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Through the characterization of many samples of the filled skutterudite compound $PrOs_4Sb_{12}$ we found that even though the double superconducting transition in the specific heat ($T_{c1} \sim 1.89$ K and $T_{c2} \sim 1.72$ K) appears in samples of good quality, there are various pieces of evidence which cast doubt on its intrinsic nature. First, three samples exhibit a single sharp transition of ~15 mK width at $T_c \sim 1.7$ K. We have clear evidence that the quality of the samples with exhibiting a single transition is better; the width of the transition is the smallest and the normalized specific heat jump $(C - C_{normal})/C_{normal})_{T_c}$ is larger than the sum of the two specific heat jumps when a double transition exists. Secondly, the ratio of the two specific heat jumps $\frac{\Delta C(T_{c1})}{\Delta C(T_{c2})}$ exhibits wide variation with samples not only among different batches but also even within a batch. Finally, this ratio was strongly reduced by polishing a sample down to 120μ pointing to bulk inhomogeneities as an origin of the spurious transition. Our X-ray diffraction analysis points to Pr-vacancies problem in the samples but it does not show that they are the origin of the double transition. We provide the superconducting phase diagram under magnetic field of a sample exhibiting a single transition and fit the curve $H_{c2}(T)$ with a two-band model taking into account the appropriate 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 $PrOs_4Sb_{12}$ ($T_c \sim 1.85$K) by Bauer et al.[1], this system has attracted much attention with particular emphasis on the possible unconventional nature of superconductivity. A significant piece of evidence for unconventional superconductivity is the double superconducting transition seen in specific heat first reported in 2003 by Vollmer et al.[2] and Maple et al.[3]. 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[4], USA[3,5], Germany[2,6–8], France[9]) and by thermal expansion[10] with samples from different origins and even in La doped or Ru substituted samples[5,11]. So whatever the origin, the double transition is a robust property of this compound.

Susceptibility measurements on a sample with a very clear double superconducting transition[9] cast the first doubts about its microscopic origin. Indeed even in this good sample, the diamagnetism is not perfect at T_{c1}: two steps in the susceptibility appear at the two transitions (T_{c1} and T_{c2}, $T_{c1}>T_{c2}$). The field dependence of T_{c2} is completely similar to that of T_{c1}[9]. The behavior of $T_{c1} - T_{c2}$ under pressure is also not conclusive[12]. 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 UPt_3 where the different field and pressure dependencies of the two transitions were decisive results).

We report here on a study of the nature of the double superconducting transition of $PrOs_4Sb_{12}$. Our main purpose is to clarify whether the double superconducting transition which appears in specific heat is intrinsic, like it is now accepted for UPt_3, or extrinsic, due to sample inhomogeneities, as shown for URu_2Si_2 (ref.[13]), and high-T_c superconductor $YBa_2Cu_3O_x$ (ref.[14]). To settle the problem, we have carried out systematic characterizations by resistivity, specific heat and susceptibility measurements. They are presented in sections II and III. Based on the results, we conclude that a double transition appears in good samples, whereas a broad transition, much larger than the splitting of the double transition, appears in lesser quality samples. But an extensive study, particularly of small samples, provides evidence which brings strong doubts about its microscopic origin. The most convincing evidence is the existence of three samples exhibiting only a single sharp superconducting transition. In section IV, we present the single crystal x-ray diffraction results. Finally in section V, 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.

Several parameters used in this paper are defined in Fig. 1. We also use the normalized specific heat which is defined as $(C - C_{normal})/C_{normal}$. We obtained the normal part of C, C_{normal}, by applying a magnetic field of about 1 T , which shifts the superconducting transition below 1.4 K. As noticed earlier[7], the shape of the specific heat in the normal part (for T$\geq T_c$) is not affected by such a magnetic field.

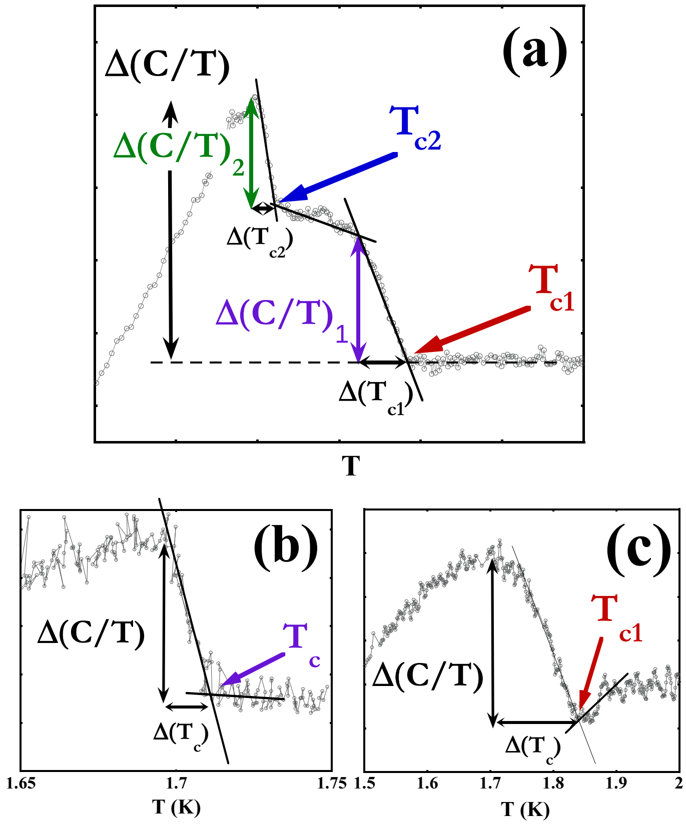


FIG. 1: (color online) Definition of the criteria we use in this paper depending on the kind of superconducting transition, (a) double, (b) single and sharp, or (c) single and broad: the superconducting transition T_c, T_{c1} and T_{c2} obtained on the onset, the specific heat jumps $\Delta(C/T)_1$ at 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.

II. GENERAL CHARACTERIZATIONS

The crystals of $PrOs_4Sb_{12}$ were grown by the Sb flux method[15–17] by 3 separate groups (P. Canfield, H. Sugawara and G. Lapertot, labeled C, S and L, respectively). 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 crystals from H. Sugawara directly underwent the last process. The samples used in earlier studies[9,12,18] are S1, L1-1A, L1-2, respectively. The sample measured in[19] has similar shape as sample C3.

The specific heat (C) measurements were performed in a ^3He calorimeter either by a quasi-adiabatic method with a Au/Au-Fe 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 as C/T of several samples of $PrOs_4Sb_{12}$. Their absolute values at $\sim$ 2 K differ strongly, varying from 2.06 J/K^2.mol to 2.94 J/K^2.mol and can vary for samples within the same batch (not shown). In the published reports[3,7], the absolute values at 2 K are between 1.3 J/K^2.mol and 3.2 J/K^2.mol, respectively. This variation cannot be explained only by the difference in amount of trapped Sb flux. We suggest that it is mainly due to the variation of the Schottky anomaly which is due to the presence of the first crystalline electric field (CEF) excited level of the 4f^2 Pr states, $\Gamma_4^{(2)}$, at $\sim\ 8K$ above the singlet ground state Γ_1 ref.[20,21].

One origin of the change in the Schottky anomaly could be the Pr-vacancies in the crystal (see section IV). It is difficult to estimate the percentage of Pr-vacancies required to explain the variation of $C/T(2K)$. Indeed, Pr-vacancies may induce some distortions which change locally the CEF and broaden the Schottky term. Moreover, the apparent dispersion in wavevectors of the crystal field excitations[22] indicates strong interactions between Pr ions; so a simple local model to describe the excitations on the Pr ions is not appropriate. Roughly a maximum of 10 % of Pr-vacancies is required to fit the specific heat of sample L3-1 to L1-1 (three upper curves of figure 2).

No upturn due to the nuclear Schottky anomaly except

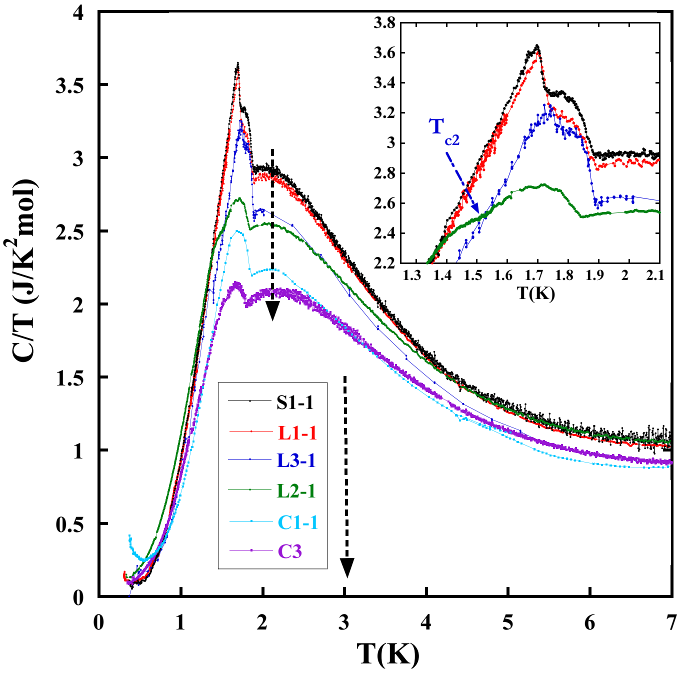


FIG. 2: (color online) Specific heat as C/T versus T for selected samples of $PrOs_4Sb_{12}$ from different batches. The names of the samples are labelled following the decreasing magnitude of C/T at 2 K where the contribution from the Schottky anomaly predominates. The insert gives a zoom around the superconducting transition for the samples having a double superconducting transition. The absolute value of C clearly depends on the sample. A double superconducting transition appears in samples S1-1, L1-1, L3-1, L2-1 while samples C1-1, C3 exhibit a broad single transition.

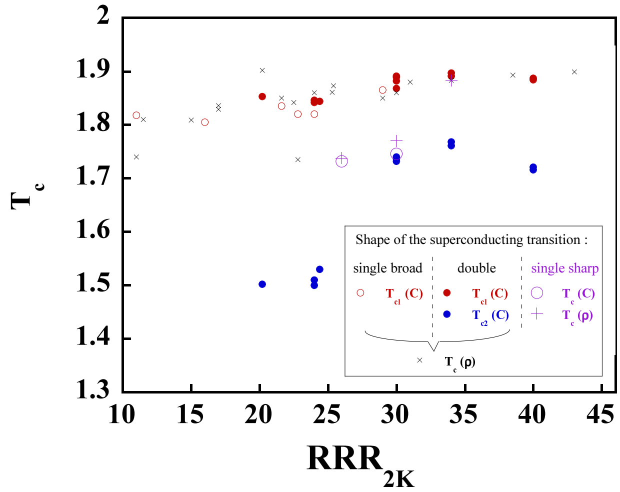


FIG. 3: (color online) Superconducting transition temperature (determined by specific heat (circle) or resistivity (cross) measurements) versus RRR_{2K}. The open red circles show the transition temperature for the samples exhibiting a single and broad superconducting transition. They exist in the low RRR_{2K} region. The full red and blue circles are T_{c1} and T_{c2}, respectively, of the double transition samples. The large purple open circles and crosses show the single sharp transitions of samples L1-5 and L1-1A, determined by the C and ρ measurements respectively. Please note the definition of the $T_c(C)$s in the Fig 1. $T_c(\rho)$ is the onset temperature. As a general trend, the double transition is realized in the sample with relatively large RRR_{2K}. NB: sample L1-6 with a single sharp transition is not included in this figure because the resistivity measurement was not performed.

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[6].

The double superconducting transitions for several samples are shown in the zoom of Fig. 2 (see insert). It is seen that the shape and height of the transition, as well as the absolute value of T_c and of the specific heat may vary even for samples of the same origin (samples L1, L2, L3), or be rather similar for samples of different origin (samples L1-1, S1-1). We associate the lowest transition temperature of batch L2 to T_{c2} because the ac susceptibility of these samples (not shown) exhibits two steps matching the transitions in the specific heat (as also observed for batch S1, Cf.[9]). This indicates that the two transitions exhibited by the samples of batch L2 can be associated with a double superconducting transition.

We discuss now the link between the existence of the double transition and the sample quality. Figure 3 shows the plot of the superconducting transition temperatures (determined by specific heat and resistivity measurements) versus the residual resistivity ratio. In this paper, the residual resistivity ratio RRR_{2K} is measured between 300 K and 2 K. When the specific heat and the resistivity were not measured on the same sample, the RRR_{2K} values taken are an average for the batch. As the spread of the RRR_{2K} is large (for instance the RRR_{2K} of batch L1 is between 17 and 34), only a general tendency can be extracted.

It is quite clear that T_{c1} increases, but only slightly, with the RRR_{2K} (its minimum and maximum values are respectively 1.805 K and 1.897 K) whereas T_{c2} is strongly sample dependent. All the samples with a single broad superconducting transition appear in the small RRR_{2K} range. These samples probably have a large distribution of T_c values which combine to form the observed broad transition. When the RRR_{2K} increases above 20, some samples exhibit a double transition. The samples having a double transition with a T_{c2} at about 1.5 K belong to batch L2 whereas those with a T_{c2} of about 1.7 K are from batches L1, L3 and S1. From table I, it appears that the double transition of these samples become sharper with increasing RRR_{2K}(from batch L2 to batches L1, L3 and S1). However, some samples exhibiting a broad single transition have higher RRR_{2K} than some double transition samples. We also notice that the samples with a single sharp transition have a T_c similar to T_{c2} and a relatively high (but not the highest) RRR_{2K}. This probably points to a large variety of possible defects in PrOS4Sb12, having different effects on the resistivity and on the superconducting properties. Moreover, resistivity is not really a bulk property. So the discussion of the relative sample quality cannot be limited to the RRR_{2K}. This will be discussed further in section III. We will now discuss the results from specific heat measurements, which may better qualify the bulk properties.

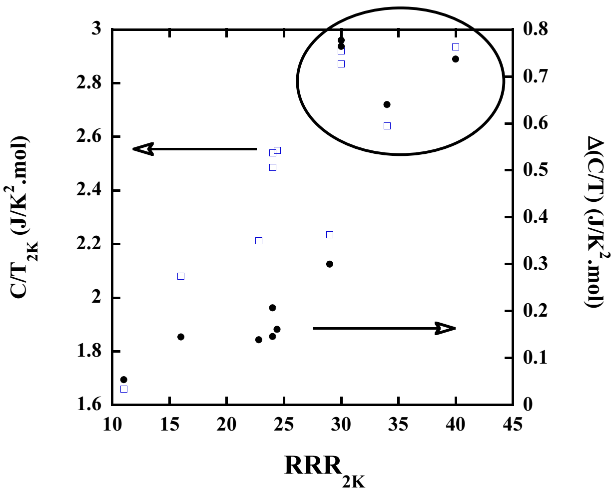


FIG. 4: C/T at 2 K and the total specific heat jump $\Delta(C/T)$ defined in Fig. 1 versus RRR_{2K}. There is apparently a positive correlation between the three quantities. All the samples exhibiting clear double superconducting transitions (batches S1, L1 and L3) are within the large circle. They are of high quality : they are characterized by a large RRR_{2K}, a large C/T at 2 K and a large specific heat jump at the superconducting transition.

Figure 4 shows the absolute value of C at 2 K and 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 RRR_{2K}. Only the samples where the absolute value of the specific heat is not known are omitted in Fig. 4 (samples which are too small for their mass to be determined precisely, which includes the sharp single transition samples). It appears that the higher the RRR_{2K}, the larger the specific heat at 2 K and the higher the specific heat jump at T_c. The large circle on Fig. 4 embodies all the samples with a clear double transition: the double transition seems to be a feature of the samples which meet all these criteria. We conclude that *the samples with a double superconducting transition are of high quality.* The samples with a broad single superconducting transition, which *always* covers the temperature range of the double transition, are clearly of less good quality.

However, we will present in the next section several pieces of evidence against an intrinsic origin of the double transition.

III. DOUBLE SUPERCONDUCTING TRANSITION

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 the T_{c1} and T_{c2} of the specific heat anomalies[6,9]. All the samples with a double transition that we have also tested by ac susceptibility (χ), i.e. batches L1, L2 and S1, also exhibit a double step matching the specific heat jumps. But there are other reasons to doubt the intrinsic (symmetry driven) scenario.

A. Ratio of the specific heat jumps

Table I provides the main parameters related with the properties of all the samples having a double transition or a single sharp superconducting transition. All of them except S1-2A and L1-1A are as grown (unpolished) samples. All the samples not reported in table I exhibit a single broad transition with a width larger than the temperature range of the double transition, as shown in Fig. 2. The criteria for T_{ci}, $\Delta(T_{ci})$ and $\Delta(C/T)_i$ are defined in the Fig. 1. The ratio $\Delta(C)/C_{normal}$ is the total specific heat jump at the superconducting transition taken on the normalized specific heat, $(C - C_{normal})/C_{normal}$, defined in the introduction.

We first notice that the double transition appears in 5 different batches from 3 origins with a similar shape for the biggest samples, L1-1, S1 and S1-1. But further investigations, especially on small samples (with a typical size of 100μm), show a wide range of the ratio of the two specific heat jumps, $\Delta(C/T)_1/\Delta(C/T)_2$, from 0.2 to 3.36. It even differs in the same batch, 0.25 to 3.36 in batch L2. One can argue that this variation is due to different sensitivity of the two superconducting states to the quality of the sample. However, in this case, other properties should be affected. And it clearly appears that we cannot connect the value of the ratio with other criteria. For instance, whereas their ratio $\Delta(C/T)_1/\Delta(C/T)_2$ differ strongly, T_{c1} and T_{c2} are similar in samples L2-1 and L2-2 and the width of the transition $\Delta_{T_{c2}}$ is the same in samples L1-3 and L3-2.

B. Sharp single superconducting transition

We focus now on the most remarkable finding shown in Fig. 5. We present here only semi-quantitative values of C because of the tiny mass of the samples. We measured the specific heat of three samples L1-5, L1-6 and L1-1A exhibiting a single sharp superconducting transition (although, for L1-1A, there remains a faint jump near 1.8 K as well as a small step in resistivity at 1.85K, ref.[18]).

sample	shape ␣ size/weight ␣ measurement	$T_{c1(\mathrm{K})}$	$T_{c2(\mathrm{K})}$	$\frac{\Delta(C/T)_1}{\Delta(C/T)_2}$	$\Delta(T_{c1})_{(\mathrm{mK})}$	$\Delta(T_{c2})_{(\mathrm{mK})}$	$\frac{\Delta(C)}{C_{normal}}$	RRR_{2K}
Double Superconducting Transition								
S1	AofC. ␣ 4mg ␣ Q-A m.	1.887	1.716	1.36	67	19	32%	∅
S1-1	AofC. ␣ 1.97mg ␣ Q-A m.	1.884	1.721	1.23	61	23	30.6%	∅
L1-1	AofC. ␣ ∼10mg ␣ Q-A m.	1.890	1.737	0.70	61	35	32.3%	∅
L1-2	p. ␣ 50*150*150μm^3 ␣ AC	1.85	1.73	0.54	36	39	≥27.2%	∅
L1-3	c. ␣ 200μm ␣ PPMS	1.868	1.74	0.29	43	40	30.7%	∅
L1-4	b. ␣ 500μm ␣ PPMS	1.889	1.732	0.20	64	35	28%	∅
L3-1	AofC. ␣ 1.25mg ␣ Q-A m.	1.891	1.761	2.8	46	21	27.3%	∅
L3-2	b. ␣ 200μm ␣ PPMS	1.897	1.76	1	60	40	32%	∅
Sharp Single Superconducting Transition								
L1-5	p. ␣ 160*200*40μm^3 ␣ PPMS	∅	1.733	**0**	∅	**17**	33%-44%	26
	␣ AC						≥28%	
L1-6	p. ␣ 50*150*150μm^3 ␣ AC	∅	1.680	**0**	∅	21	≥22%	∅
L1-1A	p. ␣ 45*150*200μm^3/∼0.1mg ␣ PPMS	1.800	1.745	∼**0** (≤0.09)	55	27	36%	30
Double Superconducting Transition with a lower T_{c2}								
L2-1	b. ␣ 9.7mg ␣ Q-A m.	1.844	1.53	3.36	150	105	16%	24
L2-2	b. ␣ 150μm ␣ PPMS	1.85	1.535	0.25	75	47	28%	∅
C1-2	c. ␣ 200μm ␣ PPMS	1.877	1.685	1.17	95	35	27%	∅
Effect of polishing : change of the relative height of the two specific heat jumps								
S1-2	p. ␣ 300μm ␣ AC	∼1.88	∼1.71	**1.9**	100	25	≥28%	43
S1-2A	p. ␣ 120μm ␣ AC	∼1.88	∼1.71	∼**1.0**	180±20	20	≥28.1%	∅

TABLE I: Main properties of the samples having a double superconducting transition or a single and sharp transition. S1-2A and L1-1A were made by polishing S1-2 and one piece of L1-1, respectively. The definition of the parameters is given in Fig. 1 or in the text. Abbreviations are: c.=cube; b.=bar, AofC.=aggregate of cubes, p.= platelet; AC=ac calorimetry measurements; PPMS=measurements by relaxation method with the Physical Property Measurement System; Q-A m.: quasi-adiabatic method; ∅=not measured or does not exist. The RRR_{2K} is taken between 300 K and 2 K.

The specific heat of a sample with the "usual" double transition (L1-1) is also presented. L1-5 and L1-6 are very small as-grown platelets with well-developed faces and with a thickness of about 50μm. L1-1A has been obtained by polishing a large cube (1 mm) of the aggregate of cubes L1-1 so that the thickness was reduced down to 45 μm, ref.[18]. Their critical temperature T_c is in the temperature range of T_{c2} of the samples exhibiting a double transition.

We characterized further sample L1-5. We confirmed the composition of the sample (see section IV) by 4 circles X-ray diffraction measurements. Figure 6 presents the normalized specific heat measured by ac method, ac susceptibility and resistivity measurements of sample L1-5. For the susceptibility measurements a tiny susceptometer was built to get a good filling ratio. The two pick-up coils connected in opposition consisting of 440 turns of 14 μm diameter copper wire are wound on a glass-fiber body with an inner diameter of 300 μm. The frequency and the amplitude of the exciting magnetic field are about 375 Hz and 0.36 mT, respectively. The insert of fig. 6a shows the specific heat in a large temperature range. It exhibits only one superconducting jump which is very sharp as shown in fig. 6a. The ac susceptibility (fig 6b and 6c) presents no sign of superconductivity above T_c. The resistivity shown in fig. 6c exhibits a sharp superconducting drop. The width of the transition is 17 mK, 16 mK and 35 mK in specific heat, resistivity and susceptibility, respectively. It is the sharpest transition of all our samples. All T_c (ρ, χ, C) are consistent at about 1.73 K. *This sample has a single and very sharp superconducting transition.*

C. Comparison of the quality of the samples with and without a double transition

We compare the quality of these single transition samples with the samples exhibiting a double transition. The first criterion we discuss is **the specific heat jump at the superconducting transition**. We are only able to consider semi-quantitative values because all samples having a single transition are too small and because the absolute value of C depends strongly on the sam-

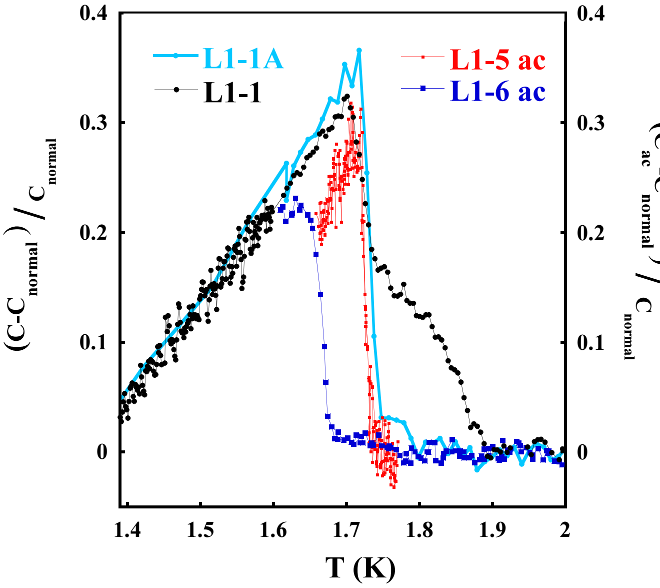


FIG. 5: (color online) Normalized specific heat (defined in the introduction) of selected samples of $PrOs_4Sb_{12}$. Sample L1-1 exhibits a double transition. Most remarkable finding is the existence of three samples L1-5, L1-6 and L1-1A exhibiting only a single sharp transition, which casts serious doubt on the intrinsic origin of the double superconducting transition. The specific heat jumps for L1-5 and L1-6 measured by ac method are underestimated. The specific heat of sample L1-5 was also determined semi-quantitatively by relaxation method (Cf. figure 9). All properties are included in table I.

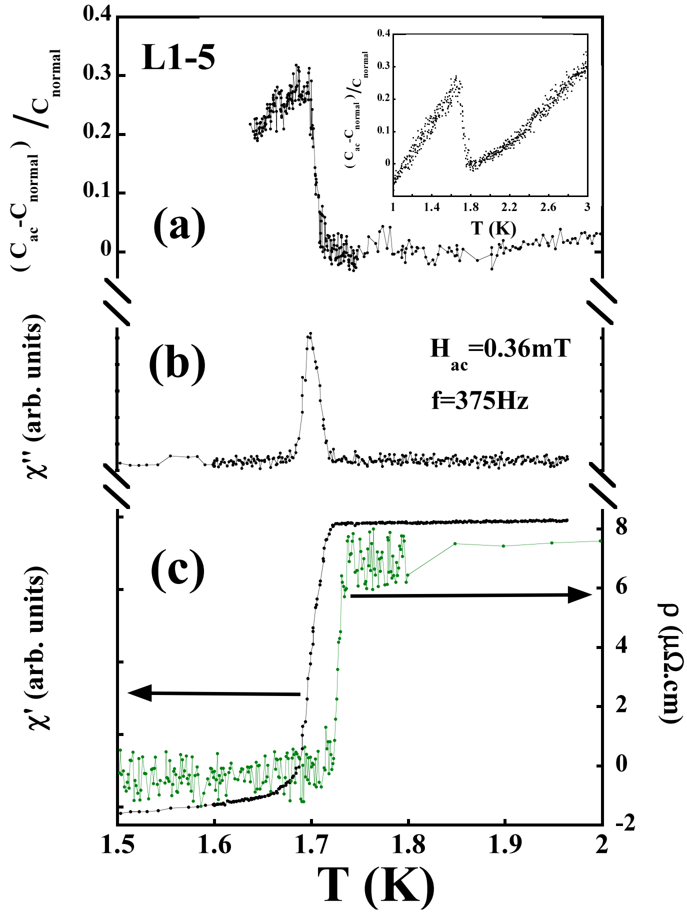


FIG. 6: Normalized specific heat, ac susceptibility and resistivity versus temperature of the sample L1-5. This sample has a single and sharp superconducting transition in all measurements with T_c of 1.733 K. T_c is consistent among all the measurements (C, ρ and χ) and is similar to T_{c2} in the samples exhibiting a double transition.

ple (see section II). The normalized specific heat jump, $\Delta(C)/C_{normal}$, of the samples exhibiting a single transition is at least as high as the entire transition of the double transition samples. Indeed, even though the specific heat measured in the PPMS (shown in Fig 9) shows a large scatter in the values, due to the tiny mass of the sample, $\Delta(C)/C_{normal}$ was found to be 33-44%, a value larger than the entire jump in any sample showing a double transition (the maximum reported in table I is $\Delta(C)/C_{normal}$=32.3%). The conclusion for L1-1A is similar, with $\Delta(C)/C_{normal}\sim$ 36%. The specific heat jump of sample L1-6 is underestimated because C was measured by ac method without subtracting the background. We also note that the normalized specific heat jump of the samples exhibiting a single and broad transition is always smaller than 19%.

As for **the width of the transition**, sample L1-5 has the sharpest ever measured (17 mK in C). Moreover the specific heat jump of the single transition sample is roughly two times larger than $\Delta(C)_{1,2}$. This implies that the slope in the transition is about two times steeper for sample L1-5 as well as for the two other single transition samples, L1-6 and L1-1A.

Comparison using this criterion as well as the normalized specific heat jump $\Delta(C)/C_{normal}$ points to a *higher quality (as regards homogeneity) of the samples exhibiting a single sharp transition.*

The **RRR**$_{2K}$ of samples L1-5 and L1-1A are respectively 26 and 30 which is smaller than the largest value we have got for a double transition sample (RRR$_{2K}$ of sample S1-2 is 43). Of course, the resistivity is not a probe of the whole volume of the sample. For instance, sample S1-2 exhibits a sharp superconducting transition in resistivity (ρ=0 at 1.82 K) but two steps in χ matching with T_{c1} and T_{c2}. Moreover we cannot exclude that another parameter, such as remaining Sb-flux or Pr-vacancies, improves the RRR$_{2K}$.

D. Effect of polishing on the double transition

We present the effect of polishing on the double transition in Fig. 5 and 7. The former shows that by extracting one cube from the aggregate of cubes L1 and by polishing it down to 45μm as described earlier [18], the transition at

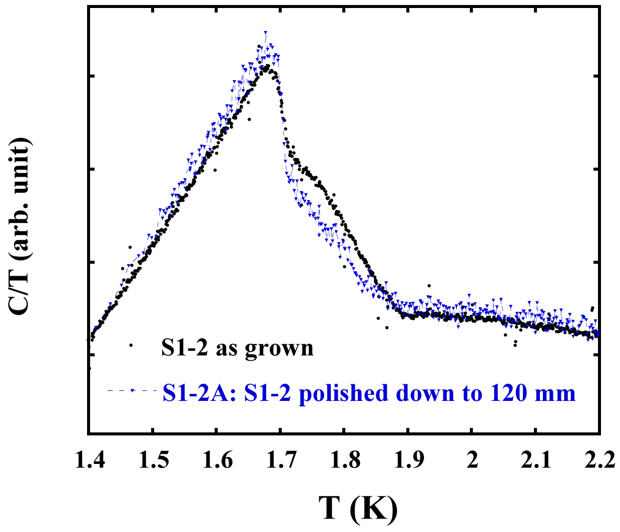


FIG. 7: Comparison of ac specific heat versus temperature between S1-2 and S1-2A. The latter was obtained by polishing S1-2 down to 120μm. The ratio $\Delta(C/T)_1/\Delta(C/T)_2$ changes clearly, from 1.9 to ~1.0.

T_{c1} in the final sample L1-1A almost completely disappears. We also confirm this tendency on a sample from another batch as presented in Fig. 7. It shows the ac specific heat of sample S1-2 before and after polishing down to 120μm (then called S1-2A). As the samples are too small to determine their mass, the curves are normalized so that the entropies in the normal phase match. The data coincide in all the temperature range from 1.3K to 4K except in the double transition region. A large decrease of the ratio of the specific heat jumps occurred on polishing the sample, going from 1.9 to ~1.0 (Table I). The transition at T_{c2} became steeper and sharper whereas we are not even able to distinguish any change of slope between T_{c1} and T_{c2} in S1-2A.

So *polishing the samples L1 and S1-2 clearly tended to remove the transition at* T_{c1}. This result points to bulk inhomogeneities as origin of the double transition.

E. Discussion

All the observations are compatible with a double transition due to different parts of the sample. The effect of polishing suggests that the two parts are macroscopically segregated. Actually the shape of the double transition (broad transition at T_{c1} and sharp transition at T_{c2}) can be rebuilt if we imagine a sample with two parts, one with a large distribution of T_c as for the single and broad transition samples (like C1-1) and the other one with a single and sharp transition at T_{c2} (sample L1-5).

We argue here that *the transition at* T_{c2} *is the intrinsic one.* First, the transition at T_{c1} is always broader than the transition at T_{c2} (Cf. table I). All the single transition samples have a T_c similar to T_{c2}. Moreover, we can exclude that the single transition is the transition at T_{c1} shifted to lower temperature by some impurities effects. Indeed, all the samples exhibiting a single sharp transition have T_c lower than 1.75 K whereas even in the worst samples (see Fig. 3) T_{c1} is not smaller than 1.805 K.

To explain the presence of such single sharp transition samples in the context of an intrinsic double transition, one could argue that the transition at T_{c1} simply disappears due to lesser quality of the samples. However then the single transition should also be broadened which is not the case. Furthermore, thermal conductivity (κ) measurements clearly indicate that the sample L1-1A exhibiting a single transition ($\kappa/T\sim$ 70 μW/K^2.cm at 100 mK, ref.[18]) is of better quality than a sample which exhibits a broad superconducting transition with T_c about 1.85 K ($\kappa/T\sim$ 250 μW/K^2.cm at 100 mK , ref.[23]).

Finally, even if our conclusion on the extrinsic nature of the double transition in PrO_4Sb_{12} is quite robust, definitive proof of this will appear if:

- we can show that the specific heat jump of the single sharp transition samples is *quantitatively* higher than the whole jump in the double transition samples. This requires bigger samples having a single sharp transition.
- the origin of the spurious transition can be identified.

Of course the absence of an intrinsic double transition does not imply that the superconductivity of this material is conventional. Particularly, following the idea that T_{c2} is the intrinsic transition, its strong sample dependence (a dispersion of 15%) might point to unconventional superconductivity. Nevertheless this observation must be carefully investigated as the superconductivity at T_{c1} and T_{c2} should have the same sensitivity to the quality of the samples but the dispersion of T_{c1} is only of 5% for all our samples.

Actually, this is one of the **main questions** we still have to answer, and the existence of samples such as L2-2 with T_{c2} shifted to much lower temperature while T_{c1} is virtually unchanged is a puzzle. Put more simply, why is T_{c1} so stable, and T_{c2} is so sample dependent? The most likely answer at present is that other impurity effects, unrelated to the appearance of the double transition, play a role.

The other main question is **the origin of the spurious 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}). Moreover, 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 another mechanism must be involved and it is not surprising that annealing the sample has no effect on the double transition[11]. We note that such observation, namely a superconducting transition which is not affected by a simple random-impurity-induced pair breaking mechanism but by another more complex one, is not an isolated case in the history of heavy fermions superconductors. The double transition of URu_2Si_2 was ruled out by Ramirez et al.[13] by isolating the lowest T_c phase when removing the surface of the sample. As for $CePt_3Si$, Kim et al. pointed out to a spurious double transition[24] due to a second phase of $Ce_3Pt_{23}Si_{11}$, and T_c decreasing from 0.75 K to 0.46 K with increasing quality of the sample[25]. Sr_2RuO_4 (ref.[26]) and $CeIrIn_5$ (ref.[27]) exhibit a much higher T_c in resistivity measurements than specific heat.

Multiple scenarios are possible like the existence of an impurity phase very similar to $PrOs_4Sb_{12}$ which superconducts at T_{c1} (not found up to now), or the presence of twin boundaries which enhance T_c, ref.[28]. For example, figure 8 shows a fit of the single and double transitions observed in samples of batch L1, using the theory of reference[28] and "cheating" to impose a finite slope of C/T below T_c (Landau theory only predicts a jump at T_c). In fact, we used the model of reference[28] as giving simply the distribution of T_c, assuming that the single transition sample gives the "intrinsic" shape of the superconducting transition. The model of reference[28] has two parameters : the maximum enhancement of T_c due to a single twin boundary, and the ratio between the zero temperature coherence length, ξ_0, and the mean distance between twin boundaries, L. We added another parameter : the percentage of the sample containing twin boundaries, the rest having a sharp transition fixed at T_{c2}. The interest of the fit is just to fix the idea about what would be needed in order to observe the double transition : the answer is about 60 percent of the sample having twin boundaries, with a mean distance of 30 ξ_0, i.e. 3500$\AA$. Validation of this scenario needs experimental observation of the twin boundaries.

Another possibility comes also from the fact that in the filled skutterudite structure RT_4X_{12}, some R-vacancies are commonly observed[29] because of a weak interaction of the R-atoms with their neighbors (as indicated by the large rattling motion of the R-atoms in the X_{12} cages). So a scenario involving such Pr-vacancies, as discussed in ref.[12], must be checked. Moreover, different percentage of Pr-vacancies in different samples could also explain the disparity in the quantitative values of the specific heat due to the Schottky anomaly. The X-ray diffraction analysis reported in section IV will help to discuss this last scenario.

As for other published results, the extrinsic origin of the double transition can account for the two steps at T_{c1} and T_{c2} seen by magnetization and resistivity measurements as well as for the highest temperature minima in flux flow resistance reported in ref.[30].

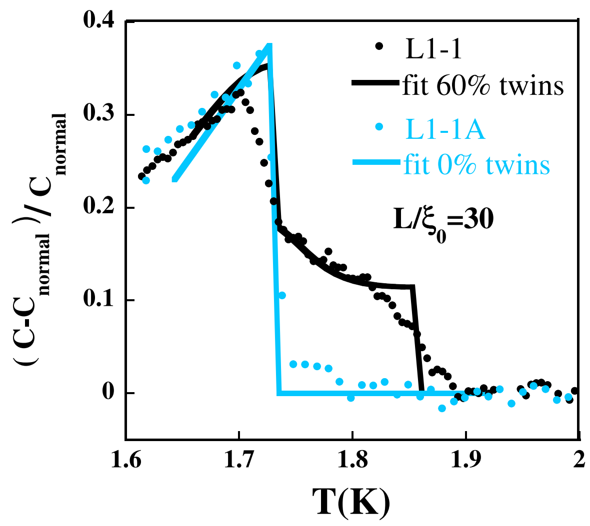


FIG. 8: Fit of the superconducting transitions in the specific heat by the model described in ref.[28]. Cf. texte.

We would like again to draw attention to the problem of the quality of the samples. Some part of the samples can still become superconducting at temperatures much lower than T_{c1} (Cf. batch L2). It is most likely the case in the samples with a broad single superconducting transition which can affect the temperature dependence of several properties in the superconducting state.

IV. 4 CIRCLES X-RAYS DIFFRACTION STUDY

We have selected three single crystals, one with a single transition L1-5 and two other ones with different ratio of the superconducting jumps $\Delta(C/T)_1/\Delta(C/T)_2$. We have subjected them to a 4 circles X-ray diffraction experiment at 300 K. Fig. 9 presents the normalized specific heat 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.

The X-ray investigation was carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromatized AgKα radiation. After sample alignment, up to 20000 Bragg reflexions were collected to a maximum sinθ/λ of 1.15 leading to a very high redundancy. After extraction of the intensities using the Eval-CCD software[31], a numerical absorption correction was applied using the crystal shape. The structure refinement was carried out using the Jana2000 software[32]. 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 $\AA^2$), and in order to test the vacancy ratio

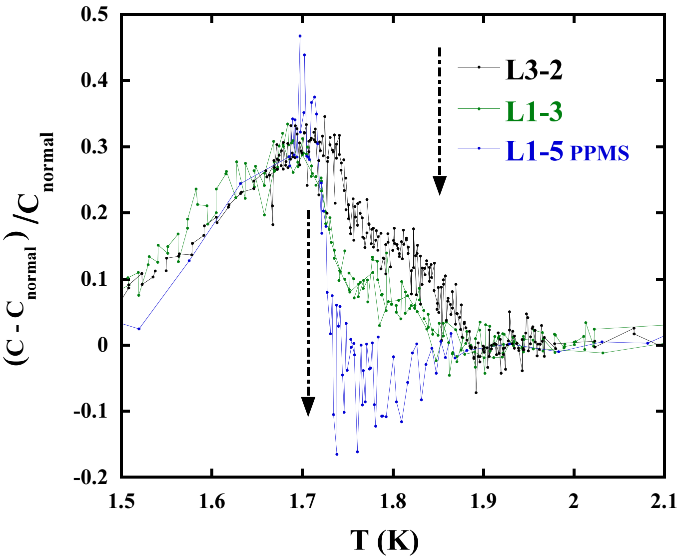


FIG. 9: Normalized specific heat versus temperature for three selected samples included L1-5 (measured with the PPMS) and with different ratios of the two specific heat jumps. The names of the samples are labeled following the decreasing magnitude of normalized C at ∼1.8 K. Results of 4 circles X-ray diffraction on these samples are presented table II.

on the Pr sites, its occupancy factor was also let to vary. This systematically leads to a slight decrease of the Pr atom occupancy (from 1 to 0.97 for sample L1-5), the a.d.p. remains practically unchanged. The agreement factors are improved, though only slightly : for crystal L1-3 having the lowest refined Pr occupancy (0.89), the goodness of the fit decreases 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).

Sample	L3-2	L1-3	L1-5
Cell parameter ($\AA$)	9.272(1)	9.288(1)	9.321(1)
occ. (Pr)	0.93(1)	0.89(1)	0.966(6)
U_{iso} (Pr) ($\AA^2$)	0.0370(5)	0.0359(7)	0.0384(3)
U_{iso} (Os) ($\AA^2$)	0.0046(1)	0.00402(5)	0.00480(3)
U_{iso} (Sb) ($\AA^2$)	0.0064(1)	0.00578(6)	0.00660(5)
x(Sb)($\AA$)	0.15608(5)	0.15613(3)	0.15608(2)
z(Sb)($\AA$)	0.34040(5)	0.34036(3)	0.34031(2)
Gof	2.24	1.95	2.33

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

These results confirm that the Pr atom has a large U_{iso}, one order of magnitude larger than that for Sb or Os atoms. So Pr atoms are in a strongly disordered position as reported in[7,33]. *Moreover, they indicate the possibility of a nearly but not completely filled Pr site in the filled skutterudite structure of $PrOs_4Sb_{12}$*. This may play a role in the large sample dependence of the Schottky anomaly. It should be noted that the large rattling motion of the Pr atoms in the Sb-cages at 300 K may reduce the accuracy of this measurement, and the values may depend slightly on the refinement model. However the occupancy factors reported in table II at least support the trend of varying Pr occupancy in these three samples.

We note that the Pr occupancy is the highest in sample L1-5 with a single sharp transition, which might indicate that the broad transition at T_{c1} is due to Pr vacancies. However the jump at T_{c1} is much higher in sample L3-2 than in sample L1-3 whereas the level of Pr vacancies is smaller in sample L3-2 than in sample L1-3. *This X-ray diffraction analysis cannot confirm the scenario based on Pr vacancies to explain the double transition in $PrOs_4Sb_{12}$.*

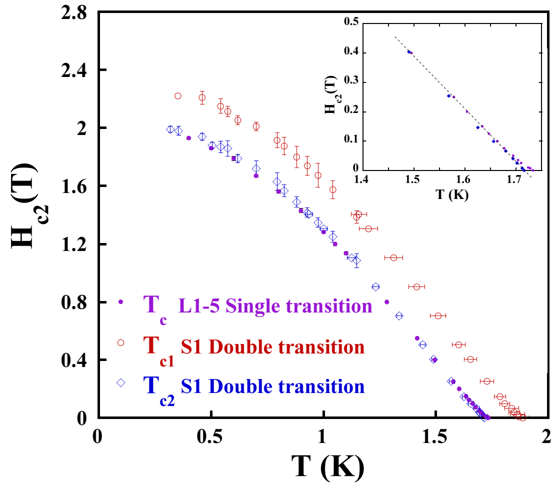
Further diffraction measurements at low temperature are required to thoroughly characterize the dynamic and static disorder at the Pr site, and to discuss more precisely the filling factor of the Pr sites.

V. SUPERCONDUCTING PHASE DIAGRAM

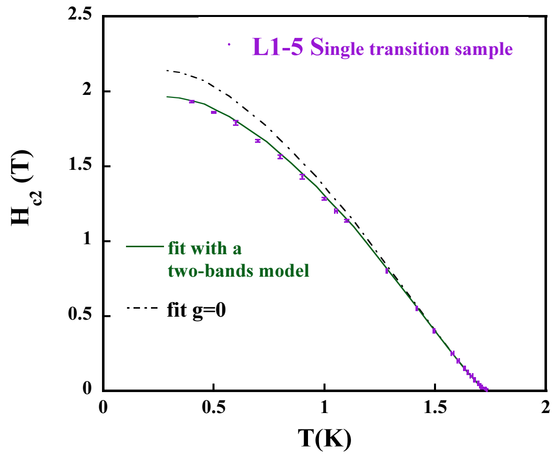
Eventually, let us conclude on a different aspect of the fascinating superconducting properties of this system, coming back to the question of multiband superconductivity. We have investigated the superconducting T_c versus H phase diagram of the single transition sample L1-5 under magnetic field by resistivity measurements as shown in figure 10(b). The transition remains very sharp (12 mK at 1.2 T and less than 30 mT at 400 mK), indicating again the high quality of this sample. The $T_c(H)$ line matches with $T_{c2}(H)$ published in[9] as shown in figure 10(a). The small positive curvature at low magnetic field is even more clearly visible (Cf. insert of figure 10(a)).

This makes it even clearer that multigap effects are disconnected from the question of the double transition. It also supports the conclusions of the recent thermal conductivity measurements on a high quality-single superconducting transition sample, L1-1A: multigap effects have been confirmed[18], 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[23]. 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[9], that it is not connected to sample inhomogeneities.

It also gives information on the inter band coupling strength different from those of the thermal conductivity experiments. For example, the fit proposed in[9] for $H_{c2}(T)$ would also apply to these new measurements, as



(a)



(b)

FIG. 10: (a) Superconducting phase diagram H-T for the single transition sample L1-5, obtained by resistivity measurements, and for the sample with a double transition S1 (ref.[9]). The insert shows the small positive curvature at low magnetic field both for L1-5 and T_{c2}(H) of the sample with a double transition. Clearly, $H_{c2}(T)$ for L1-5 follows that for the lower temperature one of the double transition sample. The small positive curvature in low fields is more clearly resolved in L1-5. (b) Fit of the superconducting phase diagram H-T of L1-5. The error bars indicate the width of the transition. A two-band model like in ref[9] was used. The new set of parameters is described in the text. The dashed dotted line shows the fit without Pauli limitation (with g=0)[34].

the data simply scale with T_c. But the set of inter and intra band coupling constants (λ_{ij}) proposed in this first work, was based on the simplest hypothesis that λ_{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[18], one needs to introduce a difference between λ_{11} and λ_{21}. The size and position of the curvature on H_{c2} then still impose a very small value of λ_{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[9], 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. 10(b)), but yields also the good values for the gap as deduced from thermal conductivity measurements. Again, it is only the ratio of the λ_{ij} which matters, the value $\lambda_{11} = 1$ being fixed arbitrarily[9]. The factor 5 between λ_{11} and λ_{21} is essentially due to the coupling strength, meaning that intra 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, λ_{12} and λ_{22} are strongly reduced by density of states effects, but the general trend which emerges from the new set of λ_{ij} imposed by the combination of thermal conductivity[18] and H_{c2} results is that multiband effects in $PrOs_4Sb_{12}$ arise 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.

VI. CONCLUSION

The general characterizations point out to a recurrent double superconducting transition in $PrOs_4Sb_{12}$ which appears in the good samples, with the best RRR_{2K} and high specific heat jump at the superconducting transition. However a study of many samples especially small ones (with a typical size of 100 μm) shows that its occurrence is most likely a phenomenon related to inhomogeneity rather than to fundamental microscopic mechanisms. The evidences are :

- the existence of three samples with a single sharp transition.
- the higher quality of these three samples than that of the samples exhibiting a double transition: their normalized specific heat jump at the superconducting transition is higher and their transitions are narrower.
- polishing a sample tends to remove the higher transition temperature (T_{c1}) without broadening of the lower transition (T_{c2}).

The samples exhibiting a double transition are most likely divided into macroscopically segregated parts, one with a large distribution of T_c below T_{c1} and one with a single sharp superconducting transition at T_{c2}. The lowest temperature transition T_{c2} seems to be the intrinsic one.

However these results leave open the questions of the origin of the double transition and of the sensitivity of T_{c2} to the quality of the samples.

Based on our 4 circles X-ray diffraction results, we conclude that Pr vacancies are certainly present in the samples, and that the percentage of the Pr deficiency varies from sample to sample, which might explain the dispersion of the hight of the Schottky anomaly above T_c. However, it seems that Pr vacancies cannot explain the presence of the double superconducting transition. Further studies, especially at low temperature, are necessary to refine these conclusions.

Finally, the superconducting phase diagram of a single transition sample was determined and fitted with a two-band model. It appears, in conjunction with thermal conductivity results, that the multiband effects in $PrOs_4Sb_{12}$ come from the difference in the f character of the bands both through density of states and pairing mechanism effects.

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