Double superconducting transition in the filled skutterudite \( \text{PrOs}_4\text{Sb}_{12} \) and sample characterizations

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A thorough characterization of many samples of the filled skutterudite compound \( \text{PrOs}_4\text{Sb}_{12} \) is provided. We find that the double superconducting transition in the specific heat \( (T_{c1} \sim 1.89 \text{ K} \) and \( T_{c2} \sim 1.72 \text{ K} \) tends to appear in samples with a large residual resistivity ratio, large specific heat jump at the superconducting transition and with the highest absolute value of the specific heat above \( T_{c1} \). However, we present evidence which casts doubt on the intrinsic nature of the double superconducting transition. The ratio of the two specific heat jumps \( \Delta C(T_{c2})/\Delta C(T_{c1}) \) shows a wide range of values on crystals from different batches but also within the same batch. This ratio was strongly reduced by polishing a sample down to \( 120 \mu \text{m} \). Remarkably, three samples exhibit a single sharp transition of \( \sim 15 \text{ mK} \) in width at \( T_c \sim 1.7 \text{ K} \). The normalized specific heat jump \( C−C_{\text{normal}}/C_{\text{normal}} \) of two of them is higher than \( \sim 32\% \) so larger than the sum of the two specific heat jumps when a double transition exists. As an evidence of better quality, the slope in the transition is at least two time steeper. We discuss the origins of the double transition; in particular we consider, based on X-ray diffraction results, a scenario involving Pr-vacancies. The superconducting phase diagram under magnetic field of a sample with a single transition is fitted with a two-band model taking into account the good values for the gap as deduced from thermal conductivity measurements.

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I. INTRODUCTION

Since the discovery of the first Pr-based heavy fermion superconductor \( \text{PrOs}_4\text{Sb}_{12} \) \( (T_c \sim 1.85\text{K}) \) by Bauer et al., this system has attracted much attention with particular emphasis on the possible unconventional nature of superconductivity. A significant piece of the evidence for unconventional superconductivity is the double superconducting transition seen in specific heat first reported in 2003 by Vollmer et al. and Maple et al. Ever since, a plethora of publications have dealt with its observation and with possible theories. This double transition has since been observed by specific heat measurements by many groups (from Japan, USA, Germany, France) and by thermal expansion with samples from different origins and even in La doped or Ru substituted samples. So whatever the origin, the double transition is a robust property of this compound and we will see that it appears in good samples.

However susceptibility measurements on a sample with a very clear double superconducting transition induced the first doubts about its microscopic origin. Indeed even in this good sample, the diamagnetism is not perfect at \( T_{c1} \), the highest superconducting transition temperature, and a second step at \( T_{c2} \), the lowest one, is visible. This caused us to look more closely at other evidence for a microscopic origin, including the magnetic field, and pressure dependences of the double transition. The phase diagram under magnetic field didn’t bring evidence for its intrinsic nature since the field dependence of \( T_{c2} \) is completely similar to that of \( T_{c1} \). The shape of \( H_{c2}(T) \) can be quantitatively understood with a two-band model and indeed the same model simply scaled with \( T_c \) has been used to fit both lines. The behavior of \( T_{c1}−T_{c2} \) under pressure is also not conclusive. At low pressure, the slope \( \partial T_{c1}/\partial P \) is at least 20% smaller than
\(\partial T_{c2}/\partial P\). However, above 1 GPa the behavior of the two transitions is similar, with \(T_{c1} - T_{c2}\) stabilizing around 200 mK. These results do not rule out an intrinsic origin but certainly provide no supporting evidence towards it, (contrary to the well documented case of UPt₃ where the different field and pressure dependences of the two transitions were decisive results).

We report here on a study of the nature of the double superconducting transition of PrOs₄Sb₁₂. Our main purpose is to clarify whether the double superconducting transition which appears in specific heat is intrinsic, like it is now admitted for UPt₃ or extrinsic, due to sample inhomogeneities, as shown for URu₂Si₂ and high-\(T_c\) superconductor YBa₂Cu₃O₇. We discuss this point from systematic characterizations by resistivity, specific heat and susceptibility measurements. From general characterizations, we conclude that the double transition appears in good samples. But an extensive study particularly of many small samples provides evidence which brings strong doubts about its microscopic origin; the most convincing one is the existence of three samples with a single sharp superconducting transition with a \(T_c\) matching \(T_{c2}\). Then we present the single crystal x-ray diffraction results. Finally we show the first measurement of the phase diagram under magnetic field for a sample with a single sharp superconducting transition, and a fit of the upper critical field with a two band model.

We would like first to introduce some criteria we will use in this paper. Figure 1 provides the main criteria depending on the kind of superconducting transition (double, single and broad, or single and sharp), i.e. the superconducting transition \(T_{c1}, T_{c2}\) and \(T_c\) obtained on the onset, the specific heat jumps \(\Delta(C/T)_1\) at \(T_{c1}\), \(\Delta(C/T)_2\) at \(T_{c2}\) and \(\Delta(C/T)\) for the whole jump, the width of the transition \(\Delta(T_{c1})\) at \(T_{c1}\), \(\Delta(T_{c2})\) at \(T_{c2}\) or \(\Delta(T_c)\) when a single transition appears, and the slope in the transition \(a\). This last criterion appears more relevant than the simple width of the transition when we compare one of the jumps in the double transition with a single sharp jump, which is probably two times higher. The residual resistivity ratio \(RRR\) is always measured between 300 K and 2 K.

**II. GENERAL CHARACTERIZATIONS**

The crystals of PrOs₄Sb₁₂ were grown by the Sb flux method by 3 separate groups (P. Canfield, H. Sugawara and G. Lapertot, respectively labelled C, S and L). The first number indicates the batch. When there were 2 different samples from the same batch we add an extra index. The crystals from P. Canfield and G. Lapertot were separated from flux by a hot spinning process. Remaining flux droplets were dissolved in hydrochloric/water solution. The samples used in ref. are respectively labelled S1, L1-1A, S3, L1-6.

The specific heat \((C)\) measurements were performed in a \(^3\)He calorimeter either by a quasi-adiabatic method.
with a Au/Fe-Au thermocouple controlled by a superconducting quantum interference device (SQUID) or by a heat-pulse relaxation technique using a Physical Property Measurement System (PPMS) from Quantum Design.

Figure 2 presents the specific heat of several samples of PrOs$_3$Sb$_{12}$. Their absolute values at 2 K differ strongly, varying from 2.06 J/K$^2$.mol to 2.94 J/K$^2$.mol and can vary on the samples in the same batch (see samples L2-1 and L2-2). Other published results report absolute values at 2 K between 1.3 J/K$^2$.mol and 3.2 J/K$^2$.mol. This discrepancy cannot be explained only by the presence of trapped Sb flux. The specific heat broad peak at 2 K is mainly due to the Schottky term due to the presence at $\sim$ 8K of the first crystalline electric field (CEF) excited level of the 4f$^2$ Pr states, $\Gamma_4^{(2)}$, above the singlet ground state $\Gamma_1$. As we point out to possible Pr-vacancies in the structure (see section III.B), we propose that the samples dependence of the specific heat is partly due to these Pr-vacancies. Quantizing the necessary percentage of vacancies to fit the curves is a difficult task. Indeed, some distortions may appear with Pr-vacancies and they may change locally the CEF, which broaden the Schottky term. Moreover the interactions between Pr ions are quite strong as shown by the dispersion of the inelastic spectrum in wavevectors, so the consequence of the Pr-vacancies cannot be reproduced by a pure local model. Roughly a maximum of 10% of Pr-vacancies is required to fit the specific heat of sample L3-1 to L1-1. No upturn due to the nuclear Schottky anomaly except a small feature for the samples of batch C1, was observed, at least above 0.4 K. We also note that no anomaly was detected at 0.6 K, temperature at which several experiments report a change of behavior.

The double superconducting transitions for several samples are shown in the zoom of Fig. 2 (see insert). The shape of the double transition of samples from different origins (L1-1 and S1-2) is similar but is quite different from sample L3-1 with similar $T_c$ and even larger deviations are found from sample L2-2 both in absolute value of $C$ and in value of $T_c$. The sample dependence of the shape of the double transition will be discussed in detail in section III.

We discuss now the link between the appearance of the double transition and sample quality. Figure 3 shows the superconducting transition temperatures determined by specific heat and resistivity measurements versus the residual resistivity ratio. In both cases $T_c$ was obtained from the onset criterion. When the specific heat and the resistivity were not measured on the same sample (which was often the case), the $RRR$ values taken are an average for the batch. As the spread of the $RRR$ is large (for instance the $RRR$ of batch L1 is included between 17 and 33.8), only a general tendency can be extracted. However it is quite clear that $T_{c1}$ increases slightly with the $RRR$ (its minimum and maximum values are respectively 1.805 K and 1.897 K) whereas $T_{c2}$ is strongly sample dependent. All the smaller $T_{c2}$ at about 1.5 K were reported from samples belonging to batch L2. The large circle indicates all the samples with a clear double transition (excluding sample L2-3) and also contains a sample with a single sharp superconducting transition L1-1A. The general tendency is that the double transition appears in the samples with the highest $RRR$.

Figure 4(a) shows the absolute value of $C$ on the Schottky anomaly at 2 K against the $RRR$. The highest the $RRR$ is, the largest the specific heat at 2 K is. Figure 4(b) presents the total jump of the specific heat at the superconducting transition ($\Delta(C/T)$), which is probably the best criterion of the quality of the samples, against the value of $C$ at 2 K. Again, the highest the specific heat jump is, the largest the specific heat at 2 K is. Moreover as indicated by the large circles on Fig. 4(a) and 4(b) which embodies all the samples with a double transition, the double transition seems to be a feature of the samples which meet all these criteria. Samples with a broad single superconducting transition, which $always$ covers the temperature range of the double transition, are clearly of worse quality than the double transition samples.

However, we will present in the next section some characterisations which provide several pieces of evidence against an intrinsic origin of the double transition, specially those carried out on very small samples (with a
III. DOUBLE SUPERCONDUCTING TRANSITION

A. Characterization results

The first doubts about the intrinsic nature of the double superconducting transition came from the results of susceptibility measurements. Indeed no published result shows perfect diamagnetism at $T_{c1}$: the ac susceptibility always exhibits a very broad superconducting transition or a double step matching with $T_{c1}$ and $T_{c2}$ of the specific heat results. All the samples with a double transition we have tested by ac susceptibility ($\chi$), i.e. batches L1, L2, S1, also exhibit a double step matching the specific heat jumps. We report here other stronger doubts, particularly based on the existence of samples with a single sharp superconducting transition. We will compare their quality with those of samples with a double transition.

Table I provides a general view and the main features of all the samples with a double transition or a single sharp superconducting transition we have tested. All of them except S1-1A and L1-1A are as grown (unpolished) samples. All the samples not reported in table I exhibit a single transition with a width larger than the temperature range of the double transition as shown in Fig. 2. The criteria for $T_{ci}$, $\Delta(T_{ci})$, $\Delta(C/T)_i$, $a_{T_{ci}}$ are defined in the Fig. 1.

Before discussing further the characterizations, we focus on our most remarkable finding which is shown in Fig. 5: we measured the specific heat of three samples L1-5, L1-7 and L1-1A with a single sharp superconducting transition (L1-1A has still a tiny jump at 1.80K as well as a small step in resistivity at 1.85K). The specific heat of a sample with a "usual" double transition (L1-1) is also presented. We notice the existence of sample L2-3 with a clear double transition but with a quite reduced $T_{c2}$. L1-5 and L1-7 are very small as-grown platelets with well-developed faces and with a thickness of about 50 $\mu$m. L1-1A has been obtained by polishing a large cube (1 mm) of the sample L1-1 so that the thickness was reduced down to 45 $\mu$m. Their critical temperature $T_c$ is 1.733 K, 1.680 K and 1.745 K, so matching $T_{c2}$ of the samples with a double transition. One of these

typical size of 100 $\mu$m and lighter than 0.1 mg).
Now we compare the quality of these single transition samples with a single sharp transition: L1-5, L1-7 and L1-1A. The superconducting transition of sample L1-5 is the sharpest. For samples L1-5 and L1-1A and relatively to the specific heat of most of the samples is indeterminable (because many samples are too small or were measured by ac calorimetry), we have subtracted the normal part obtained under magnetic field subtracting the background; the specific heat jump is unmeasured.

A large range of ratio of the two specific heat jumps appears. Three samples with a single sharp transition exist: L1-5, L1-7 and L1-1A. The superconducting transition of sample L1-5 is the sharpest. For samples L1-5 and L1-1A and relatively to the specific heat in the normal state, the specific heat jump is higher than the sum of the two specific heat jump in the double transition samples. The slope in the superconducting transition at $T_{c2}$, $a_{T_{c2}}$, increases with decreasing ratio $Δ(ΔC/T_c)/Δ(ΔC/T_c)_1$, reaching the highest values for the 3 samples with a single transition (the transition is even three times steeper for the single transition sample L1-5).

TABLE 1: Main features of the specific heat of the samples with a double superconducting transition or a single sharp transition. To get SI-1A and L1-1A, SI-1 and one piece of L1-1 were respectively polished. Abbreviations are: c.=cube; b.=bar, AoF.C.=aggregate of cubes, p.= platelet; AC=ac calorimetry measurements. The slope at $T_{c1}$, $a_{T_{c1}}$, is taken on the specific heat jump normalized to its normal value. The criteria are indicated in the Fig. 1.

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samples L1-5 was further characterized by single crystal x-ray diffraction, ac susceptibility and resistivity measurements. We confirmed the composition of the sample (see section III.B). For the susceptibility measurement a tiny susceptometer in glass fiber was built to get a good filling ratio. The secondary coil has an external diameter of 500 μm and hole of 300 μm. 440 turns of 14 μm diameter copper wires were wound on each part on the secondary coil. The frequency of the exciting magnetic field of 0.36 mT is about 375 Hz. Ac susceptibility and resistivity results are visible in Fig. 2. From these results, we checked that this sample has a single superconducting transition. Indeed, the susceptibility exhibits no sign of superconductivity above $T_c$. All $T_c$ ($\rho$, $\chi$, $C$) are consistent.

Now we compare the quality of these single transition samples with the samples with a double transition. As the quantitative value of the specific heat of most of the samples is indeterminable (because many samples are too small or were measured by ac calorimetry), we have subtracted the normal part obtained under magnetic field up to 1 T then normalized to this value. We are only able to consider semi-quantitative values because, as we discussed in section II, the absolute value of the specific heat depends strongly on the sample. The ac calorimetry results of samples L1-7 and L1-6 provide only a bottom limit of the normalized specific heat jump as the background was not subtracted. As for the sample L1-5, a semi-quantitative measurement of $C$ (its mass, about 0.1 mg, was too small to be measured precisely) was performed with the PPMS (Cf. figure 3). The most important feature is certainly that the normalized specific heat jump, $Δ(ΔC/T_c)/T_c$, is at least as high as the entire transition of the double transition samples. Indeed even if the smallness of the sample L1-5 implies a noisy specific heat measurements by the PPMS (shown in Fig 3), the specific heat jump at $T_c$ was found to be 33-44% of the normal state specific heat, a value larger than the entire transition of the double transition samples. The conclusion for L1-1A is similar with a $Δ(ΔC/T_c)/T_c$ of 36%. The specific heat of L1-7 was only measured by ac method without subtracting the background; the specific heat jump is underestimated.

As for the width of the transition, sample L1-5 has the sharpest ever measured (16 mK in $\rho$, 17 mK in $C$...
transition. The values obtained for a smaller transition than the steepest transition in the samples with a double transition increases with increasing steepness of the transition at the samples of table I: the ratio $\Delta(C/T)/C/T_{\text{normal}}$.

We think that the transition at $T_{c1}$ is the intrinsic one. Indeed the transition at $T_{c1}$ is always broader and less steep than the transition at $T_{c2}$ (Cf. table I). All the single sharp transition samples exhibit $T_{c}$ lower than 1.8 K for L1-1A. It clearly questions the intrinsic nature of the double transition. Two single transition samples L1-5 and L1-7 were measured by an ac method. Their specific heat jumps are underestimated. The specific heat of sample L1-5 was also determined semi-quantitatively by relaxation method (Cf. figure 5). All features are reported in table I and comparison of the quality of the samples is provided in the text.

and 35 mK in $\chi$). One remarkable feature is that the transition is three times steeper ($a_{T}$, three times larger) than the steepest transition in the samples with a double transition. The values obtained for a may be influenced to some extent by the range of values of $C$ in the normal state, but insufficiently to change this semi-quantitative conclusion. Actually, this tendency is confirmed for all the samples of table I: the ratio $\Delta(C/T)/\Delta(C/T_{\text{normal}})$ decreases with increasing steepness of the transition at $T_{c2}$ reaching zero for the three steepest transitions. This criterion as well as the specific heat jump $\Delta C/C_{T_{c}}$ points to a higher quality of the samples with a single transition.

We think that the transition at $T_{c2}$ is the intrinsic one. Indeed the transition at $T_{c1}$ is always broader and less steep than the transition at $T_{c2}$ (Cf. table I). All the single sharp transition samples have $T_{c}$ lower than 1.75 K whereas even in the worst samples (see Fig. 5) $T_{c1}$ is not smaller than 1.805 K. From this observation, we exclude that the single transition is the transition at $T_{c1}$ shifted to smaller temperature by some impurities effects. It would also be quite surprising that in these single transition samples the transition at $T_{c1}$ simply disappears due to worse quality of the samples; because the single transition should also be broadened and because the thermal conductivity ($\kappa$) measurements clearly point to a higher quality for sample with a single transition called L1-1A ($\kappa/T_{c} \sim 70 \mu W/K^{2}.cm$ at 100 mK) than for a sample which exhibits a large superconducting transition with $T_{c}$ about 1.85 K ($\kappa/T_{c} \sim 250 \mu W/K^{2}.cm$ at 100 mK).

Finally only two points could leave some doubt. First, the RRR of samples L1-5 and L1-1A are respectively 26 and 30 whereas the largest value we have got (43) is in a double transition sample (S1-1). Of course, the resistivity is not a probe of the whole volume of the sample. For instance, sample S1-1 exhibits a sharp superconducting transition in resistivity ($\rho=0$ at 1.82 K) but two steps in $\chi$ matching with $T_{c1}$ and $T_{c2}$. Moreover we cannot exclude that another parameter, such as remaining flux or Pr-vacancies, has the opposite effect on the RRR. Secondly, if we assume that the intrinsic $T_{c}$ is $T_{c2}$, we can compare $T_{c}$ of the single transition samples with $T_{c2}$ of the double transition samples. It appears that the transition in the single transition samples is shifted to smaller temperature than the transition at $T_{c2}$ of the double transition samples of batch L3 ($T_{c}$ is smaller than $T_{c2}$ and the transition in batch L3 is not much broader). One can argue that the parts of the sample with different $T_{c}$ may be affected independently by others impurities not related to the appearance of the double transition. This hypothesis...
would also explain the existence of such samples as L2-2 and L2-3 with a $T_{c2}$ 15% smaller than the highest one but with similar $T_{c1}$. Finally, the rareness of the samples with a single sharp transition (to our knowledge, no other observation was reported) is certainly due to their smallness and all the consecutive experimental difficulties.

Of course ruling out the existence of an intrinsic double transition doesn’t imply that its superconductivity is conventional. In particular, following the idea that $T_{c2}$ is the intrinsic transition, its strong sample dependence (1.76 K for L3-1, 1.71 for S1-1, 1.68 for L1-7 and 1.53 K for L2-2, i.e. a dispersion of 15%) might point to unconventional superconductivity. Nevertheless this observation must be carefully investigated as the dispersion of $T_{c1}$ is only of 5% for all our samples.

So we have accumulated evidence for an extrinsic double superconducting transition in PrOs$_4$Sb$_{12}$. Thus, in addition to account for the two steps visible in magnetic or resistivity results, the presence of normal part in the sample above $T_{c2}$ would explain the highest temperature minima in flux flow resistance reported in reference\textsuperscript{\ref{22}}.

It happens that a definitive conclusion may emerge from a quantitative measurement of the specific heat of a single transition sample, specially by validating our semi-quantitative observation that the single jump at $T_c$ is higher than the sum of the two jumps in the double transition samples. But finding the origin of the extrinsic superconducting transition would provide the definitive answer.

B. Origin of the Double superconducting transition:

As discussed above, the low temperature superconducting transition $T_{c2}$ seems to be the intrinsic one. So a simple random-impurity-induced pair breaking mechanism cannot be responsible for the appearance of the extrinsic transition which occurs at higher temperature ($T_{c1}$) and, whatever the intrinsic transition is at $T_{c1}$ or $T_{c2}$, the narrowness of the lowest-temperature jump rules out this hypothesis, since such an effect would simultaneously broaden and lower $T_c$. So it is not surprising that annealing the sample has no effect on the double transition\textsuperscript{\ref{23}}. We note that this case is not isolated in the history of heavy fermions superconductors. The double transition of URu$_2$Si$_2$ was ruled out by Ramirez et al\textsuperscript{\ref{24}} by isolating the lowest $T_c$ phase when removing the surface of the sample. As for CePt$_3$Si, Kim et al. pointed out to a spurious double transition\textsuperscript{\ref{25}} due to a second phase of Ce$_5$Pt$_{23}$Si$_{11}$, and $T_c$ decreases from 0.75 K to 0.46 K with increasing quality of the sample\textsuperscript{\ref{26}}. Sr$_2$RuO$_4$\textsuperscript{\ref{27}} and CeIrIn$_5$\textsuperscript{\ref{28}} exhibit a much higher $T_c$ in resistivity measurements than on the specific heat results.

Multiple scenario are possible like the existence of an impurity phase very similar to PrOs$_4$Sb$_{12}$ and superconductor at $T_{c1}$, or the presence of twins which enhance $T_{c2}$. We test here another hypothetic scenario involving the existence of praseodymium vacancies in the structure, in relation with the disparity of the quantitative value of the specific heat on the Schottky anomaly. Actually in the filled skutterudite structure RT$_4$X$_2$, because of a weak interaction of the R-atoms with its neighbours (as

![Diagram](attachment:image.png)

**FIG. 7:** AC specific heat versus temperature of samples S1-1 and S1-1A we got after polishing S1-1 down to 120μm. The ratio of the two specific heat dramatically changes from 1.9 to ∼1.0. Our last proof is presented figure\textsuperscript{\ref{17}} showing the ac specific heat of sample S1-1 before and after polishing down to 120μm (then called S1-1A). As the samples are too small to determine their mass, the curves are normalized so the entropies in the normal phase match. The data fit in all the temperature range from 1.3K to 4K except in the double transition. By polishing, a dramatic decrease of the ratio of the specific heat jumps occurred, going from 1.9 to ∼1.0. The transition at $T_{c2}$ became steeper and sharper whereas we aren’t even able to distinguish any change of slope between $T_{c1}$ and $T_{c2}$ in S1-1A. So polishing the sample S1-1 clearly tended to remove the transition at $T_{c1}$.

Finally all these observations are compatible with a double transition due to two part of the sample. The effect of polishing presented here as well as reported in\textsuperscript{\ref{12}} (we got a single transition sample L1-1A by reducing the thickness down to 50μm) suggest that the two parts are macroscopically segregated.

We would like again to draw attention to the problem of the quality of the samples and on possible spurious analyses of the temperature dependence in the superconducting state of the sample with a large single transition. Indeed from the specific heat measurements of batch L2, it appears that some part of the samples can still become superconductor at temperature much lower than $T_{c1}$ (1.52 K for batch L2) and it would not be surprising that it is also the case in the samples with a large single superconducting transition.
points out by the large rattling of the R-atoms in the $X_{12}$ cages), some R-vacancies are commonly observed. Moreover as discussed in section II, the large dispersion of the specific heat value around 2 K could be ascribed to varying ratio of Pr-vacancies which may strongly affect the Schottky anomaly. Based on these observations, we suggest the overall scenario discussed in, namely the transition at $T_{c1}$ appears in the part of the samples with only partial occupancy of the Pr site.

In order to test this hypothesis, we have selected three single crystals with different shapes of the superconducting transition and we have submitted them to a single crystal x-ray diffraction experiment. Fig. 8 shows the superconducting transition in the specific heat normalized to its value in the normal state of these three samples. From sample L3-2 to L1-3, the ratio $\Delta(C/T)_1/\Delta(C/T)_2$ decreases strongly from 1 to 0.29 reaching zero in sample L1-5. If the hypothesis of Pr vacancies is true, the jump at $T_{c1}$ should increase when the vacancies on the Pr sites becomes larger.

The X-ray investigation was carried out with a No-Nius KappaCCD diffractometer equipped with graphite monochromatized AgKo radiation. After sample alignment, up to 20000 Bragg reflexions were collected to a maximum $\sin \theta/\lambda$ of 1.15 leading to a very high redundancy. After extraction of the intensities using the EvalCCD software, a numerical absorption correction was applied using the crystal shape. The structure refinement was carried out using the Jana2000 software. An isotropic extinction correction (type I, Lorentzian distribution) was applied and all atoms were given anisotropic atomic displacement parameters (a.d.p.). Finally, since an anomalously large a.d.p. was observed for the Pr atom (about 0.04 $\text{Å}^2$) and to test the vacancy ratio on the Pr sites, its occupancy factor was also let to vary. This systematically led to a slight decrease of the Pr atom occupancy (from 1 to 0.97 for sample L1-5) and the a.d.p. remained practically the same. The agreement factors were improved, though only slightly : for crystal L1-3 having the lowest refined Pr occupancy (0.89), the goodness of the fit decreased from 2.05 to 1.95 by letting the Pr occupancy parameter free. Table II reports the parameters obtained for the three single crystals when the Pr occupancy is refined and the Pr position is set at (0,0,0). Gof is the goodness of fit.

Table II: Structural parameters and refinement agreement factors for three crystals. The position of Pr atoms is setting at (0,0,0). $U_{iso}$ : isotropic thermal parameters. The occupancy (occ.) of Os and Sb was set to 1. Gof is the goodness of fit.

![Graph](image)

**FIG. 8:** Zoom on the superconducting transition in the specific heat normalized to its normal part obtained under magnetic field for the three samples we have selected (for their different ratios of the 2 specific heat jumps) for the 4 circles X-ray diffraction. Results of 4 circles X-ray diffraction are presented in.

| Sample | L3-2 | L1-3 | L1-5 |
|--------|------|------|------|
| Cell parameter ($\text{Å}$) | 9.272(1) | 9.288(1) | 9.321(1) |
| occ. (Pr) | 0.93(1) | 0.89(1) | 0.966(6) |
| $U_{iso}$ (Pr) ($\text{Å}^2$) | 0.0370(5) | 0.0359(7) | 0.0384(3) |
| $U_{iso}$ (Os) ($\text{Å}^2$) | 0.0046(1) | 0.0040(2) | 0.0048(3) |
| $U_{iso}$ (Sb) ($\text{Å}^2$) | 0.0064(1) | 0.0057(6) | 0.0060(5) |
| $x$(Sb)($\text{Å}$) | 0.15608(5) | 0.15613(3) | 0.15608(2) |
| $z$(Sb)($\text{Å}$) | 0.34040(5) | 0.34036(3) | 0.34031(2) |
| Gof | 2.24 | 1.95 | 2.33 |

C. Superconducting phase diagram

We have followed the superconducting transition of the single transition sample L1-5 under magnetic field by resistivity measurements. In figure [9(b)] we report $T_c$ versus $H$, determined by onset criterion. The transition remains very sharp (12 mK at 1.2 T and less than 30 mT...
at 400 mK) pointing out again to the high quality of this sample. The $T_c(H)$ line matches with $T_{c2}(H)$ published in\textsuperscript{10}, as shown in figure 9(a). The small positive curvature at low magnetic field is even more clearly visible (Cf. insert of figure 9(a)).

It also backs up the conclusions of the recent thermal conductivity measurements on a high quality-single superconducting transition sample, L1-1A: multigap effects have been confirmed\textsuperscript{12}, with a very low field scale associated with the light carrier/small gap band, of the same value as found in a previous inhomogeneous (wide specific heat transition) sample\textsuperscript{11}. Moreover, the fact that the small positive curvature close to $T_c$ is found also in homogeneous samples and with the similar amplitude is a definite proof, beyond the reproducibility of the measurements\textsuperscript{10}, that it is not connected to sample inhomogeneities.

It also brings information on the inter band coupling strength different from those of the thermal conductivity experiments. For example, the fit proposed in\textsuperscript{12} for $H_{c2}(T)$ would also apply to these new measurements, as the data simply scale with $T_c$. But the set of inter and intra band couplings ($\lambda_{ij}$) proposed in this first work, was based on the simplest hypothesis that $\lambda_{ij}$ is proportional to the density of states of band $j$, so that $\lambda_{11} = \lambda_{21}$ and $\lambda_{12} = \lambda_{22}$. In such a case, a simple calculation of the two gaps in a weak-coupling scheme shows that they are equal. In order to be consistent with the thermal conductivity results, which find a factor three between the small and large gap\textsuperscript{12}, one needs to introduce a difference between $\lambda_{11}$ and $\lambda_{21}$. The size and position of the curvature on $H_{c2}$ then still impose a very small value of $\lambda_{12}$ (we take still for simplicity ($\lambda_{12} = \lambda_{22}$).

So, instead of the set of parameters : $\lambda_{11} = \lambda_{21} = 1$, $\lambda_{12} = \lambda_{22} = 0.04$ proposed in\textsuperscript{12}, we propose the new set : $\lambda_{11} = 1$, $\lambda_{21} = 0.2$, $\lambda_{12} = \lambda_{22} = 0.07$ and $g=2$, which yields a fit of the same high quality (see fig. 9(b)), but yields also the good values for the gap as deduced from thermal conductivity measurements. Again, it is only the ratio of the $\lambda_{ij}$ which matters, the value $\lambda_{11}$ = 1 being arbitrarily fixed\textsuperscript{12}. The factor 5 between $\lambda_{11}$ and $\lambda_{21}$ is essentially due to the coupling strength, meaning that inter band coupling in the band with heavy effective masses (having f character) is much stronger than inter band coupling from this band to the band with a small mass (weak f character). Of course, $\lambda_{12}$ and $\lambda_{22}$ are strongly reduced by density of states effects, but the general trend which emerges from the new set of $\lambda_{ij}$ imposed by the combination of thermal conductivity\textsuperscript{10} and $H_{c2}$ results is that multiband effects in PrOs$_4$Sb$_{12}$ are coming from the difference in the f character of the bands both through density of states and pairing mechanism effects. This conclusion is quite robust as it relies on measurements independent of the sample homogeneity and the number of transitions.

\section{Conclusion}

Although general characterizations point out to a recurrent double superconducting transition in PrOs$_4$Sb$_{12}$ appearing in the samples with the best $RRR$ and high specific heat jump at the superconducting transition, so in good samples, a study of many samples specially small
ones (with a typical size of 100 µm) shows that its occurrence could be a phenomenon related to an inhomogeneous effect rather than to fundamental microscopic mechanisms. More precisely we think the lowest temperature transition $T_{c2}$ is the intrinsic one. Based on our 4 circles X-ray diffraction results, we conclude that Pr vacancies are certainly present in the samples and with various percentages which might explain the discrepancy between quantitative specific heat results. But establishing a clear relationship between Pr vacancies and the occurrence and magnitude of the jump in specific heat at $T_{c1}$ needs further studies, specially at low temperature.

Finally, the superconducting phase diagram of a single transition sample was determined and fitted with a two-band model. It appears in connection with thermal conductivity results that the multiband effects in PrOs$_4$Sb$_{12}$ come from the difference in the $f$ character of the bands both through density of states and pairing mechanism effects.

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