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Superconducting phase diagram of the filled skutterudite PrOs$_4$Sb$_{12}$

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We present new measurements of the specific heat of the heavy fermion superconductor PrOs$_4$Sb$_{12}$, on a sample which exhibits two sharp distinct anomalies at $T_{c1} = 1.89$K and $T_{c2} = 1.72$K. They are used to draw a precise magnetic field-temperature superconducting phase diagram of PrOs$_4$Sb$_{12}$ down to 350 mK. We discuss the superconducting phase diagram of PrOs$_4$Sb$_{12}$ and its possible relation with an unconventional superconducting order parameter. We give a detailed analysis of $H_{c2}(T)$, which shows paramagnetic limitation (a support for even parity pairing) and multiband effects.

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I. INTRODUCTION

The first Pr-based heavy fermion (HF) superconductor PrOs$_4$Sb$_{12}$ ($T_c \sim 1.85$K) has been recently discovered. Evidence for its heavy fermion behavior is provided mainly by its superconducting properties, like the height of the specific heat jump at the superconducting transition or the high value of $H_{c2}(T)$ relative to $T_c$. PrOs$_4$Sb$_{12}$ is cubic with $T_h$ point group symmetry, and has a nonmagnetic ground state, which in a single ion scheme can be either a $\Gamma_{23}$ doublet or a $\Gamma_1$ singlet, a question which remains a matter of controversy. Presently, most measurements in high field seem to favor a singlet ground state, $\Gamma_1$. In any case, whatever the degeneracy of this ground state, the first excited state (at around 6K) is low enough to allow for an induced electric quadrupolar moment on the Pr$^{3+}$ ions, that could explain the heavy fermion properties of this system by a quadrupolar Kondo effect. Thus, while the pairing mechanism of usual HF superconducting compounds (U or Ce-based) could come from magnetic fluctuations, the superconducting state of PrOs$_4$Sb$_{12}$ could be due to quadrupolar fluctuations. Yet at present, this attractive hypothesis is backed by very few experimental facts, both as regards the evidence of a quadrupolar Kondo effect in the normal phase and as regards the pairing mechanism in the superconducting state. Even the question of the unconventional nature of its superconductivity is still open. Indeed, several types of experiments have already probed the nature of this superconducting state, but with apparently contradictory results. Concerning the gap topology, scanning tunneling spectroscopy measurements point to a fully open gap, with some anisotropy on the Fermi surface. Indication of unconventional superconductivity might come from the distribution of values of the residual density of states (at zero energy) on different parts of the sample surface. This could be attributed to a pairing breaking effect of disorder. The same conclusion as regards the gap size was reached by $\mu$SR measurements and NQR measurements, although unconventional superconductivity is suggested in the latter case by the absence of a coherence peak below $T_c$ in $1/T_1$.

This should be contrasted with recent penetration depth measurements, that would indicate point nodes of the gap, or the angular dependence of the thermal conductivity which suggests an anisotropic superconducting gap with a nodal structure. This latter measurement also suggests multiple phases in the temperature ($T$) - field ($H$) plane, which could be connected to the double transitions observed in zero field. Recent $\mu$SR relaxation experiments detected a broadening of the internal field distribution below $T_c$, suggesting a multi-component order parameter or a non unitary odd parity state, with a finite magnetic moment.

In this context, our results bring new insight on the question of the parity of the order parameter, and draw a definite picture of the (H,T) phase diagram as deduced from specific heat measurements. With reference to the historical case of UPt$_3$, we emphasize that the present status of sample quality may explain the discrepancies between the various measurements: definite claims on the nature of the superconducting state in PrOs$_4$Sb$_{12}$ are at the very best too early, the key point being the sample quality.

II. EXPERIMENTAL DETAILS

We present results on single crystals of PrOs$_4$Sb$_{12}$ grown by the Sb flux method. These samples are aggregates of small single crystals with well developed cubic faces. They have a good RRR of about 40 (between room temperature and 2K), a superconducting transition (onset of $C_p$ or $\rho$) at 1.887 K and, they present a very sharp double superconducting transition in the specific heat.
Two different techniques have been used for the specific heat measurements. The first is a quasi-adiabatic method with a Au/Fe-Au thermocouple controlled by a superconducting quantum interference device (SQUID) in a $^3$He calorimeter. It is well suited to quantitative studies in zero field (the addenda are precisely known), and was used on samples with a total mass of 8 mg. The second technique was ac calorimetry, used to follow the superconducting transitions under magnetic field in order to draw a complete phase diagram of the two superconducting transitions. This ac calorimetry uses a strain gauge heater (PtW alloy), a sensitive SiP thermometer (silicon doped with phosphorus close to the critical concentration of the metal-insulator transition), and a long gold wire (25 µm diameter) as a heat leak. For the ac method, we choose a frequency of 0.04 Hz and a large integration time of 350 s. The SiP thermometer is measured with a four lead resistance bridge at 500 Hz, whose analog output is sent to the lock-in detection. The heating power was chosen so that the SiP temperature oscillations remain smaller than 6 mK in order to avoid broadening of the transitions. Thermometry under field was controlled by thermometers located in the (zero field) compensated region of the magnet.

III. SPECIFIC HEAT RESULTS

Figure 2 displays the specific heat $C_p(0, T)/T$ of 3 samples of the same batch measured together, of total mass 8 mg. The inset of fig. 2 is the ac specific heat $C_p(0, T)$ of one of these three samples (hereafter called sample n°1). As it has been previously observed, PrOs$_4$Sb$_{12}$ shows a Schottky anomaly with a maximum in $C_p/T$ near $T = 2.2 K$. Absolute values of $C_p/T$ are the highest ever reported: at $T = 1.7 K$, $C_p/T = 3.65 J/K^2 mol$ and at $T = 2 K$, $C_p/T = 2.9 J/mol.K^2$. Sample n°2 has a well defined double transition: to our knowledge, it is the sharpest ever reported in the literature, although we are aware of similar (yet unpublished) results by Y. Aoki on samples grown in the same group. The width of the two transitions was estimated to be 16 mK and 58 mK, with respectively $T_{c1} = 1.716 K$ and $T_{c1} = 1.887 K$ (with the junction criterion).

Shown in fig. 2 and fig. 3 are the ac specific heat measurements $C_p/(H, T)$ at, respectively, constant magnetic field ($T_{c1} \geq 1.16 K$) and constant temperature ($T_{c1} \leq 1.15 K$) of the same sample n°1. The normal state specific heat, or an arbitrary line between the two transitions, has been subtracted for the temperature or field sweeps respectively. Even under field, the transitions remain very sharp, so that we were able to detect them down to 350 mK and to draw a precise phase diagram (Fig. 3). The width of the two transitions does not exceed $\Delta H_{c2} = 80 mT$ and $\Delta H' = 50 mT$ at 500 mK.

The phase diagram has the same features as reported by Tayama et al. from magnetization measurements. The advantage of specific heat is to give an unambiguous signature of a bulk phase transition, that cannot be confused with other physical phenomena like peak-effect. The two transition lines remain almost parallel and we will see that they can be deduced from each other simply by scaling $T_c$. 

V. PHASE DIAGRAMS

The advantage of specific heat is to give an unambiguous signature of a bulk phase transition, that cannot be confused with other physical phenomena like peak-effect. The two transition lines remain almost parallel and we will see that they can be deduced from each other simply by scaling $T_c$. 

![Fig. 1](image1.png) FIG. 1: Specific heat of samples of the same batch including sample n°1 as $C_p/T$ versus $T$ at zero field measured with a quasi-adiabatic method. The inset is a zoom on the double superconducting transition of sample n°1 measured with an ac method: $T_{c1} = 1.887 K$ and $T_{c2} = 1.716 K$.

![Fig. 2](image2.png) FIG. 2: Temperature sweeps of the ac specific heat of sample n°1 at several fields below 1.4 T. The normal state was subtracted. The arrows indicate the double transition $T_{c1}$ and $T_{c2}$. 

![Fig. 3](image3.png) FIG. 3: Phase diagram of the two superconducting transitions, has been subtracted for the temperature or field sweeps respectively. Even under field, the transitions remain very sharp, so that we were able to detect them down to 350 mK and to draw a precise phase diagram (Fig. 3). The width of the two transitions does not exceed $\Delta H_{c2} = 80 mT$ and $\Delta H' = 50 mT$ at 500 mK.

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![Fig. 4](image4.png) FIG. 4: Phase diagram of the two superconducting transitions, has been subtracted for the temperature or field sweeps respectively. Even under field, the transitions remain very sharp, so that we were able to detect them down to 350 mK and to draw a precise phase diagram (Fig. 3). The width of the two transitions does not exceed $\Delta H_{c2} = 80 mT$ and $\Delta H' = 50 mT$ at 500 mK.
FIG. 3: Field sweeps of the ac specific heat of sample n°1 at several temperatures. An arbitrary line between the two transitions was subtracted. We follow the two transitions ($H_{c2}$ and $H'$) down to 350 mK.

FIG. 4: $H - T$ superconducting phase diagram of PrOs$_4$Sb$_{12}$ determined by specific heat measurements on sample n°1. The field dependence of $T_{c1}$ and $T_{c2}$ are completely similar. The lines are fits by a two-band model of the upper critical field (Section V B 2). Only $T_c$ has been changed from $H_{c2}$ to $H'$.

IV. SAMPLE CHARACTERIZATION

Three pieces of sample n°1 have been used for further characterizations, called 1a, 1b and 1c. As well as the specific heat of sample n°1a (2 mg), we have measured the resistivity of samples n°1b (0.2 mg) and n°1c, and the ac susceptibility and dc magnetization of samples n°1a and n°1b.

Concerning the specific heat, the high absolute value of $C_p$ as well as the large height of the two superconducting jumps ($\Delta(C_p/T) = 350$ mJ/mol.K$^2$ at $T_{c1}$ and $\Delta(C_p/T) = 300$ mJ/mol.K$^2$ at $T_{c2}$) must be linked to the high quality of these samples (absence of Sb-flux and/or good stoichiometry). Moreover, the heights of the two steps of sample n°1a are quantitatively similar to those of the entire batch (7.5 mg) as Vollmer has already pointed out.

Like in previous work, we have noticed that the resistivity at 300K is very sample dependent (from 200 to 900 $\mu\Omega$.cm). On all samples, the value of $\rho$ at 300 K seems to scale with the slope at high temperature ($T \geq 200$K), i.e. the phononic part of the resistivity, as if the discrepancies were due to an error on the geometric factor. This error could be explained by the presence of microcracks in the samples. We have taken this problem into account by normalizing all data to the slope at high temperature ($T \geq 200$K) of sample n°1c, chosen arbitrarily. For samples n°1b and n°1c respectively (Fig. 3), the RRR (ratio between 300K and 2K values) are 44 and 38, the onset $T_c$ are 1.899 K and 1.893 K (matching the critical temperature obtained by specific heat), and the temperatures of vanishing resistance ($T_{R=0}$) are 1.815 K and 1.727 K. $T_{R=0}$ of sample n°1c is equal to $T_{c2}$ and this remains true under magnetic field. So, in sample n°1c, the resistive superconducting transition is not complete between $T_{c1}$ and $T_{c2}$.

Figure 3 shows the superconducting transition for samples n°1a and n°1b by ac-susceptibility ($H_{ac} = 0.287$Oe), corrected for the demagnetization field. The onset temperature is the same for the two samples (1.88K). The transition is complete only at around 1.7K and two transitions are visible. The field cooled dc magnetization of samples n°1a and n°1b ($H_{dc} = 10$Oe), shown in fig. 3, gives a Meissner effect of, respectively, 44% and 55%, indicating (like specific heat) that the superconductivity is bulk. The two transitions are also visible.

V. DISCUSSION

A. Double superconducting transition

Let us first discuss the nature (intrinsic or not) of the double transition observed in our specific heat measurements. The remarkable fact, compared to previous reports, is the progress on the sharpness of both transitions. If for previous reports, a simple distribution of $T_c$ due to a distribution of strain in the sample could
have explained the transition width, it is not the case anymore for the sharp features observed on these new samples. Also the explanation recently proposed that the lower transition at \( T_{c2} \) would be induced by Josephson coupling of one sheet of the Fermi surface to another with transition temperature \( T_{c1} \) is excluded, owing to the sharpness of both transitions and particularly of that at \( T_{c2} \): see the broadening calculated by the authors for the Josephson induced transition. Nevertheless, some of our results still cast serious doubts on the intrinsic nature of the double transition. Indeed, the susceptibility also shows a "double" transition, and resistivity becomes zero only at \( T_{c2} \). If the first transition at \( T_{c1} \) was bulk-homogeneous, the resistivity should immediately sink to zero below \( T_{c1} \), and the susceptibility (\( \chi \)) should also show perfect diamagnetism far before \( T_{c2} \): the sample diameter is at least 1000 times larger than the penetration depth (\( \lambda \)) so that the temperature dependence of \( \lambda \) cannot explain such a transition width of \( \chi \) (contrary to the statements of E.E.M. Chia). So both resistivity and susceptibility are indicative of remaining sample inhomogeneities.

Nevertheless, in our opinion, even the comparison of the various characterizations of the superconducting transition by resistivity, susceptibility and specific heat on the same sample does not allow for a definite conclusion.

Two historical cases are worth remembering. URu\(_2\)Si\(_2\) showed a double transition in the specific heat in some samples, with inhomogeneous features detected in the susceptibility. In that case, the authors of reference could clearly show that it was not intrinsic (maybe arising from internal strain?) because different macroscopic parts of the same sample showed one or the other transition. In PrOs\(_4\)Sb\(_{12}\), the specific heat results are reproducible among various samples of the same batch (see samples \( n^1 \) and \( n^1a \) of the present work), and such an easy test does not work.
The second case is of course UPt₃: it is now well established that the two transitions observed in zero field are intrinsic and correspond to order parameters of different symmetries. But the first results on samples that were not homogeneous enough showed exactly the same behaviour as the present one in PrOs₄Sb₁₂: two features in the susceptibility and a very broad (covering both transitions) resistive transition. It was not until the sample quality improved significantly that resistivity and susceptibility transitions matched the higher one. The puzzling result for PrOs₄Sb₁₂, compared to UPt₃, is that despite the sharpness of the specific heat transitions, resistivity and susceptibility reveal inhomogeneities, which means that this new compound probably has unusual metallurgical specificities.

Continuing the parallel with UPt₃, basic measurements rapidly supported the intrinsic origin of the two transitions: they were probing the respective field and pressure dependence of both transitions. Indeed, a complete (H-T) phase diagram was rapidly drawn, showing that in UPt₃, like in U₁₋ₓThₓBe₁₂, the two transitions observed in zero field eventually merged under magnetic field, due to a substantial difference in \(dT_c/dH\). It is even more true for the pressure dependence of \(T_{c1,2}\), as the thermal dilation has jumps of opposite sign at the two transitions, indicating opposite variations of \(T_{c1,2}\) under pressure (Ehrenfest relations). So in this compound, the two transitions could be rapidly associated with a change of the symmetry of the order parameter indicating the unconventional nature of the superconducting state.

We are not so lucky in the case of PrOs₄Sb₁₂: indeed, the field dependence of \(T_{c2}\) seems completely similar to that of \(T_{c1}\) (fig. 4), a claim that will be made quantitative below. It is the same situation as in URu₂Si₂ and nothing in favor of an intrinsic nature of the double transition can be deduced from this phase diagram. Another phase diagram has already been established by transport measurements, with a line \(H^*(T)\) separating regions of twofold and fourfold symmetry in the angular dependence of thermal conductivity under magnetic field. It may seem likely that this line would merge with the double transition in zero field. From the line \(H^*(T)\) drawn from our specific heat measurements (\(T_{c2}(H)\), fig. 5), we can conclude that this is not the case: \(H^*(T)\) does not match the line \(H^*(T)\) drawn in reference, unless there is an unlikely strong sample dependence of these lines.

Comparison of the pressure dependence of \(T_{c1}\) and \(T_{c2}\) seems more promising: contrary to case of UPt₃, the jump of the thermal expansion at the \(T_{c1}\) superconducting temperatures does not change sign, but from the relative magnitude of these jumps and our specific heat peaks, we get a value \(dT_{c1}/dp \approx -0.2K/GPa\), and twice as much for \(dT_{c2}/dp\). This supports a different origin for both transitions. The weak point is that the thermal expansion measurements were done on two samples mounted on top of each other, that were early samples with rather broad specific heat transitions. Thus, the question of the intrinsic nature of the double superconducting transition remains open.

### B. Upper critical field

Another quantity which has not been thoroughly discussed is the upper critical field \(H_{c2}(T)\). In heavy fermion superconductors, \(H_{c2}(T)\) has always proved to be an interesting quantity, mainly due to the large mass enhancement of the quasiparticles. Indeed, the usual orbital limitation is very high in these systems, due to the low Fermi velocity, so that the authors of reference could, from their \(H_{c2}(T)\) data, confirm the implication of heavy quasiparticles in the Cooper pairs (revealed also by the specific heat jump at \(T_c\)). They also gave an estimate of the heaviest mass: \(\approx 50m_0\), where \(m_0\) is the free electron mass.

But, as the orbital limitation is very high, \(H_{c2}(T)\) is also controlled by the paramagnetic effect. A quantitative fit of \(H_{c2}(T)\) easily gives the amount of both limitations, except that on this system, \(H_{c2}(T)\) has an extra feature: a small initial positive curvature close to \(T_c\). This feature has been systematically found, whatever the samples and the techniques used to determine \(H_{c2}(T)\) (\(\rho, \chi\) and \(C_p\)). Our data, obtained by \(\rho\) on sample \(n^1c\) and \(C_p\) on sample \(n^12\), matches all other published results. So we can now consider this curvature of \(H_{c2}(T)\) as intrinsic, and not due to some artifact of transport measurements, or coming from inhomogeneity in the sample. Such an intrinsic positive curvature also appears in MgB₂ or in borocarbides like YNi₂B₂C and LuNi₂B₂C.

#### 1. Physical inputs

We propose an explanation based on different gap amplitudes for the different sheets of the Fermi surface of PrOs₄Sb₁₂, which is made quantitative through a "two-band" model. Microscopically, STM spectroscopy also reveals an anisotropic gap, with zero density of states at low energy (fully open gap) but a large smearing of the spectra. Recent microwave spectroscopy measurements also discuss a two band model, but in order to explain the double transition. We insist that our model has nothing to do with the double transition, which clearly involves heavy quasiparticles both at \(T_{c1}\) and at \(T_{c2}\) (see the size of the two specific heat jumps): our aim is a quantitative understanding of \(H_{c2}(T)\), based on the normal state properties of PrOs₄Sb₁₂, as in MgB₂ or borocarbides where no double transition has ever been observed. The physical input of a multi-band model for \(H_{c2}(T)\) is to introduce different Fermi velocities and different inter- and intra band couplings. As a result, \(T_{c}\) is always larger than for any of the individual bands. The slope of \(H_{c2}\) at \(T_c\) is larger for slower Fermi velocity (heavier) bands. Positive curvature of \(H_{c2}(T)\) is easily obtained.
if the strongest coupling is in the heaviest bands (large $H_{c2}$), with a slight $T_c$ increase due to the inter band coupling to the lightest bands (small initial slope)\[54x-491\].

2. The two-band model:

There are at least three sheets for the Fermi surface of PrOs$_4$Sb$_{12}$, but in the absence of a precise knowledge of the pairing interaction, a full model would be unrealistic, having an irrelevan number of free parameters. A two band model is enough to capture the physics of anisotropic pairing, although only the correspondence with band calculations becomes looser. In our model, band 2 would correspond to the lightest ($\beta$) band detected by de-Haas van Alphen measurements, and band 1 would be a heavy band having most of the density of states. Indeed, the de Haas-van Alphen experiments on PrOs$_4$Sb$_{12}$ reveal the presence of light quasiparticles (band $\beta$) and heavier particles (band $\gamma$). The heaviest quasiparticles are at present only seen by thermodynamic measurements ($C_p$ or $H_{c2}$). Anisotropic coupling between the quasiparticles is considered in the framework of an Eliashberg strong coupling two-band model in the clean limit, with an Einstein phonon spectrum (characteristic "Debye" frequency $\Omega$). Let us point out that the results do not depend on (and a fortiori do not probe) the pairing mechanism, which is likely to be much more exotic than the usual electron-phonon mechanism. Compared to a single band calculation, there is now a matrix of strong coupling parameters $\lambda_{i,j}$ describing the diffusion of electrons of band $i$ to band $j$ by the excitations responsible for the pairing.

What matters for $H_{c2}(T)$ is the relative weight of the $\lambda_{i,j}$, not their absolute value: we consider $T_c$ or the renormalized Fermi velocities as experimental inputs. $\lambda_{i,j}$ depends both on the interaction matrix elements between bands $i$ and $j$, and on the final density of states of band $i$, $\lambda_{1,j}$. In MgB$_2$, it is claimed that electron-phonon coupling is largest within the $\sigma$ bands. Here, knowing nothing about the pairing mechanism, we assume constant inter and intra band coupling, so that the relative weight of the $\lambda_{i,j}$ is only governed by the density of states of band $j$. This density of states is itself proportional to the contribution of that band to the specific heat Sommerfeld coefficient $\gamma$, except $\Omega$, adjusted to give $T_c=1.716$K. There is a good agreement with all data except at very low temperature or near $T_c$ where the curvature is reduced compared to $H_{c2}(T)$. However, these deviations are weak, and this is why we claim that $H'(T)$ has the same behavior as $H_{c2}(T)$, which does not help to identify the second transition with a symmetry change of the superconducting order parameter.

3. Interpretation

Shown also in fig. are the calculations of $H_{c2}(T)$ for a single band model: $v_F$, the characteristic frequency $\Omega$ and $\lambda_{i,j}$ have the same values as before, but all other $\lambda_{i,j}$ coefficients have been turned down to zero, eliminating the effects of the light electron band. $T_c$ is then reduced (down to 1.78 K) and the positive curvature disappears. We also observe that the fit of $H_{c2}$ is basi-
cally unchanged above 1 T, meaning that low fields suppress the superconductivity due to the light electron band restoring a "single band" superconducting state. This is the same effect observed more directly in MgB$_2$ with specific heat measurements under magnetic field: the smaller gap rapidly vanishes, leading to a finite density of states at the Fermi level under magnetic fields due to the $\pi$ band. This suppression of the light quasiparticle superconductivity would have here an effect on specific heat too small to be observed (contribution of the light quasiparticles to the specific heat of order $4\%$). But it may have much larger effects on transport. Let us note that the clean limit is a posteriori justified: from experiments performed at high field, we find a coherence length $\xi_0 \sim 110\AA$, whereas from a residual resistivity $\rho_0$ and specific heat coefficient $\gamma \sim 0.5J/K^2/mol\sim 2.10^3 J/K^2.m^3$, we get $v_F l \sim \frac{3L_0}{\rho_0} \sim 2.10^{-3} m^2/s$ yielding a mean free path $l \sim 1300 \AA > 10\xi_0$.

More interestingly, the quantitative fit of $H_{c2}$ also allows a discussion of the purity of the order parameter in PrOs$_4$Sb$_{12}$. Indeed, like other heavy fermion superconductors, despite the low-$T_c$ value, $H_{c2}$ can be sensitive to the Pauli limit in case of singlet pairing. The fit in fig. 3 includes this paramagnetic limitation, with the conventional free electron value for $g$ ($g = 2$). Also shown in fig. 3 is the calculation of $H_{c2}(T)$ with the same parameters but for $g = 0$, i.e. without any paramagnetic limit. The strong deviations observed demonstrate that the paramagnetic effect controls $H_{c2}$ at low T in PrOs$_4$Sb$_{12}$. Quantitatively, the paramagnetic effect depends on the coupling strength. Yet, we choose arbitrarily $\lambda = 1$. A rather strong coupling regime is supported by NQR experiments. Even for a weak coupling picture ($\lambda = 0.6$), the fit yields $g = 1.55$. In both cases, the paramagnetic limit remains important, supporting a singlet nature of the superconductivity, contrary to what had been suggested in previous works and in agreement with the supposition in fig. 4. This result should be quite robust, independent of the two band model. It could be invalidated if the mass renormalization mechanism was field dependent, which could be an explanation for the difference in the large specific heat Sommerfeld coefficient obtained in low field, and the de Haas-van Alphen measurements performed at high field. In such a case, the "saturation" of $H_{c2}(T)$ at low temperature could arise from a reinforcement of the orbital limitation alone.

VI. CONCLUSION

To conclude, we have drawn a very precise superconducting phase diagram of PrOs$_4$Sb$_{12}$ down to 350 mK, by a specific heat measurement. We have yet no clear evidence of the unconventional nature of the superconducting order parameter from this phase diagram. The superconducting phase diagram with the symmetry change of the order parameter drawn by K. Izawa et al. from transport measurements does not seem related to the double transition observed with specific heat measurements. Despite the high quality of the sample, we cannot completely exclude that there are still two parts with different $T_c$ in our sample, as $H^c(T)$ is just scaled from $H_{c2}$ with respect to $T_c$. The puzzling result is that despite sharp specific heat transitions, inhomogeneities are still present in the samples. This calls for caution in the claim of various types of nodes of the gap by different sophisticated techniques: the most urgent task is to understand the problem of sample quality. Contrarily, the upper critical field is very reproducible, independent of samples and types of measurements. It has been analyzed with a strong coupling two-band model taking account of the spread in the effective masses of the quasi-particles and of the pairing strength as suggested also by STM spectroscopy measurements. The strong influence of the paramagnetic limit on $H_{c2}$ is the first experimental argument for a singlet superconducting order parameter.

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