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Dependence of the superconducting transition temperature of the filled skutterudite compound $PrPt_4Ge_{12}$ on hydrostatic pressure

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ABSTRACT

The temperature-dependent ac susceptibility of the filled skutterudite superconductor $PrPt_4Ge_{12}$ has been measured under hydrostatic He-gas pressure to 0.58 GPa. The superconducting transition temperature T_c decreases linearly with pressure P from 7.91 K at ambient pressure to 7.83 K at 0.58 GPa, giving the rate $dT_c/dP = -0.19 \pm 0.03$ K/GPa. Evidence is presented that suggests that the value of T_c in this compound is slightly reduced due to magnetic pair-breaking effects from the Pr^{3+} cations.

1. Introduction

The filled skutterudite compounds have attracted much attention during the past three decades due to the wide variety of interesting electronic and magnetic properties they exhibit [1–6]. Recently, a new series of platinum germanide filled skutterudite compounds MPt_4Ge_{12} (M = Sr, Ba, La, Ce, Pr, Nd, Eu, Th) were synthesized and their properties studied, revealing that the compounds with M = Sr, Ba, La, Pr, and Th are superconducting [7–10]. The compounds $LaPt_4Ge_{12}$ and $PrPt_4Ge_{12}$ have been characterized as strong-coupling superconductors with the highest values of the superconducting transition temperature T_c among the MPt_4Ge_{12} skutterudites of 8.27 K and 7.90 K, respectively [7,10].

Whereas the normal-state magnetic susceptibility of the compounds with M = Sr, Ba, and La is diamagnetic, that of $PrPt_4Ge_{12}$ is paramagnetic and conforms to a Curie–Weiss law above 30 K due to the presence of well localized 4*f* magnetic moments on each Pr^{3+} ion. Below 30 K, however, the magnetic susceptibility levels off and saturates, indicative of a nonmagnetic ground-state that is consistent with a Pr^{3+} singlet ground state arising from crystal-field splitting of the Pr^{3+} Hunds rule multiplet, which is often observed for Pr in the filled skutterudites [7]. The calculated total density of states (DOS) for $LaPt_4Ge_{12}$ and $PrPt_4Ge_{12}$ [7] indicates that the electronic structure derived from the Pt–Ge framework is, in the first approximation, independent of the atom in the M-site [11].

Parallels have been drawn between the properties of $PrPt_4Ge_{12}$ and $PrOs_4Sb_{12}$. The latter compound is the only known example of a Pr-based, heavy fermion, unconventional superconductor ($T_c \approx 1.85$ K) with an effective mass, inferred from the electronic specific heat coefficient, of $\sim 50\ m_e$, where m_e is the mass of the free electron [12,13]. Unlike $PrOs_4Sb_{12}$, $PrPt_4Ge_{12}$ does not have a large electronic specific heat coefficient and is not classified as a heavy fermion compound. However, both compounds appear to exhibit unconventional, time-reversal-symmetry-breaking superconductivity, with nodes in the superconducting energy gap [14–16]. High pressure experiments can potentially play an important role in advancing our understanding of the superconducting state in a given system [17]. To our knowledge, the only MPt_4Ge_{12} filled skutterudites thus far studied under high pressure are $SrPt_4Ge_{12}$ and $BaPt_4Ge_{12}$, both of which are superconducting at ambient pressure. In both compounds, the pressure dependence of T_c to 2 GPa is small but markedly non-monotonic [18]. The T_c of $PrOs_4Sb_{12}$ is suppressed linearly with pressure up to 2.5 GPa at a rate of $\sim$0.15 K/GPa [19].

In this paper we report measurements of the temperature-dependent ac magnetic susceptibility of $PrPt_4Ge_{12}$ under the application of purely hydrostatic He-gas pressure as high as 0.58 GPa. Determining $T_c(P)$ using He as pressure medium gives benchmark values with which future studies to higher pressures can be compared. Such studies, using less hydrostatic or non-hydrostatic pressure media, may introduce strains in the sample and falsify the intrinsic $T_c(P)$ dependence [17]. We find that the T_c in $PrPt_4Ge_{12}$ decreases slowly and linearly with He-gas pressure at the rate -0.19 ± 0.03 K/GPa. This modest rate of depression of T_c with P is

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insufficient to account for the difference in T_c between $LaPt_4Ge_{12}$ and $PrPt_4Ge_{12}$ as being due to a lattice pressure effect alone.

2. Experimental details

Similar to the procedure described in a previous report [20], polycrystalline $PrPt_4Ge_{12}$ was synthesized by arc melting high purity elemental starting materials on a water-cooled copper hearth under argon atmosphere. The arc-melted boule was flipped over and re-melted a total of 5 times in order to promote homogeneous mixing. Following arc melting, the boule was sealed in a quartz tube under 200 Torr of argon gas and annealed at 800 °C for 2 weeks. Powder X-ray diffraction confirmed the cubic $LaFe_4P_{12}$-type crystal structure with a lattice constant of 8.61 Å. $PtGe_2$ is present as an impurity at the ~1% level.

To generate hydrostatic pressures as high as 1 GPa, a three-stage He-gas compressor system (Harwood Engineering) located at room temperature (RT) was connected by a flexible capillary tube to a CuBe pressure cell (Unipress) located in a He-gas vaporizing cryostat capable of reaching temperatures as low as 1.5 K. All pressures were determined at temperatures near T_c using a calibrated digital manganin gauge in the compressor system at RT. The small decrease in pressure as the pressure cell is cooled below the freezing point of He is determined from the published He isochore [21].

AC magnetic susceptibility measurements at 0.1 Oe rms and 1023 Hz were carried out under pressure to the same high accuracy as measurements at ambient pressure by surrounding the sample with a calibrated primary/secondary compensated coil system connected to a Stanford Research SR830 digital lock-in amplifier via a SR554 transformer preamplifier. Measurements were carried out by slowly warming up through the superconducting transition at the rate ~110 mK/min. All susceptibility measurements were repeated at least once to verify that the measured value of T_c is reproducible to within 20 mK. Further details of the high-pressure and measurement techniques used are given elsewhere [22].

3. Results and discussion

In Fig. 1, the real part of the ac susceptibility for $PrPt_4Ge_{12}$ is plotted versus temperature at four different hydrostatic pressures. The midpoint of the superconducting transition is used to define T_c. The values of T_c obtained in all 8 high-pressure runs are shown in Fig. 2. The superconducting transition temperature T_c decreases linearly with pressure at the rate −0.19 ± 0.03 K/GPa, taking on the values of 7.91 K at ambient pressure and 7.83 K at the highest pressure of 0.58 GPa. The value of T_c at ambient pressure agrees well with the values reported in previous studies [7,9].

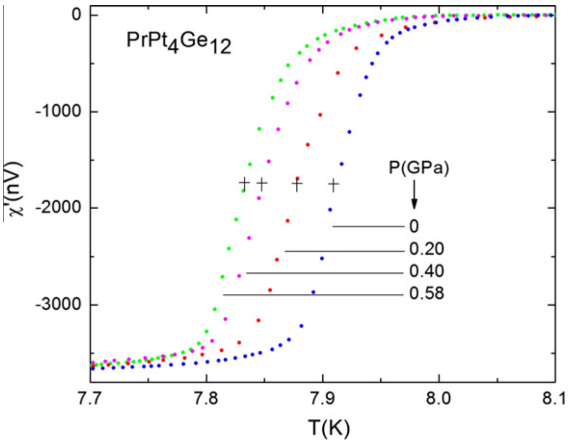

Fig. 1. Real part of the ac magnetic susceptibility χ' versus temperature T at different pressures P for $PrPt_4Ge_{12}$. Numbers give the order of measurements and plus signs (+) give the location of T_c, defined as the transition midpoint.

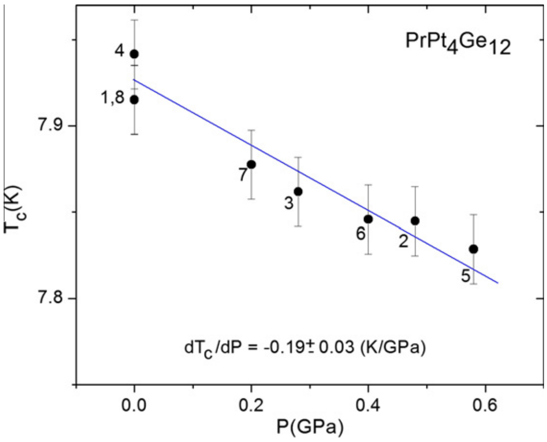

Fig. 2. Superconducting critical temperature T_c versus pressure P for all data taken. Numbers give order of measurement (see text for details).

We now discuss in more detail the data presented in Fig. 2 where the numbers give the order of measurement. After determining the value of T_c at ambient pressure (point 1), a pressure of 0.61 GPa was applied at RT before cooling down to measure $T_c = 7.84$ K (point 2) at which temperature the pressure had decreased to 0.48 GPa. The pressure was then successively reduced at low temperatures (65 K for points 2 → 3 and 55 K for 3 → 4) before cooling down further to measure T_c. Point 4 appears to lie ~30 mK higher than point 1; however, both values are the same within the experimental error of ±20 mK.

The experiment was then continued by applying pressure at RT (point 5) and then releasing pressure at 60, 55 and 45 K to obtain points 5 → 6, 6 → 7, and 7 → 8. T_c is seen to fully revert (point 8) back to its initial value 7.91 K (point 1) at ambient pressure. To 0.58 GPa pressure, T_c is thus found to depend reversibly and linearly on pressure. The value of T_c at a given pressure does *not* depend on the temperature where the pressure is changed, unlike what is observed for many high-temperature copper-oxide superconductors where pressure-induced oxygen ordering effects may cause $T_c(P)$ to depend sensitively on the entire temperature/pressure history of the sample [17].

We would now like to compare the values of T_c for the platinum germanide filled skutterudites MPt_4Ge_{12} (M = La, Pr, Ba, Sr). Interestingly, $PrPt_4Ge_{12}$, where each Pr^{3+} ion possesses a local magnetic moment, has a value of $T_c = 7.91$ K which is only slightly (0.36 K) less than that of nonmagnetic $LaPt_4Ge_{12}$ ($T_c = 8.27$ K). Note that the above compounds with the divalent cations Sr and Ba have lower values of $T_c \approx 5.0$ K. It has been suggested that the higher values of T_c for the platinum germanide filled skutterudites with the trivalent cations M = La and Pr may arise from their higher electronic density of states [7].

The nonmonotonic pressure dependences $T_c(P)$ observed for $BaPt_4Ge_{12}$ and $SrPt_4Ge_{12}$ to 2 GPa [18] may be the result of pressure-induced structural changes, but could also arise from non-hydrostaticity at low temperatures in the frozen pressure medium used (daphne oil). The present experiments on $PrPt_4Ge_{12}$, which use dense He, the most hydrostatic pressure medium known, show a linear dependence of T_c on pressure to 0.58 GPa. We cannot speculate on whether this linear dependence would continue for $PrPt_4Ge_{12}$ to higher pressures.

In the present studies, we have shown that the T_c of $PrPt_4Ge_{12}$ decreases with increasing pressure. Since, due to the lanthanide contraction, the lattice parameter of $PrPt_4Ge_{12}$ (a = 8.6111(6) Å) is less than that of $LaPt_4Ge_{12}$ (a = 8.6235(3) Å) by Δa = 0.0124 Å or 0.14%, it is interesting to ask whether the lower value of T_c in $PrPt_4Ge_{12}$ (ΔT_c = 0.36 K) might be due to a lattice pressure effect. From the present high-pressure experiment, the size of such an effect can be estimated to be $\Delta T_c = (\Delta a/a)(3B)(dT_c/dP) = 0.164$ K, where, in lieu of a measurement of the bulk modulus for $PrPt_4Ge_{12}$, the reasonable estimate $B = 200$ GPa has been used, based on bulk modulus values for related skutterudite compounds [23,24]. This estimated value of ΔT_c is less than half that observed (ΔT_c = 0.36 K). It follows that the lower value of T_c for $PrPt_4Ge_{12}$ at ambient pressure compared to that for $LaPt_4Ge_{12}$ does not arise from the difference in lattice parameters alone, but may be due to magnetic pair-breaking effects from the Pr cations or differences in the electron structure between the two compounds.

The rate that T_c is suppressed in $PrPt_4Ge_{12}$ ($dT_c/dP \approx -0.19$ K/GPa) is nearly the same as that for $PrOs_4Sb_{12}$ ($dT_c/dP \approx -0.15$ K/GPa). The suppression of T_c with pressure in $PrOs_4Sb_{12}$ has been attributed to competition between the superconducting state and the high-field antiferroquadrupolar ordered phase [25]. This scenario depends critically on the small splitting between the singlet ground state and the first excited state ($\Delta \approx 7$ K). The similarity in dT_c/dP between the two compounds is interesting then, given that the CEF splitting between the ground state singlet and first excited states in $PrPt_4Ge_{12}$ ($\Delta \approx 130$ K) [20] is more than an order of magnitude larger than for $PrOs_4Sb_{12}$. This would seem to suggest that pressure effects the superconducting states of both compounds in a similar way that is not related to the details of the crystal field level scheme.

In summary, we have measured the dependence of T_c of $PrPt_4Ge_{12}$ on hydrostatic pressure. The superconducting critical T_c is found to decrease reversibly under pressure at the rate $dT_c/dP = -0.19 \pm 0.03$ K/GPa. This rate is less than that expected from the decrease in lattice parameter of $PrPt_4Ge_{12}$ relative to $LaPt_4Ge_{12}$, suggesting that magnetic pair-breaking effects may play a role in the former compound or that differences in electronic structure may be involved.

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