Superconducting $PrOs_4Sb_{12}$: a thermal conductivity study

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The superconducting state of the heavy fermion $PrOs_4Sb_{12}$ is studied by heat transport measurements on a highly homogeneous single crystal exhibiting only one transition peak in the specific heat. The field *and* temperature dependence of the thermal conductivity confirm multiband superconductivity and point to fully open gaps on the whole Fermi surface.

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Several unusual features have been reported on the superconducting state of $PrOs_4Sb_{12}$, the first Pr-based heavy fermion (HF) superconductor [1]: a double superconducting transition in the specific heat has been observed on different samples [2, 3, 4, 5], like in the well-known case of UPt_3, but its intrinsic nature has not been clearly established yet [4, 6]. Other experiments also point to *unconventional* superconductivity in this compound: thermal conductivity (κ) measurements in a rotated magnetic field [7], London penetration depth studies [8] and flux-line lattice distortion [9] support nodes of the gap. These results contrast with scanning tunneling spectroscopy (STM) [10], Sb nuclear quadrupole resonance (NQR) [11] or muon spin relaxation (μSR) [12] which measured a fully opened gap. Our first very low temperature κ measurements under magnetic field (sample A) provided strong evidence for multiband superconductivity (MBSC) in $PrOs_4Sb_{12}$, but sample quality did not allow analysis of the gap topology from the low temperature regime of κ [13].

In this Letter, we report a new study of thermal transport at very low temperatures on a highly homogeneous $PrOs_4Sb_{12}$ single crystal. Supplementary specific heat measurements of this sample show only one single, sharp superconducting jump at T_c, supporting an extrinsic origin for the double transition reported so far. Improved sample quality also has profound impact on thermal transport, mainly on the temperature dependence $\kappa(T)$ in zero field. It provides compelling evidence for a rather "conventional" MBSC scenario with fully opened gaps on the whole Fermi surface.

Our thin, platelet-shaped $PrOs_4Sb_{12}$ single crystal (sample B2, $\sim 760 \times 340 \times 45\ \mu m^3$, $T_c \simeq 1.75$ K, residual resistivity (ρ) ratio $\rho(300\ K)/\rho(T_c) \sim 30$ instead of ~ 15 in sample A) has been extracted (gently "grinded down" against the disk of a diamond saw) from a conglomerate of several small cubes of $PrOs_4Sb_{12}$ (sample B1 $\sim 1 \times 0.75 \times 0.6\ mm^3$), grown by the Sb-flux method [7]. Specific heat (C_p) in zero field has been measured on a PPMS, first the entire conglomerate (B1) and then sample B2 alone (see fig. 1). $\kappa(T, H)$ of sample B2 parallel to the magnetic field has been measured in a dilution refrigerator by a standard two-thermometers-one heater steady-state method down to 30 mK and up to 3 T ($\mu_0 H_{c2}(T \to 0) \simeq 2.2$ T). The carbon thermometers were thermalized on the sample by gold wires, held by silver paint on gold stripes evaporated on the surface of the sample after ion gun etching. The gold stripes are essential for the stability and the quality of the electrical contacts (resistance $R_c^e \approx 10\,m\Omega$ at 4 K). The same contacts and gold wires were used to measure the electric resistivity of the sample by a standard four-point lock-in technique. The reliability of the experimental setup was checked against the Wiedemann-Franz law, giving quantitatively similar results for L/L_0 as reported in [13].

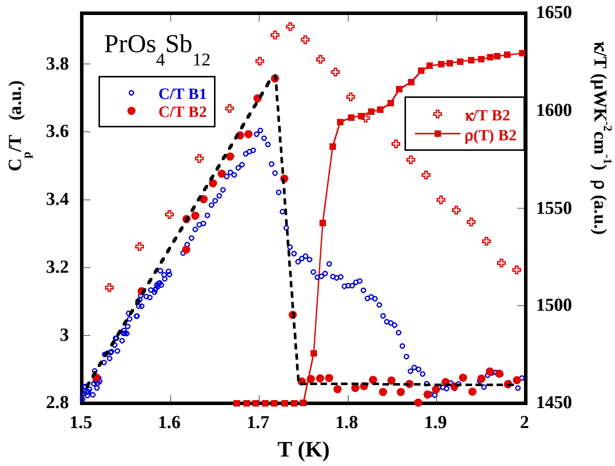

FIG. 1: Specific heat C_p/T, electric resistivity ρ and thermal conductivity $\kappa(T)/T$ in zero field around T_c, documenting the collapse of the double transition (observed only in sample B1) and the high homogeneity of sample B2. Nevertheless, a kink at 1.9 K on $\rho(T)$ reveals some "traces" of the upper transition in sample B2, but the bulk superconducting transition clearly corresponds to the lower T_c in C_p/T(T) of sample B1.

The excellent homogeneity of our sample B2 is documented by the fact that the bulk superconducting transition appears at exactly the same temperature on C_p, κ/T and ρ (see fig. 1 and below). Another criterion regarding crystal purity is the residual value of κ/T in the $T \to 0$ limit. For platelet B2, it is smaller than $1.6\,\mu W\,K^{-2}\,cm^{-1}$, which corresponds to 0.07% of

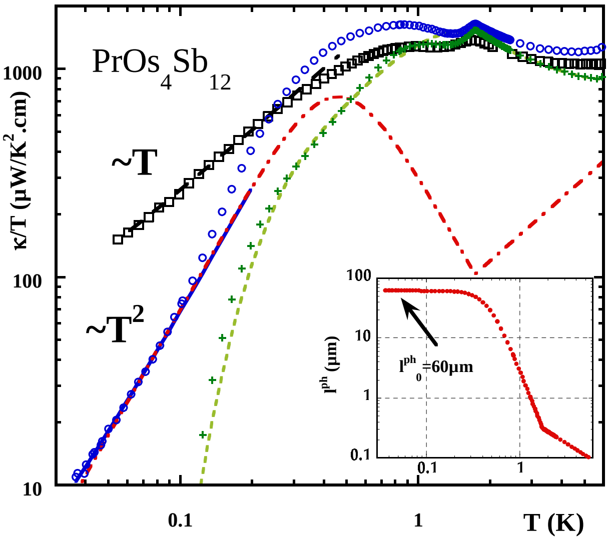

FIG. 2: $\kappa/T(T)$ in zero field: comparison of former (A, open squares) and present (B2, open circles) sample. For sample B2, we separate phonon κ^{ph} (dash-dotted line) and electronic κ^{el} (crosses) contribution. The dashed line is a fit of κ^{el} within the MBSC scenario, see text. The inset shows the estimated temperature dependence of the phonon mean free path.

$\kappa/T(T \to 0, \mu_0 H = 2.5\,\mathrm{T} > H_{c2})$ and is significantly lower than in former sample A. These signatures of high sample quality allow us to use thermal transport at very low temperatures as a sensitive probe of the low lying energy excitations in $PrOs_4Sb_{12}$.

Figure 1 displays the superconducting transition at zero magnetic field as seen by specific heat for samples B1 and B2, and in addition for sample B2 the corresponding κ/T and $\rho(T)$ curves. The specific heat of sample B1 exhibits a double transition, comparable to those reported in [4]. The fact that both transitions behave similarly under magnetic field, and that the upper one always appears inhomogeneous [4] had cast doubt on the intrinsic nature of this double transition. The remarkable result is that the double transition collapses to a single, sharp jump of C_p (at the lowest T_c and of about the same overall height) just by reducing the crystal dimensions (sample B1 $\to$ B2). Obviously, areas with a single and a double transition coexist within the same sample. It suggests that, like in URu_2Si_2 [14], the observed double superconducting transition in $PrOs_4Sb_{12}$ is related to sample inhomogeneity. A hint for extracting samples with a single transition comes from the preparation stage: in order to remove all small cavities appearing during the sawing process of B1, we had to reduce the thickness of B2 down to only 50 μm. Similarly, such tiny dimensions were reported for another sample exhibiting a single C_p jump [6]. Further systematic (structural) investigations are required to determine the nature of defects which might be at the origin of the sharp double transition in $PrOs_4Sb_{12}$.

In figure 2, we compare the temperature dependence of κ/T in zero field of samples A (former) and B2 (present). For B2, κ/T has dropped by about two orders of magnitude from T_c down to 30 mK, with a clean T^3 behavior of κ below 100 mK. In sample A, the low temperature behavior of κ/T is probably dominated by impurities, defects and/or other inhomogeneities, resulting in a sort of cross-over regime $\kappa/T \sim T$ [13]. By contrast, at higher temperatures, κ/T is qualitatively the same for both samples, except that there is now a sharp peak in κ/T precisely at the superconducting transition (as seen by C_p and ρ). In sample A, these features were much broader and the local maximum of κ/T appeared below the resistive T_c or the onset of the specific heat jump.

In figure 3, we compare the normalized $\kappa(H)/T$ data at 50 mK of samples A and B2: in this temperature region, the quasiparticle mean free path is governed by elastic impurity scattering [13]. The very fast increase of thermal conductivity at low fields is perfectly reproducible, and even more pronounced in sample B2 because of the significant drop of κ/T for $T \ll T_c$ in zero field (see fig. 2): a magnetic field of only 5% of $H_{c2}(0)$ is enough to restore about 40% of the normal state heat transport. This robust feature, similar to observations in MgB_2 [15], confirms MBSC in $PrOs_4Sb_{12}$ [13]. The plateau at $0.4\kappa_n$ can be interpreted as the "normal state" contribution of the small gap band at $T \to 0$, observed once the vortex cores of that band completely overlap. Moreover, despite improved sample quality, testified by the sharp change of slope at T_c, there is clearly no sign of a phase transition in the mixed state as suggested in [7]: $\kappa(H, T \to 0)$ has no anomaly at the proposed H^* line ($H^*(T \to 0) \approx 0.8\ T$), whereas the $B \to C$ transition in UPt_3 was clearly seen on $\kappa(H)$ [16]).

Because of improved sample homogeneity, it is now worth analyzing the temperature behavior of κ/T. Just above T_c, $L/L_0 \lesssim 1$ [13], which indicates a phonon thermal conductivity (κ^{ph}) negligible compared to the electronic heat transport (κ^{el}) in the neighborhood of T_c. The change of slope observed at T_c ($d(\kappa_S/\kappa_N)/d(T/T_c)$) is of order 1.4. In conventional superconductors, it is generally ascribed to the combined effects of the opening of the gap and the energy dependence of the electron-phonon scattering rate on κ^{el}[17, 18]. In the BCS weak-coupling limit, its maximum value is of order 1.4, when lattice scattering is the limiting mechanism for κ^{el} (see measurements on very pure In [19, 20, 21]). For $PrOs_4Sb_{12}$, electronic inelastic scattering may replace the effect of electron-lattice scattering. Nevertheless, taking into account the relative weight of elastic to inelastic scattering, as well as MBSC (negligible effect of gap opening in the small gap band), the value of $d(\kappa_S/\kappa_N)/d(T/T_c) \approx 1.4$ appears very large. It is likely a signature of strong-coupling effects, as observed (and calculated) for example in lead ($d(\kappa_S/\kappa_N)/d(T/T_c) \approx 7$ [17, 22]). Indeed, Sb NQR [11] or heat capacity analysis [5] have already stressed strong-coupling effects in

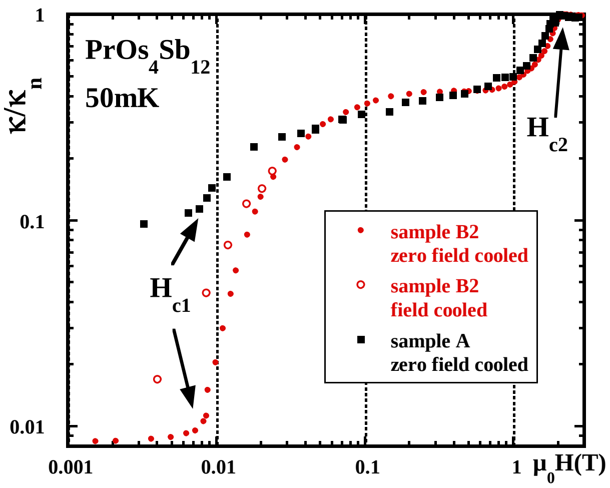

FIG. 3: $\kappa/T(H)$ (normalized to its value at the superconducting transition) at 50 mK for samples A and B. The arrows indicate the lower (H_{c1}) and upper (H_{c2}) critical field. The data in the "field cooled" mode reveal residual flux pinning below 50 mT and a sensitivity of κ to fields as low as 5 mT.

$PrOs_4Sb_{12}$.

As regards now the origin of the local maximum of κ/T slightly below 1 K, it had been ascribed to enhanced inelastic mean free path due to the condensation of electronic scattering centers for $T < T_c$. But the question of phonon or electronic origin (or both) was left open [13]. It is now possible to give a quantitative estimate of the phonon contribution: indeed, a maximum of κ/T below T_c followed by a T^3 behavior of κ at low temperature is well-documented from superconducting Pb and Nb [22, 23], from the rare earth nickel borocarbides RNi_2B_2C (R=Lu, Y) [24, 25, 26] and many other materials.

On cooling the phonon mean free path l^{ph} increases from a law $l^{ph} \sim T^{-1}$ (when it is limited by electron-phonon interactions above T_c) up to a typical crystal dimension at the lowest temperature. But an intermediate regime, described empirically by $l^{ph} \sim T^{-1}(T_c/T)^n$, starts below T_c due to the reduction of scattering by electrons (see inset of fig. 2). Quantitatively, an estimation for κ^{ph}/T is plotted in fig. 2 from:

$$\frac{1}{\kappa^{ph}_{sc}/T} = \frac{1}{\kappa^{ph}_{normal}/T}\left(\frac{T}{T_c}\right)^{n=3} + \frac{1}{bl_0^{ph}T^2}, \qquad (1)$$

We used $\kappa^{ph}_{normal} = aT^2$ with a=60 μW/K^{3}cm (from deviation of the Lorenz number above T_c [13]), bl_0^{ph} is fixed by κ/T at lowest temperatures ($T < 100\,$mK), yielding $l_0^{ph} \sim 60\ \mu$m ($b = 10.9 \times 10^3\,\mathrm{W\,K^{-4}\,m^{-2}}$). l_0^{ph} is of order the smallest crystal dimension. The adjustable parameter is mainly the power law (n) for the boosted temperature dependence of l^{ph} : it proved impossible (adjusting n) to account for the local maximum only by the phonon contribution, so that a situation similar to that of Pb [22] or the high-T_c oxydes [27, 28, 29] is recovered. In any case, it is seen that κ^{ph} should follow a T^3 behavior up to 0.3 K, giving, in the temperature range 0.1-0.3 K, a robust estimate of the electronic contribution κ^{el}/T.

Nevertheless, we tried to understand the normalized electronic contribution $\kappa^{el}/\kappa^{el}_{2.5\,\mathrm{T}}$ up to $T \leq 0.6\,$K (region with dominant elastic impurity scattering). The most striking feature is that it is not possible to fit $\kappa^{el}(T)$ if one assumes a BCS gap corresponding to $T_c = 1.729\,$K: κ^{el}/T starts to rise at much lower temperatures than expected, requiring a smaller gap value. Of course, this cannot be compensated by strong coupling effects (which only make it worse, increasing the ratio Δ/T_c), nor by another estimation of the phonon contribution ($\kappa^{ph}(T)$ cannot be larger than $bl_0^{ph}T^3$, which is constrained by the measurements below 0.1 K). The data points can be quantitatively reproduced within a MBSC scenario, when we include a small $\Delta_\mathrm{s}(T)$ and a large $\Delta_\mathrm{l}(T)$ gap function with the same T_c, and two associated conduction channels: $\kappa^{el}/T = n_s \cdot \kappa^{el}_{\Delta_s}/T + (1-n_s) \cdot \kappa^{el}_{\Delta_l}/T$. The best data fit is then obtained for a zero temperature gap ratio of about $\Delta_\mathrm{l}/\Delta_\mathrm{s}(T \to 0) \sim 3$ with $\Delta_\mathrm{s}(T \to 0) \sim 1\,$K, and a "weight" for the small gap band $n_s \sim 0.35$. This value is close to the 40% deduced from the "plateau" of $\kappa(H, T \to 0)$ (fig. 3). The characteristic field scale H^S_{c2} for the vortex core overlap of the small band gap can now be estimated from $H_{c2}/H^S_{c2} \sim \left(\frac{\Delta_\mathrm{l} \cdot \mathrm{v}^F_\mathrm{s}}{\Delta_\mathrm{s} \cdot \mathrm{v}^F_\mathrm{l}}\right)^2$, where v_i^F is the average Fermi velocity of band i. In [4] we assumed that the small gap band is also a light carrier band, with $\mathrm{v_{F,s}/v_{F,l}} \sim 5$. We then get $H^S_{c2} \sim 10\,$mT, which is of the order of H_{c1} and seems reasonable owing to the data of $\kappa(H)$. So the main outcome of the analysis of this new data is the existence of a small but finite gap Δ_s in $PrOs_4Sb_{12}$, quantitatively consistent with the MBSC scenario deduced from $\kappa(H)$.

Various measurements on the superconducting state of $PrOs_4Sb_{12}$ have been interpreted either as pointing to gap nodes [7, 8, 9] or fully open gaps [10, 11, 12]. Focusing on the latest, we can compare the extracted gap values. The NQR [11] as well as the μSR [12] studies propose large ratios of $2\Delta/k_BT_c$, respectively ~ 5.2 and ~ 4.2, supporting strong coupling effects but not the presence of a small gap. Nevertheless, the NQR data shows a large residual relaxation rate ($1/T_1$) below 0.5 K, which may point, as for our sample A, to crystal inhomogeneities which prevent observation of the smallest gap. Moreover, like specific heat, the nuclear relaxation rate should be rather sensitive to bands with large density of states. So if our interpretation [13] of the small gap band as being also a "light mass" band is correct, it may have indeed little contribution to $1/T_1$. The muon relaxation rate (σ_s) measured with μSR is controlled by the field distribution which may not put more weight on the heavy than on the light bands. But the measurements were performed in a residual field of 20 mT, already larger than

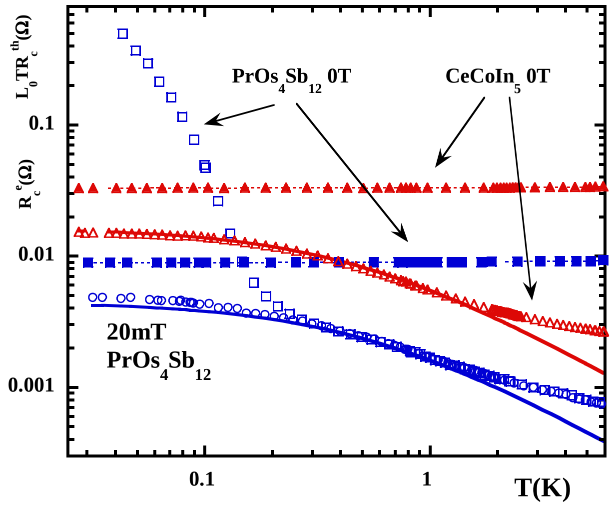

FIG. 4: Electric $R_c^e(T)$ (full symbols) and thermal $R_c^{th}(T).L_0T$ (open symbols) resistance of the Au-$PrOs_4Sb_{12}$ or Au-$CeCoIn_5$ contacts. Full lines: fits of $R_c^{th}(T)$ according to equation (2). $R_c^e(T)$ are temperature and field independent, but $R_c^{th}(T)$ shows a highly singular behavior in zero field below 200mK on $PrOs_4Sb_{12}$. This further supports a fully open gap in this system (see text).

H_{c2}^S, so that again $\sigma_s(T)$ is probably governed by the high energy excitations. But the "unusual" non linear field dependence of $\sigma_s(T = 0.1$ K) compares well with $\kappa(H)$: the MBSC scenario, with the small gap band associated to light carriers can even "explain" the increase of σ_s at low fields as $\sigma_s \propto 1/m^*$. Eventually, the STM measurements [10] proposed a gap distribution, which may extend from 120 μV to 325 μV ($2\Delta/k_BT_c$ ~1.5-4.1), not so far from our analysis of $\kappa(T)$ ($2\Delta_S/k_BT_c \sim 1.15$, $2\Delta_L/k_BT_c \sim 3.5$).

A further robust and reproducible [13] experimental observation supports a *fully open* gap in $PrOs_4Sb_{12}$. Indeed, we can also measure on our setup the electrical contact resistance ($R_c^e(T)$) between the sample and the gold wire of the thermometer thermalisation, as well as its *thermal* contact resistance R_c^{th}. R_c^{th} is defined as $P/\Delta T$, with P the Joule power dissipated in $R_c^e(T)$ and ΔT the thermal gradient produced by P. For large contact areas, we expect that at low temperature

$$R_c^{th} \approx 1/2 \frac{1}{\frac{L_0T}{R_c^e} + aT^2} \tag{2}$$

(aT^2 being the phonon contribution to the thermal conductivity of the contact). Figure 4 shows that this is well observed below 1 K for $PrOs_4Sb_{12}$ in a field of 20 mT, or $CeCoIn_5$ in zero field (new measurements on this same setup). But for $PrOs_4Sb_{12}$ in zero field, an unexpected divergence is observed below 200 mK, with no correspondence on $R_c^e(T)$ (field and temperature independent). On the same footing, $CeCoIn_5$ in zero field, like $PrOs_4Sb_{12}$ in 20 mT, could be cooled below 10 mK whereas $PrOs_4Sb_{12}$ in zero field remained stuck above 25 mK. A reason could be that electronic heat transport is suppressed at the normal-superconducting interface when $k_BT \ll \Delta_s$ (whereas electric current can always go through thanks to Andreev processes [30]): of course, this barrier is suppressed in very low field in $PrOs_4Sb_{12}$ (multiband effects) or in zero field in $CeCoIn_5$ which has line nodes of the gap [31].

In conclusion, we measured the thermal conductivity of a highly homogeneous $PrOs_4Sb_{12}$ single crystal exhibiting a *single* jump on C_p at T_c. The reproducible field dependence $\kappa(H)$ at $T \ll T_c$ confirms the proposed MBSC scenario. Further support now comes from the low temperature $\kappa(T)$ and $R_c^{th}(T)$ data which both point to isotropic, fully opened gap functions, in comparison with other measurements (NQR, μSR, STM). Owing to the still mysterious homogeneity problems in this compound and to the strong field sensitivity, analysis of the data requires a close look at the experimental conditions (sample, field and temperature range) which may explain the remaining divergences of interpretations.

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[1] E.D. Bauer *et al.*, Phys. Rev. B **65**, 100506(R) (2002)
[2] M.B. Maple *et al.*, J. Phys. Soc. Jpn. **71** Suppl., 23 (2002)
[3] R. Vollmer *et al.*, Phys. Rev. Lett. **90**, 057001 (2003)
[4] M.A. Méasson *et al.*, Phys. Rev. B **70**, 064516 (2004)
[5] K. Grube *et al.*, Phys. Rev. B **73**, 104503 (2006)
[6] M.A. Méasson *et al.*, Physica B, **378-380**, 56 (2006)
[7] K. Izawa *et al.*, Phys. Rev. Lett. **90**, 117001 (2003)
[8] E. E.M. Chia *et al.*, Phys. Rev. Lett. **91**, 247003 (2003)
[9] A. Huxley *et al.*, Phys. Rev. Lett. **93**, 187005 (2004)
[10] H. Suderow *et al.*, Phys. Rev. B **69**, 060504(R)(2004)
[11] H. Kotegawa *et al.*, Phys. Rev. Lett. **90**, 027001 (2003)
[12] D.E. MacLaughlin *et al.*, Phys. Rev. Lett. **89**, 157001 (2002)
[13] G. Seyfarth *et al.*, Phys. Rev. Lett. **95**, 107004 (2005)
[14] A.P. Ramirez *et al.*, Phys. Rev. B **44**, 5392 (1991)
[15] A.V. Sologubenko *et al.*, Phys. Rev. B **66**, 014504 (2002)
[16] H. Suderow *et al.*, J. Low Temp. Phys. **108**, 11 (1997)
[17] J. Beyer Nielsen *et al.*, Phys. Rev. Lett. **49**, 689 (1982)
[18] V. Ambegaokar *et al.*, Phys. Rev. **139**, A1818 (1965)
[19] R.E. Jones *et al.*, Phys. Rev. **120**, 1167 (1960)
[20] L. Tewordt, Phys. Rev. **128**, 12 (1962)
[21] L.P. Kadanoff *et al.*, Phys. Rev. **124**, 670 (1961)
[22] M.H. Jericho *et al.*, Phys. Rev. B **31**, 3124 (1985)
[23] A. Connolly *et al.*, Proc. Roy. Soc. (London) **A 266**, 429 (1962)
[24] M. Sera *et al.*, Phys. Rev. B **54**, 3062 (1996)
[25] E. Boaknin *et al.*, Physica C **341-348**, 1845 (2000)
[26] B.D. Hennings *et al.*, Phys. Rev. B **66**, 214512 (2002)
[27] J.L. Cohn *et al.*, Phys. Rev. B **45**, 13144 (R) (1992)
[28] K. Krishana *et al.*, Phys. Rev. Lett. **75**, 3529 (1995)
[29] R.C. Yu *et al.*, Phys. Rev. Lett. **69**, 1431 (1992)

[30] A.F. Andreev, J. Exptl. Theoret. Phys. (U.S.S.R.) **46**, 1823 (1964), Sov. Phys. JETP **19**, 1228 (1964).

[31] R. Movshovich *et al.*, Phys. Rev. Lett. **86**, 5152 (2001)