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Heavy fermions, quantum criticality, and unconventional superconductivity in filled skutterudites and related materials

Final Technical Report

$PrOs_4Sb_{12}$ is the first, and only one known, Pr-based heavy fermion superconductor whose physical properties cannot be understood in terms of classical condensed matter physics and which provides convenient ground for studying novel states and behaviors. $PrOs_4Sb_{12}$ is one of two known superconductors that undergo two superconducting phase transitions. Its normal state has heavy fermion character, which is difficult to reconcile with Pr-crystalline electric field ground state, nonmagnetic singlet. The goals of this program was to establish the relationship between the two superconducting order parameters and to determine how the unconventional superconductivity is related to the unconventional normal state.

In-house prepared single-crystalline samples were investigated by X-ray diffraction, microprobe analysis, specific heat in ambient and wide range of magnetic fields, dc- and ac-magnetic susceptibility and electrical resistivity. For some of the crystals, de Haas van Alphen quantum oscillations were investigated in collaboration with S. Julian from Toronto. In case of materials on the verge of quantum instability such as $PrOs_4Sb_{12}$, quality of materials is of paramount importance. By comparison structural, transport and thermodynamic measurements we have determined that electrical resistivity and specific heat near the lower temperature superconducting transition can be used to describe crystal quality. We have provided additional arguments for inhomogeneous superconductivity using entropy and ac-susceptibility measurements. Temperature variation and frequency variation of the imaginary component of ac-susceptibility is similar to those previously observed for granular superconductors.

The previously reported unusual **size effect** was investigated on well characterized crystals polished to different thicknesses. This size effect is observed below 100 μm, which is much larger than characteristic length scales for superconductivity. Reducing sample thickness below 100 μm has no effect on normal state specific heat and magnetization, but a small but measurable increase in the residual resistivity (decrease of *RRR*) was observed in two cases, consistent with an increase of the concentration of defects in the sample. On the other hand, this size reduction had pronounced effect on the superconducting state, such that no bulk transition at T_{c1} was observed in crystals with one of the dimensions smaller than 50 μm. However, weak magnetic shielding was observed in all crystals including those polished to about 20 μm, with unchanged value of the onset temperature of the shielding (T_c,).

Results of this project shed new light on previously claimed exotic behavior of $PrOs_4Sb_{12}$. Among others, this study established that

- There is no significant variation, from crystal to crystal, in the value of the upper superconducting transition T_{c1}. We suggest that this alleged distribution is due to unconventional character of this transition, whose temperature is sensitive to the measurement technique.
- The upper superconducting transition is intrinsic; it is observed most clearly in high quality crystals, which exhibit also very narrow transition at T_{c2}.
- Previously claimed strong negative curvature in $H_{c2}(T)$ near T_c, which lead to two-band model of superconductivity in this system, is sample dependent. This curvature is large in crystals with two bulk transitions but is very small or not measurable in crystals with a single bulk transition (at T_{c2}). Specific heat investigation in fields shows that for any

crystal this curvature is relatively large when transition temperature is estimated from equal entropy construction and small when estimated from the onset of the transition.

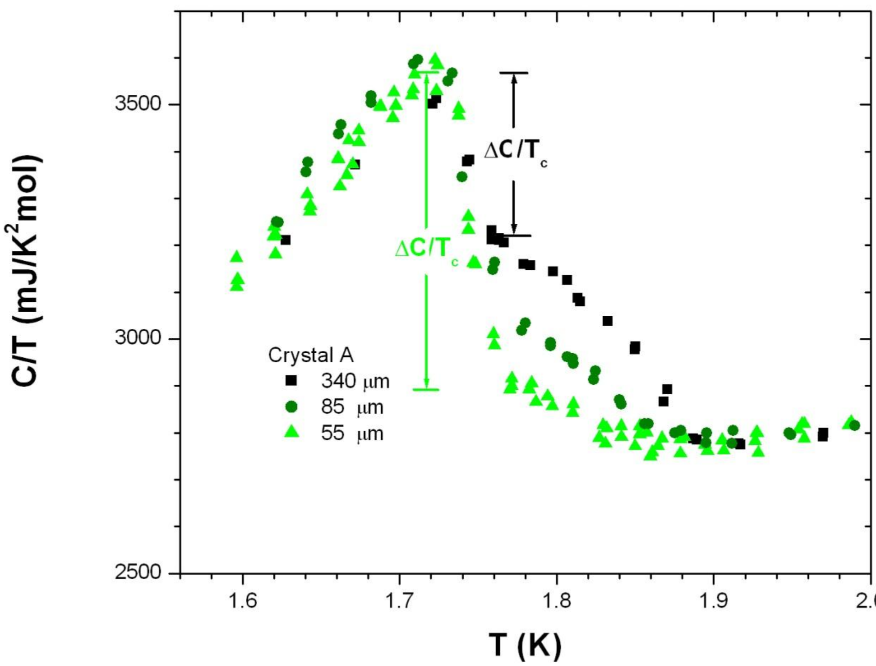
- Frequency and temperature variation of the imaginary component of ac-susceptibility is reminiscent of that for granular superconductors. Magnetic susceptibility study provides strong arguments for inhomogeneous superconductivity.

However, **this inhomogeneous superconductivity emerges from a homogenous normal state**. Contrary to expectations, strongly defected samples exhibit homogenous superconductivity with a single superconducting transition only.

The quality of the crystals used in this investigation was indirectly confirmed by de Haas- van Alphen oscillations study. Unusually clean quantum oscillations were observed in a wide range of temperatures and fields (to 15 T) on crystals with two superconducting transitions and small residual resistivity.

For the first time ever, quantum oscillations were observed in three different phases of the same material. It was demonstrated that $PrOs_4Sb_{12}$ provides unprecedented opportunity for investigation of quantum oscillations while crossing phase boundaries as a function of temperature or magnetic field. In particular, it was shown that one of the Fermi surfaces (β sheet) expands or shrinks when underlying local order parameter changes. Based on this observation it was suggested that quantum oscillations might be an important new tool in the study of materials with the so-called “hidden order

Strong and nearly linear temperature variation of the phase of quantum oscillations between 4.5 and 12 T and temperatures below 300 mK (down to 30 mK, at least) offers the opportunity to use the phase of quantum oscillations in $PrOs_4Sb_{12}$, as a convenient in-situ high field/high pressure



thermometry.

Fig. 1. The effect crystal size reduction on the specific heat neat T_c. Reducing sample thickness always reduces the signature of the upper temperature transition and increases the discontinuity in C/T at the lower transition temperature.

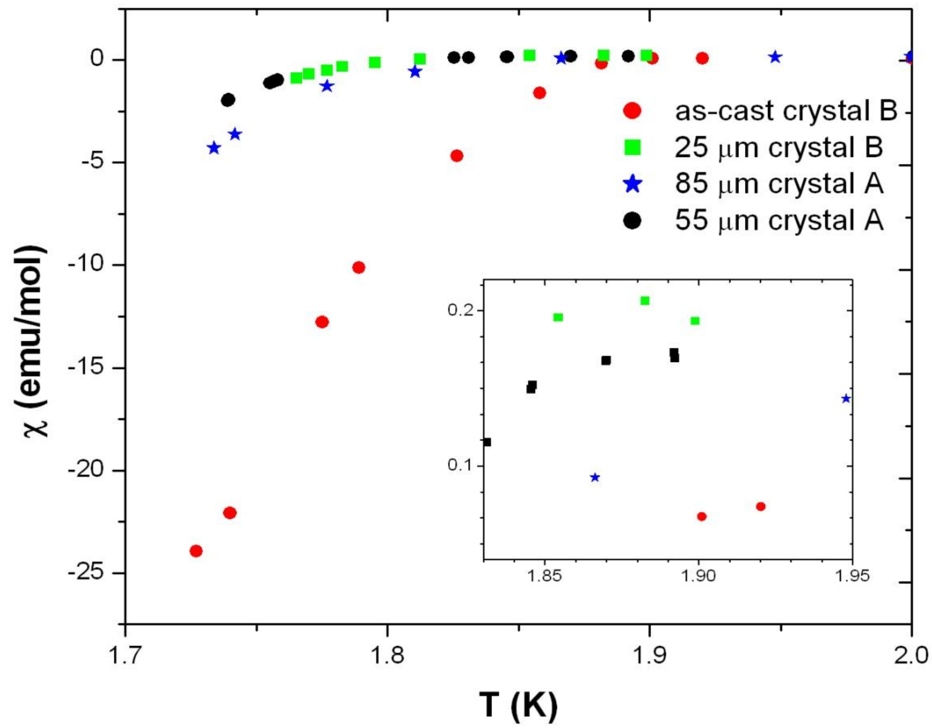


Fig. 2. Magnetic shielding studied by zero-field-cooled, low temperature dc magnetic susceptibility for as-cast crystal B, crystal B polished to 25 μm and crystal A polished to 85 and 55 μm. Measurements were performed in H=10 Oe. Note very small shielding observed in crystals with thickness reduced below 100 μm, consistent with specific heat study (Fig. 1). This size reduction corresponds to an increase of magnetization measured just above T_{c1} (inset; $\chi \equiv M/H$) due to the appearance of uncompensated magnetic moments.

Future studies and studies in progress

Further progress in understanding this fascinating system can be achieved by improvements in sample synthesis and devising a different method of sample making than currently used Sb flux-growth technique. Despite considerable efforts we were not able to reduce Pr-vacancies below 2%, using different temperature ranges of the crystal growth. Restricting this temperature growth region to narrower windows and lower temperatures results in crystals with larger concentration of defects. Therefore, we are currently experimenting with narrow temperature ranges above 850 C.

It is believed that significant progress in understanding the normal heavy fermion state can be achieved via low level alloying studies of $Pr_{1-x}L_xOs_4Sb_{12}$, with small values of x of order 0.01. However, the nominal composition (flux) in this range usually disagrees with actual composition approximated by microprobe analysis.

Publications supported by this grant

"Evidence for intrinsic superconductivity at T_{c1} in $PrOs_4Sb12$", B. Andraka and K. Pocsy, *J. Appl. Phys*. **111**, 07E115 (2012).

"Fermi volume as a probe of hidden order", A. McCollam, B. Andraka, and S.R. Julian, *Phys. Rev.* B **88**, 075102 (2013). (Editor's choice)

Manuscripts submitted

"Unconventional superconductivity of $PrOs_4Sb_{12}$: Inhomogeneous coexistence of two intrinsic superconducting phases", B. Andraka and K. Pocsy, submitted to Journal of Physics: Condensed Matter (JCPM 103844).

Presentations

"Using the phase of quantum oscillations for high-field thermometry", A. Sutton, A. McCollam, B. Andraka and S.R. Julian, abstract submitted for the 11th International Conference "Research in High Magnetic Fields", Grenoble, July 1-4, 2015. Manuscript in preparation.

"Quantum oscillation studies of quantum criticality in PrOs4Sb12", S.R. Julian, A. Sutton, B. Andraka, and A. McCollam, abstract submitted for Canadian Association of Physicists Annual Congress, Edmonton, Alberta, June 14-17, 2015.

"Quantum oscillation studies of quantum criticality in PrOs4Sb12", S.R. Julian, A. Sutton, B. Andraka, and A. McCollam, to be presented at 20th International Conference on Magnetism, Barcelona, July 5-10, 2015.

Personnel supported

Bohdan Andraka – Associate Research Professor

Ken Pocsy – student