

Magnetic ordering at anomalously high temperatures in selected lanthanides: what about Pr?

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Received 13 October 2019, revised 29 January 2020

Accepted for publication 25 February 2020

Published 27 March 2020



CrossMark

Abstract

Recent experiments have given evidence that for elemental Nd, Tb, and Dy the application of sufficient pressure pushes their magnetic ordering temperatures to anomalously high values. Pr metal has a dhcp structure and is trivalent with the $4f^2$ configuration. Its singlet ground state suppresses magnetic order from the 15 K anticipated from de Gennes scaling to 50 mK. Four-point electrical resistivity measurements were carried out on Pr for temperatures 1.5–295 K under pressures to 48 GPa. Although no clear evidence for magnetic order (or superconductivity) is observed above 1.5 K, the temperature dependence of the resistivity gives evidence that Pr may enter a dense Kondo state above 10 GPa.

Keywords: high pressure, magnetic ordering, dense Kondo state

(Some figures may appear in colour only in the online journal)

1. Introduction

The majority of lanthanide metals have a partially filled 4f shell that supports a localized magnetic moment on each ion. The Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interactions between these ions normally lead to magnetic ordering at temperatures well above 1 K. A notable exception is Pr with its $4f^2$ configuration where magnetic ordering occurs at $T_o = 50$ mK [1–3] instead of the 15 K anticipated from de Gennes scaling [4]. This drastic reduction in T_o occurs since in Pr's dhcp structure the crystalline electric field results in a singlet (nonmagnetic) ground state at both the locally hexagonal and cubic lattice sites [5]. Under pressure, however, the character of Pr's ground state may change appreciably.

At ambient pressure Pr takes on the dhcp structure. The equation of state and structural phase transitions in Pr have been determined to pressures as high as 311 GPa at ambient temperature [6]. Following a transition at 4 GPa from dhcp to fcc [7], the following transitions have been established [8] (see

legend at top in figure 3): fcc to distorted fcc (d-fcc) equivalently hR24 at 7.4 GPa, to Pr-VII body-centered orthorhombic at 13.7–18 GPa, to α -U at 20.5 GPa with 8.3% volume collapse, and to primitive orthorhombic at 147 GPa [6]. These changes in crystal structure under pressure, plus the accompanying variation in the electronic structure, could potentially result in a non-singlet (magnetic) ground state and thus to a sizable enhancement in the magnetic ordering temperature T_o from 50 mK [2], possibly similar to the anomalous magnetic ordering in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ that is due to the unusual electronic structure [9, 10]. In fact, in Nd [11], Tb [12], and Dy [13] T_o is found to soar to anomalously high values if sufficient pressure is applied.

Previous high-pressure resistivity studies on Pr have either been restricted to relatively narrow regions of pressure (9.8–22.6 GPa) [14], (21–32 GPa) [15]) or to a few values of pressure over a wide pressure range (22–120 GPa) [16]. In these studies it is difficult to systematically track the evolution of the magnetic properties in the resistivity over a wide pressure range beginning near ambient pressure.

In this paper we report temperature-dependent resistance $R(T)$ measurements on Pr metal at 11 different values of the

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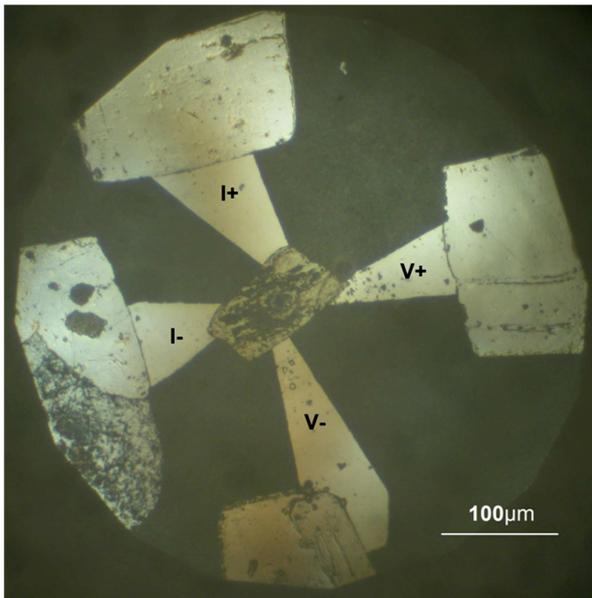


Figure 1. Image of a Pr sample $100 \times 60 \times 6 \mu\text{m}^3$ at ambient pressure resting on four flat Pt leads ($5 \mu\text{m}$ thick) on an insulated Re gasket.

applied pressure from 0.6 GPa to 48 GPa for temperatures between 1.5 K and 295 K. Although no clear sign of magnetic order is observed, the evolution of $R(T)$ with pressure, as well as the strong superconducting pair breaking in the dilute magnetic alloys Y(Pr) [17] and La(Pr) [18], give evidence that pressures near 20 GPa suffice to turn on strong Kondo many-body correlations in Pr, possibly leading to a dense Kondo state.

2. Experimental methods

Four-point dc electrical resistivity measurements with 10 mA excitation current were carried out on samples cut from bulk Pr (99.9% Ames Lab [19]). To generate pressures as high as 48 GPa at ambient temperature, a diamond anvil cell (DAC) made of CuBe alloy was used [20]. In all measurements pressure was generated by two opposing diamond anvils (1/6-carat, type Ia) with 0.5 mm diameter culets. The Re gasket (6–7 mm diameter, 250 μm thick) was preindented to 80 μm and a 260 μm -diameter hole electrospark-drilled through the center. The center section of the preindented gasket surface was filled with a 4:1 cBN-epoxy mixture to insulate the gasket and serve as pressure medium. As seen in figure 1, the thin Pr sample (approximate dimensions $100 \times 60 \times 6 \mu\text{m}^3$) was then placed on top of four 5 μm -thick Pt strips to allow a four-point dc electrical resistivity measurement over the temperature range 1.5–295 K using a custom-built Oxford flow cryostat. A small ruby sphere was placed at the center of the sample. The pressure at room temperature was determined both by ruby fluorescence [21] and diamond vibron measurements [22].

The electrical measurements were normally carried out with increasing pressure from 4 K to 295 K upon warming. At 30 GPa and 35 GPa the lowest temperature was extended

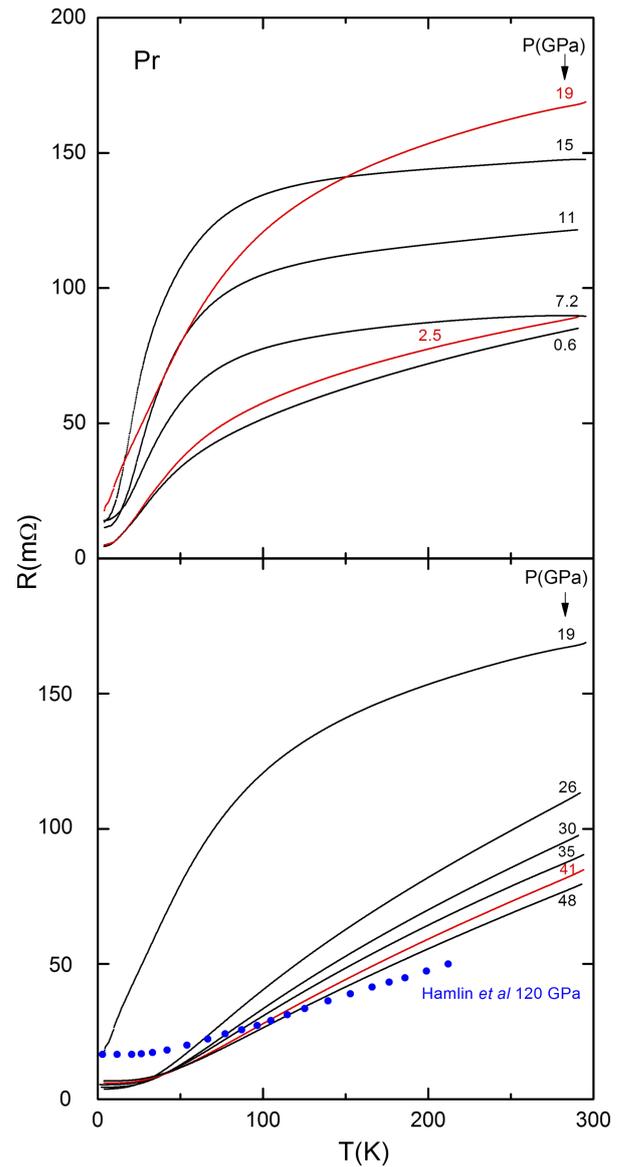


Figure 2. Measured resistance of Pr versus temperature at different pressures. The blue dotted line is reproduced from Hamlin *et al* (reference [16]).

to 2.5 K and 1.5 K, respectively. No evidence for superconductivity in Pr was found in any measurement, consistent with the results from previous experiments [14, 16]. Further details of the non-hydrostatic pressure technique are given elsewhere [23].

3. Results and discussion

In figure 2 the resistance $R(T)$ of Pr is plotted versus temperature for pressures between 0.6 GPa and 48 GPa. The temperature dependence $R(T)$ at 0.6 GPa shows a strong negative curvature, very similar to that for Pr at ambient pressure from James *et al* [24]. With increasing pressure the negative curvature near 100 K increases sharply but then begins to decrease above 15 GPa, dropping rapidly as the sample enters the α -U phase just above 20 GPa. Between 11 and 26 GPa the

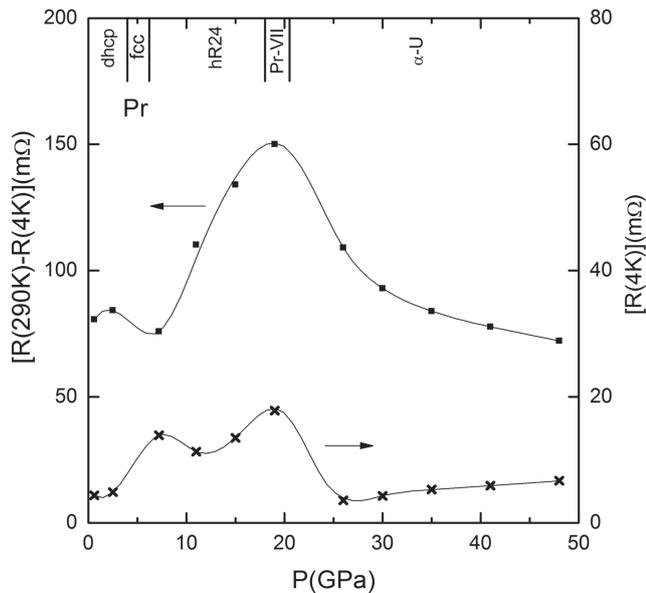


Figure 3. (left scale) Using data from figure 2, the change of resistance of Pr from 290 K to 4 K versus pressure to 48 GPa is plotted. (right scale) Resistance at 4 K versus pressure. Solid lines are guides to the eye. The legend at the top shows the crystal structure of Pr from reference [8] over the present pressure range.

present $R(T)$ data agree reasonably well with those of Wittig [14]. In the pressure range 30–48 GPa $R(T)$ in figure 2 exhibits the modest negative curvature typical for metals, such as the transition metals or some lanthanides, with significant d-electron character in the conduction band. An inspection of the data of Hamlin *et al* [16] to 120 GPa reveals that the gradual suppression of the $R(T)$ -dependence seen in figure 2 between 30 GPa and 48 GPa continues to pressures as high as 120 GPa, all in the α -U structure.

In figure 3 the resistance of Pr at ambient temperature (with $R(4\text{ K})$ subtracted off) is plotted versus pressure, along with $R(4\text{ K})$ itself. The rapid rise of the resistance above 10 GPa is clearly seen to occur within the hR24 phase whereas the rapid fall above 20 GPa begins upon entering the α -U phase. We note that in both the lanthanides and actinides the transition into the α -U structure has been interpreted as a sign that the ion's f-orbital is delocalizing through a strongly enhanced hybridization with the conduction electrons such as occurs when the negative covalent mixing exchange becomes dominant, thus turning on Kondo phenomena [11].

Of particular interest are the significant changes in $R(T)$ between 10 and 30 GPa in figure 2. The rounded downturn in $R(T)$ below 100 K at 7.2, 11, 15, and 19 GPa would appear to be much too broad to indicate magnetic order. It would more likely point to coherence effects [25–27] in the conduction electron–Pr ion system, such as are known to occur in Kondo lattices. In the dense Kondo system, below a certain temperature, the effect of the interactions between local magnetic moments (the coherence effect) is to markedly disturb the build-up of the delicately balanced Kondo resonance, causing the resistivity to fall off. See, for example, the $R(T)$ dependence for the dense Kondo system CeB_6 between 20 and 43

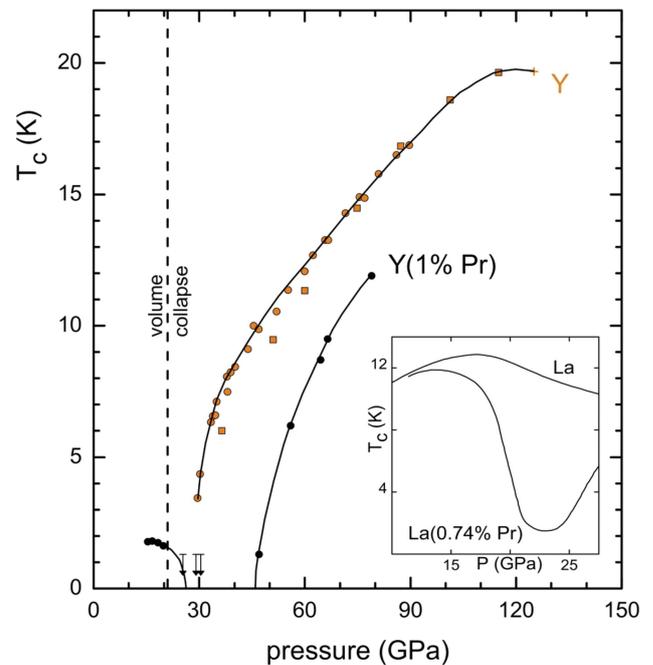


Figure 4. Pressure dependence of the superconducting transition temperature for Y(1 at% Pr) compared to that for Y [17, 30]. The vertical dashed line shows the critical pressure for the volume collapse in Pr. The downward arrows indicate no superconductivity was observed down to 1.5 K at those pressures. The inset shows data for La and La(0.74 at% Pr) adapted from figure 2 of reference [18]. Reprinted with permission from [18], Copyright by the American Physical Society.

GPa in figure 2 of reference [28]. The rise and fall of $R(T)$ would then be interpreted as the result of the Kondo temperature increasing rapidly with pressure through the temperature range of the present experiment. Pr starts to deviate from the non-magnetic singlet ground state and 4f electrons start to show the negative covalent exchange interaction with conduction electrons under pressure that serves as an additional scattering resource. Below 20 GPa, as pressure increases and the negative covalent exchange interaction becomes dominant, the Kondo effect emerges. In such a dense system the Kondo effect on Pr ions acts coherently below a certain temperature. With the increase of temperature, the coherence is thermodynamically destroyed, so the resistance rises rapidly, exhibiting a large negative curvature. As pressure increases above 20 GPa, the negative exchange interaction becomes so strong that the local 4f local moment can be completely screened by conduction electrons with opposite spins, i.e. Kondo screening occurs. As a result, the Pr ions can be treated as non-magnetic impurities by conduction electrons. Thus, the negative curvatures in the $R(T)$ curves are dramatically suppressed.

Further evidence that Pr becomes a dense Kondo system or Kondo lattice under pressure is given by high-pressure studies of superconducting pair-breaking effects in dilute magnetic Y(Pr) [17] and La(Pr) [18] alloys. Even though dhcp Pr assumes a singlet ground state at ambient pressure, the addition of 1 atomic percent (at%) Pr into superconducting La (dhcp or fcc structure) causes La's superconducting transition temperature to decrease by about 0.5 K or 10% [29]. This pair

breaking is a sign that Pr has become magnetically active, at least in La and Y. As seen in the inset in figure 4, the suppression of La's superconductivity, quantified by $[T_c(\text{La}) - T_c(\text{La-Pr})]$, increases dramatically in La(Pr) when pressures above 15 GPa are applied, reaching a maximum value at 22 GPa [18]. Figure 4 highlights similar results for the dilute magnetic alloy Y(Pr) [17]. This gives unequivocal evidence that applying pressure turns on Kondo interactions in La(Pr) and Y(Pr), and possibly also in pure Pr, turning it into a Kondo lattice.

Strong pair breaking is also found in the dilute magnetic alloys Y(Nd) [11], Y(Tb) [12], and Y(Dy) [13] near a value of the pressure where the magnetic ordering temperature T_o of Nd, Tb, and Dy, respectively, begins to rise dramatically to anomalously high values. In fact, for Y(Nd) the degree of pair breaking takes on the record-high value of -38 K/at% Nd!

In summary, we have carried out electrical resistivity measurements on Pr metal under high pressures in the temperature range 1.5 to 295 K using a diamond anvil cell. Unlike Nd, Dy, Tb and Gd, there is no clear evidence for magnetic ordering in Pr between 1.5 and 295 K to 48 GPa. However, the anomalous temperature dependence of the resistance $R(T)$ seen in figure 2 between 10 and 30 GPa gives evidence that Pr may have entered into a dense Kondo state.

Acknowledgments

This work is supported by the National Science Foundation (NSF) through Grants No. DMR-1104742 and No. DMR-1505345 as well as by the Carnegie/U.S. Department of Energy Alliance Center (CDAC) through NNSA/DOE Grant No. DE-FC52-08NA28554.

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