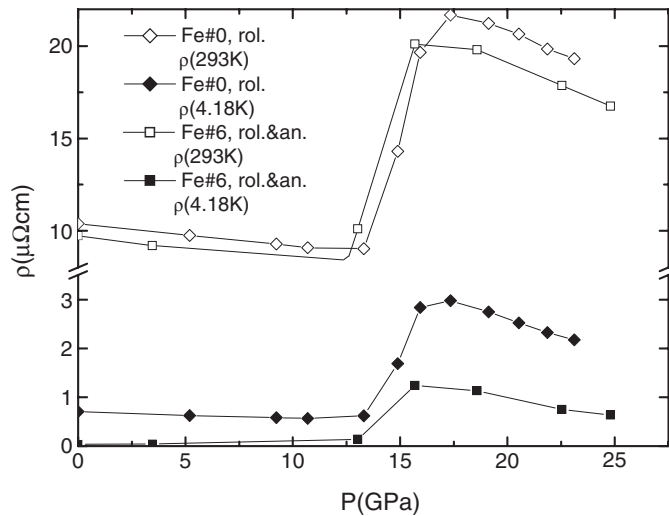

Figure 3. Resistivity signature of the α–ε transition of iron with increasing pressure at 4.18 and 293 K.

α–ε transition should start at $P < 10$ GPa in a steatite medium according to Mössbauer effect experiments [10]. The kink observed in ρ at higher pressures, around 12 GPa, with no precursor signs is therefore unexpected. It could nevertheless be attributed to the disconnection of the conducting α region by the growing amount of ε phase.

After a rounded maximum, the resistance at both temperatures drops quickly and more or less linearly with pressure, and in both cases can be extrapolated to the α-Fe values at pressures close to the disappearance of superconductivity.
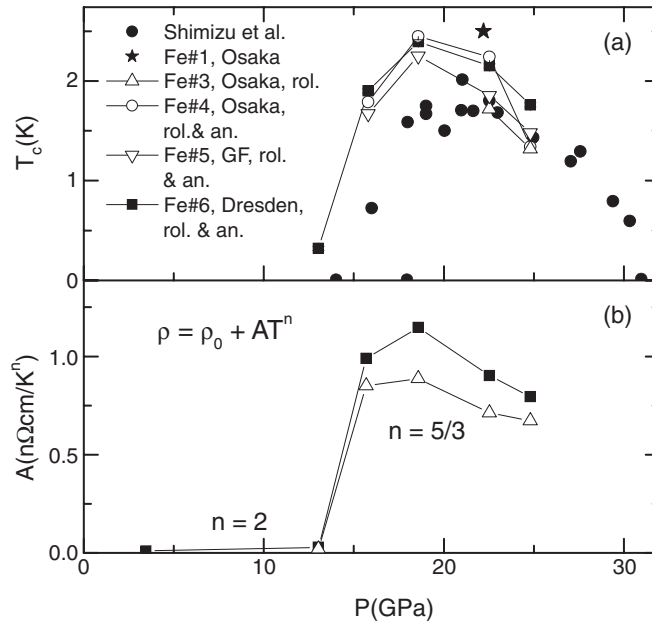
Figure 4. Pressure dependence of (a) the superconducting transition of various Fe samples and (b) the A coefficient in the law $\rho = \rho_0 + AT^{5/3}$.

The origin of the pressure-induced change in resistivity at room temperature might be due to a change in the electron–phonon coupling, or more likely to the large increase in spin disorder when passing from the magnetically ordered α-state to the ε phase. The effect of magnetic ordering on the resistivity has been explored in metastable non-magnetic γ-Fe at ambient pressure [11], where a large difference is found in the room-temperature resistivity between the magnetically ordered and non-magnetic states. We might therefore expect ε-Fe to be analogous.

At low temperature, where the phonon contribution is negligible, the increase in ρ is associated with additional disorder, but the very similar pressure dependence of ρ at these two temperatures suggests that the scattering is at least in part of the same magnetic origin.

The two samples shown in figure 3 behave similarly at room temperature, apart from a shift ascribed to the residual term. At 4.2 K, interestingly, the increase in resistivity associated with the α–ε transition is smaller for a lower ρ_0. Single-crystalline iron whiskers, which can be prepared with RRRs around 1000 [12], therefore offer a good path to obtaining a higher T_c.

Figure 4 shows T_c as a function of pressure, compared with the A coefficient of a fit to the resistivity using a T^2 power law in the α phase and a $T^{5/3}$ law in the ε phase. The $T_c(P)$ phase diagram in [1] is confirmed by our measurements. The superconductivity started to emerge exactly at the kink in $\rho(P)$.

As the resistive transitions were highly current dependent and partial in most cases, the onset was used as a criterion for T_c, i.e. T_c was defined where the resistivity curve started to deviate visibly from the normal state temperature dependence. Surprisingly, the onset of superconductivity was found to be much less sensitive to current than other criteria, such as a 50%, or even 1%, drop in resistance from the normal state. The resistivity drop became larger in every sample as the pressure increased, even beyond the maximum in T_c.

The very large value of A in the SC domain (figure 4(b)) is evidence of a strongly correlated electronic phase. The value of A reflects the strength of interaction between the electrons and
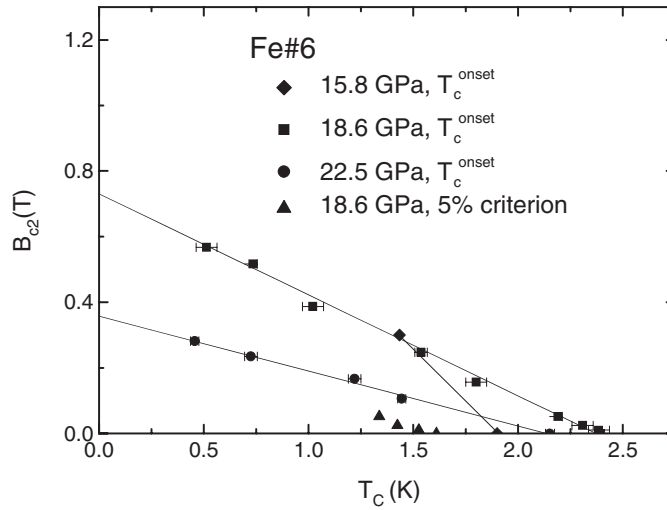
Figure 5. The critical field of ε-Fe at selected pressures. Two T_c criteria are used at 18.6 GPa.

spin fluctuations, thus the correlation seen between $A(P)$ and $T_c(P)$ is strong evidence for a magnetically mediated pairing scenario. Moreover, there appears to be a positive correlation between A and T_c in different samples (including those not shown). It is somewhat surprising that the value of A would vary between samples, but as they were all measured in the same cell, and their resistivities normalized at ambient pressure, we can have some confidence that this is a genuine observation.

Spin-fluctuation-mediated superconductivity is usually associated with a well defined quantum critical point at a particular critical pressure P_c, where non-Fermi liquid behaviour of the resistivity is expected [13]. In contrast, a T^2 dependence was never recovered in the entire SC domain in our measurements.

In a narrow pressure window, both the superconductivity and normal phase of iron show features which point to a key role for spin fluctuations. The closest similar example seems to be ZrZn$_2$ ($T_c \sim 0.3$ K) [7]. The higher T_c of iron may result from stronger magnetic interactions, reflected for example in the large Curie temperature of iron's ferromagnetic phase. Experimentally, it is not clear whether superconductivity is an intrinsic property of ε-Fe or is related to the martensitic transition.

Figure 5 shows the upper critical field B_{c2} for sample No 6 determined using an onset criterion for T_c. The extrapolated value of $B_{c2}(T = 0)$ (0.73 T at 18.6 GPa and $\sim$0.35 T at 22.5 GPa) is much larger (by a factor of up to 70) than that of the lead manometer, which has a nearly identical T_c. B_{c2} is also linear, without the usual curvature, at least down to $T_c/5$. Interpretation of this is difficult, because the internal magnetic field in the sample itself may be higher still. Hints that this is the case come from the current dependence of the resistance within the transition. This could be fitted very well to a flux-flow type linear current–voltage relation, accompanied by a small quadratic term, i.e. $V = a(I - I_0) + bI^2$ where $a \gg b$, and I_0 was very small (an equivalent current density of 0.17 A cm^{-2}), indicating an extremely low pinning density. This flux-flow-like behaviour was present even with no externally applied magnetic field.

Taking a value of 0.73 T for $B_{c2}(T = 0)$, the coherence length ξ is around 20 nm, which is comparable to the mean free path l, derived from band structure calculations [14].

A requirement for the clean limit, i.e. $\xi \leqslant l$, is another feature of unconventional superconductivity.

The initial slope $B'_{c2} = \partial B_{c2}/\partial T_c$, which is proportional to the electronic effective mass in a clean limit scenario, appears to be larger for a pressure below the T_c maximum, suggesting a critical region close to the emergence of superconductivity. In any case, B'_{c2} reaches values larger than that observed in any other SC element in the periodic table.

4. Conclusions

We have presented four pieces of evidence which support the hypothesis of unconventional pairing in superconducting ε-iron: extreme sensitivity to scattering from disorder; the large upper critical field; an anomalous exponent n in a fit $\rho = \rho_0 + AT^n$ of the resistivity and finally the correlation between the coefficient A and T_c.

Iron is the first simple element to be observed exhibiting non-Fermi liquid behaviour in its resistivity, and to be a candidate for spin-mediated superconductivity.

References

[1] Shimizu K, Kimura T, Furomoto S, Takeda K, Kontani K, Onuki Y and Amaya K 2001 *Nature* **412** 316
[2] Mazin I I, Papaconstantopoulos D A and Mehl M J 2002 *Phys. Rev.* B **65** 100511
[3] Jarlborg T 2002 *Phys. Lett.* A **300** 518
[4] Jarlborg T 2003 *Physica* C **385** 513
[5] Bose S K, Dolgov O V, Kortus J, Jepsen O and Andersen O K 2003 *Phys. Rev.* B **67** 214518
[6] Jaccard D, Holmes A T, Behr G, Inada Y and Onuki Y 2002 *Phys. Lett.* A **299** 282
[7] Grosche F M, Pfleiderer C, McMullan G J, Lonzarich G G and Bernhoeft N R 1995 *Physica* B **206/207** 20
    Pfleiderer C 2003 *Acta Phys. Pol.* B **34** 679
[8] Cohen R E 2003 *Preprint* cond-mat/0301615
[9] Wang F M and Ingalls R 1998 *Phys. Rev.* B **57** 5647
[10] Taylor R D, Pasternak M P and Jeanloz R 1991 *J. Appl. Phys.* **69** 6126
[11] Bohnenkamp U, Sandström R and Grimvall G 2002 *J. Appl. Phys.* **92** 4402
[12] Taylor G R, Isin A and Coleman R V 1968 *Phys. Rev.* **165** 621
[13] Millis A J 1993 *Phys. Rev.* B **48** 7183
[14] Jarlborg T 2002 personal communication