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Transport evidence for pressure-induced superconductivity in $CePd_2Si_2$

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Abstract

Resistivity measurements performed under pressure on high quality single crystals of $CePd_2Si_2$ are reported. Pressure-induced superconductivity is observed in the range 2–7 GPa with an optimal T_c of 520 mK at 5.1 GPa. The superconducting properties of the sample as well as its peculiar zero pressure resistivity are tentatively linked to its preparation.

Keywords: A. Superconductors; D. Electronic transport; D. Heavy fermions; E. Strain, high pressure

1. Introduction

Superconductivity, appearing at the verge of magnetic instability, is an exciting topic in condensed matter physics since it definitively provides new routes for electronic pairing apart from the BCS electron–phonon interaction [1,2]. Among these systems, the so-called heavy fermion (HF) compounds are good candidates for exotic superconductivity because of the effects of strong Coulomb repulsion and spin–orbit coupling. These compounds are named after the realization, at low temperatures, of a coherent state among localized (4*f* or 5*f*) and conduction (d) electrons, which is experimentally well described in the framework of the Landau Fermi-liquid theory. More and more HF compounds are known to undergo a superconducting transition under pressure [3]. The extensively studied CeM_2T_2 family (where M is a transition metal and T = Si, Ge) provides the opportunity to realize various kind of antiferromagnetic order by changing M and T [4]. It is then possible to drive the Néel temperature, T_N, to zero (by doping or applying pressure) and to reach a quantum critical point (QCP) where superconductivity may emerge. Among these compounds, $CeCu_2Si_2$ is an ambient pressure superconductor [5]. With a larger unit-cell volume, its isoelectronic counterpart $CeCu_2Ge_2$ [6] was subsequently found superconductor under pressure at 7.7 GPa. The same kind of behavior was also found for $CeRh_2Si_2$ [7] at 0.9 GPa. $CeNi_2Ge_2$ is still under investigation and may show some traces of superconductivity at ambient pressure [12] as well as above 1.5 GPa [13–15]. The discovery of superconductivity in $CePd_2Si_2$ under a pressure of 2.7 GPa [8,9] was a "tour de force" since this compound was studied for more than a decade with a lack of reproducibility in the experimental results obtained [10,11]. Our motivation was thus to carry out extensive metallurgical investigation on this compound. In this work, we confirmed the pressure-induced superconductivity in high quality samples of $CePd_2Si_2$, a behavior only observed so far by the Cambridge group [8]. We will focus here on the link between the *T*–*P* phase diagram obtained and the metallurgy. Results relevant to heavy fermion physics (effective mass, non-Fermi liquid behavior, critical field) will appear in a forthcoming publication.

2. Sample preparation

Polycrystalline ingots of $CePd_2Si_2$ were synthesized starting from high purity starting elements (Ce 4N, Pd 4N, Si 6N) melted on a water-cooled silver boat in an induction furnace under Argon atmosphere. Sufficiently large

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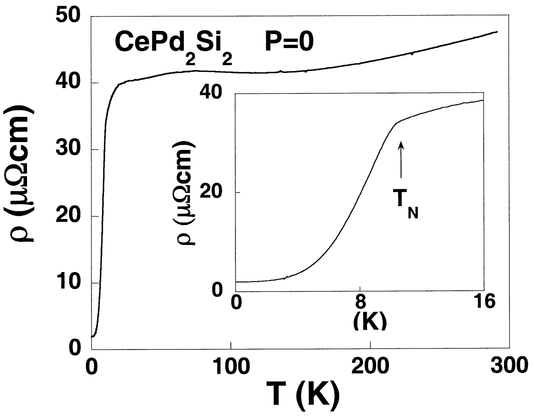

Fig. 1. Basal plane resistivity versus temperature of $CePd_2Si_2$. The low temperature part is shown in the inset. The arrow indicates the antiferromagnetic transition at $T_N = 10.6$ K.

quantities (≈ 5 g) were melted in order to get a weak curvature on the top of the ingot. This allows the self-nucleation of platelets, which turn out to be monocrystalline grains with the *c*-axis of the tetragonal structure perpendicular to the platelet as established by X-ray Laue technique. The polycrystalline batches were hung with a tungsten wire inside a susceptometer of a high vacuum furnace (10^{-8} mbar) for an annealing treatment of 48 h at 1200°C. Afterwards, a selection was made among the platelets obtained from the batch taken for criterion, their resistivity ratio $\rho(300\text{ K})/\rho(4.2\text{ K})$. For this purpose four indium contacts were soldered on tens of platelets. The best ratio obtained was nearly equal to 20 while most of the platelets have a ratio of the order of 8. The platelets selected in this way were cut and polished to the desired size for high-pressure measurements, typically $450 \times 70 \times 20\ \mu m^3$. This allows us to measure the resistivity within an accuracy of 10%. It is worthwhile to note that such good resistivity ratios are obtained only with the preparation method described above and notably a relatively high heat treatment temperature. For example, annealing at 900°C for 10 days does not significantly produce such resistivity ratios. Single crystals of $CePd_2Si_2$ obtained with the Czochralsky pulling method have so far low resistivity ratio [10,16].

3. Sample characterization

X-ray diffraction experiment on a powder sample crushed from the initial batch was performed at the Swiss-Norvegian beamline of the European Synchrotron Radiation Facility, Grenoble. The wavelength used was $\lambda = 0.69706$ Å and the counting time was 5 s/step for a spinning capillary of diameter 0.3 mm. Such measurements allow us to study with a great precision the structure of the sample. In particular, the low background and the absence of any impurity peaks implies that the amount of impurities is lower than ≈ 2% in volume. A good refinement was made with the $ThCr_2Si_2$ structure (space group *I*4/*mmm*) [17]. The lattice parameters found are $a = 4.2001(2)$ Å, $c = 9.87982(9)$ Å and the fractional coordinate of Si is $z = 0.3789(31)$. No inversion disorder was found with the Ce, Pd and Si on the 2a, 4d and 4e sites, respectively. The Bragg peaks were found to be larger along the *c* direction, a size effect due to the platelet structure of the crystal growth.

SEM imaging, together with microprobe analysis, were carried out on platelets of the same batch. These measurements confirm the overall good quality of the sample. In particular no other phases were found within a platelet and between the sheets that compose the platelets. On the typical pressure-cell sample size (100 μm), the platelet corresponds to a single grain. The composition is very close to 20–40–40 with an apparent deficiency in Si for some platelets. It is of the order of 1.5% for a piece adjacent to our sample, that is to say within the accuracy of the method.

Finally, a third characterization was made via the ambient pressure (basal plane) resistivity measurement itself. A platelet ($415 \times 110 \times 70\ \mu m^3$) with a resistivity ratio ($\rho(300\text{ K})/\rho(4.2\text{ K})$ of 13 was measured at ambient pressure using a d.c. technique with a traditional four-point method down to 50 mK. The temperature variation of the resistivity is shown in Fig. 1 up to 300 K. If we now consider the residual resistivity ratio, RRR, i.e. $\rho(300\text{ K})/\rho_0$, a value as large as 24 is found. It means that the resistivity drops by a factor of almost 2 (24/13) between 4.2 K and the lowest temperatures. The room temperature basal plane resistivity of $CePd_2Si_2$ is $47 \pm 2\ \mu\Omega$ cm (a value we confirmed on several platelets). The $\rho(T)$ curve is significantly different from previously reported results [10,16,18] since no increase (ascribed to Kondo scattering) is found above T_N. On the contrary, the resistivity of our sample is found to monotonically decrease from 80 K down to the lowest temperature. To this respect the behavior found is closer to the one reported by the Cambridge group for samples where superconductivity is induced by pressure. Another common feature is the quite large value of T_N marked by a kink in the resistivity curve at 10.6 K as shown in the inset of Fig. 1. Values down to 8.5 K were found in samples which show a lower RRR [10,16,18]. Compared to these earlier studies, it seems that samples with a low residual resistivity have a slightly higher T_N and no maximum of resistivity above T_N.

4. *T–P* phase diagram

Two samples ($450 \times 70 \times 20\ \mu m^3$) were put in a tungsten-carbide anvil cell using steatite as the pressure transmitting medium and a pyrophyllite gasket. Pressure was measured via the superconducting transition of a lead manometer. Four-point d.c. resistivity measurements were carried out with picovoltmeters P12 from EM electronics. Resistivity

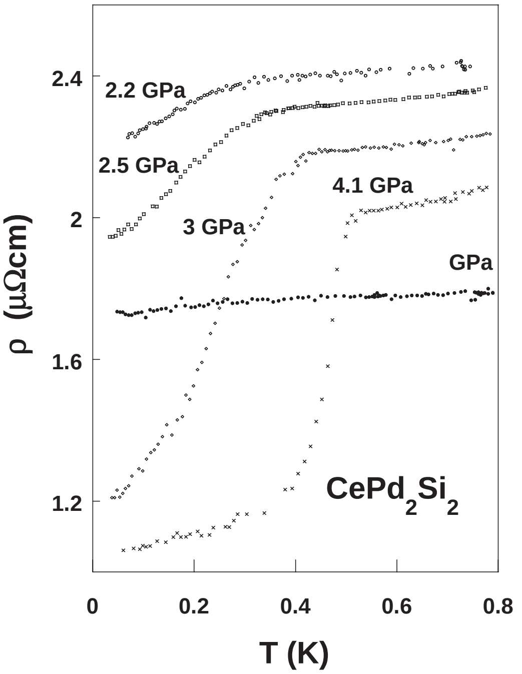

Fig. 2. Low temperature basal plane resistivity of $CePd_2Si_2$ for various pressures showing the superconducting transition.

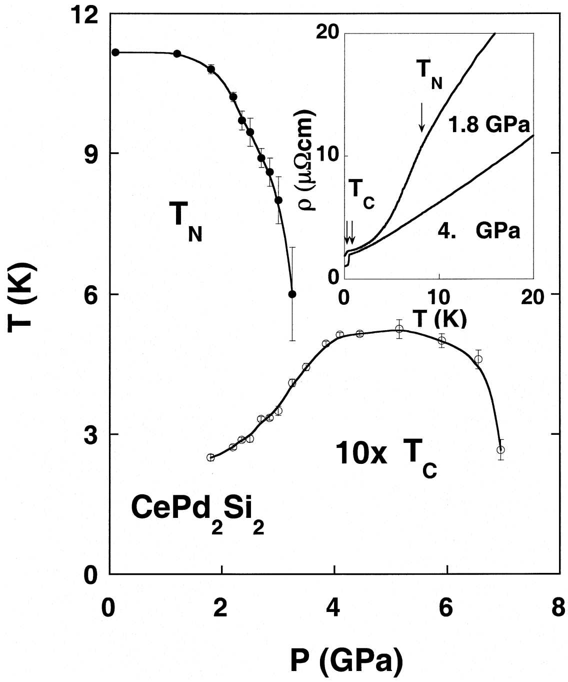

Fig. 3. The temperature–pressure phase diagram of $CePd_2Si_2$. Lines are guides for the eyes. The inset shows the basal plane resistivity for two pressures where superconductivity is observed. At 1.8 GPa both an antiferromagnetic and a superconducting transition temperature can be defined.

is measured in the basal plane due to the geometry of the platelets. The value of the measuring current was between 10 μA and 1 mA depending on the temperature range. Since the results obtained on the two samples are very similar, we will describe here the behavior of one of them and will briefly comment on the differences with the other in Section 5. The first point to note is the degradation of the RRR when the sample is pressurized. In such a cell, the electrical contact between the sample and the measurement wires is supplied by the pressure itself. We thus do not have the ambient pressure RRR of the sample made out of the platelet with a $\rho(300\,\mathrm{K})/\rho(4.2\,\mathrm{K})$ ratio of 20 that is to say an expected RRR of 30–40. Nevertheless an extrapolation of the RRR measured under pressure to $P = 0$ would give an ambient pressure RRR of 17, i.e. half the expected value. Either the small cut sample does not reflect the properties of the larger platelet, or the polishing and cutting work alters the sample quality. Compared to the literature, this result is still good and superconductivity was indeed observed under pressure in this sample.

Low temperature resistivity data are shown in Fig. 2 for various applied pressures. For the upper curve corresponding to an applied pressure of 2.2 GPa, a 15% drop of the resistivity is observed at $T_c^{\mathrm{onset}} = 300$ mK and is interpreted as the entrance in the superconducting state following the results of the Cambridge group. This drop is in fact already observed at 1.8 GPa (not shown for clarity). At higher pressure, the value of the drop increases and reaches a value of 40% at 4.1 GPa. For this pressure the resistivity ultimately shows an upturn and almost a saturation at lower temperature (below 350 mK). At 4.1 GPa, the width of the “transition” between the upper and lower plateau is of the order of 150 mK, that is twice the width measured on the lead manometer. This emphasizes the occurrence of an intrinsic physical width beyond the one of the pressure gradient in the cell (of about 0.1 GPa at 1 GPa evaluated from the manometer). Finally this transition disappears at higher pressure and is no more observed at 7.5 GPa.

The transition temperatures T_c (obtained via a tangent criterion i.e. similar to an onset criterion) and T_N (obtained via the first derivative of the resistivity) are shown in Fig. 3. An optimum T_c of 520 mK is reached at 5.1 GPa. Another finding of these measurements is that signs of magnetism and superconductivity coexist at low pressure. This is shown in the inset of Fig. 3 for a pressure of 1.8 GPa where both a kink and a drop of the resistivity are observed allowing to define at a same time a T_N and a T_c value without any hint on the nature of this coexistence (intrinsic or phase separation). A curve at 4.1 GPa in the non-magnetic state is shown in the same figure for comparison. The other important result is the large pressure range where superconductivity is observed (2–7 GPa).

5. Discussion

First, we emphasize the differences with the work of the Cambridge group where the pressure-induced superconductivity is observed in a narrow range (2.2–3 GPa) [8]. Here, we observed a much larger superconducting domain, a result compatible with measurements performed on $CeCu_2Si_2$ using the same technique [20]. Indeed, the "unified" picture of pressure-induced superconductivity in the CeM_2T_2 compounds was already stressed out from resistivity and thermopower measurements [6,7]. The simplest picture is that pressure alone allows to match the behavior of these compounds with different unit-cell volume whatever the complexity of their electronic structure. Such an idea is based on the Doniach diagram from where only one parameter, the f–d exchange J, is relevant to describe the magnetic non-magnetic boundary [21]. A consequence of this large domain observed is an apparent separation between the magnetic QCP estimated to be at 3.5 GPa, by extrapolating T_N to 0 K, and the optimal pressure for superconductivity i.e. 5.1 GPa. The drawback of our measurement is the finite resistivity found at the lowest temperature and the upturn toward a saturation of the resistivity seen around the optimal pressure for superconductivity. We do not correlate this result with any structural or metallurgical properties of the sample. In particular, X-ray and SEM imaging do not reveal other phases in the platelets or exhibit hints for filamentary originated effects. Concerning the effect of the pressure gradient, the initial slope of $T_N(P)$ can give some evidence for the occurrence of shear stress on our sample. Using the Ehrenfest relation, dT_N/dP can be linked to the jump of the coefficient of thermal expansion at T_N. Measurements of this last quantity [16] give $dT_N/dP_a = -0.83$ K/GPa and $dT_N/dP_c = 0.84$ K/GPa that is for hydrostatic pressure $dT_N/dP = -0.82$ K/GPa, which is four times the value measured here. This emphasizes the occurrence, at least at low pressures, of strong uniaxial stress perpendicular to the sample in our cell.

Compared to classical metals, HF compounds suffer from high residual resistivities (of the order of a $\mu\Omega$ cm at best) due to the dramatic effect of impurities on the coherent state realized at low temperatures. Among others, a channel of enhanced scattering at low temperatures is provided by vacancies on the magnetic sites which acts as Kondo centers (Kondo holes) [19]. This also has consequences on the superconductivity, since the electronic mean free path can be reduced down to the superconducting correlation length, impurities acting then as pair-breaking centers. Such a phenomenon was recently clearly reported and well documented for the strongly correlated electron system Sr_2RuO_4 [22]. The value of T_c and ρ_0 were related via a simple theory of pair breaking of d-wave superconductivity by non-magnetic impurity. From the two samples of $CePd_2Si_2$ we measured, the same picture emerges. These two samples have almost the same pressure behavior. The only differences lie in the values of T_c and ρ_0 around the maximum of the $T_c(P)$ curve. For example at 4.5 GPa, the two samples show 30% difference in ρ_0 with a difference of T_c of about 30 mK. If this is due to impurity pair-breaking effect, the corresponding rate of depression of T_c is 0.07 K/$\mu\Omega$ cm which is of the order of a crude estimate in a scenario of impurity pair-breaking for HF compounds [23]. This may point out, among other phenomena, the importance of pair-breaking effect on the coherent HF state and the need for low RRR in order to induce the superconductivity with pressure in $CePd_2Si_2$ in particular.

6. Conclusion

In this work, the pressure-induced superconductivity of $CePd_2Si_2$ was reproduced on high quality single crystals. The new points stressed by this study are: (i) the coexistence of signs of magnetism and superconductivity at low pressure; and (ii) the large pressure range (2–7 GPa) of superconductivity. We linked this behavior to a low ambient pressure residual resistivity. It seems also that a good candidate for superconductivity has peculiar ambient pressure behavior: a high T_N (10.6 K) and no increase of the resistivity above T_N. These results need further investigation, for instance the use of more hydrostatic condition using helium as transmitting pressure medium.

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