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Low temperature electrical resistivity of praseodymium at pressures up to 120 GPa

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Under ambient conditions, praseodymium metal possesses a localized $4f^2$ electron configuration. Near 20 GPa, the lattice volume collapses by $\sim$10 % into the α-uranium crystal structure, and the electrical resistivity drops dramatically. This behavior is similar to that observed in cerium metal and has been taken as evidence for $4f$ delocalization, although the precise nature of such volume collapse transitions in rare-earth metals is still a matter of debate. Since cerium metal develops superconductivity in the collapsed phase, we undertook a search for superconductivity in praseodymium metal at high pressure. Using designer diamond anvils, we measured the electrical resistivity of high purity praseodymium metal to pressures above 1 megabar and millikelvin temperatures. No evidence for superconductivity was found in any of the measurements. The lack of superconductivity may derive from magnetic pair-breaking effects related to incomplete screening/delocalization of the $4f$ electron state.

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To date, more than half of the elements of the periodic table have been found to be superconductors, either at ambient or sufficiently high pressure.[1] The list of pressure-induced elemental superconductors even includes elements, which, at ambient pressure, are non-metallic (*e.g.*, sulfur[2] and iodine[3]), magnetic (*e.g.*, iron[4]), or both non-metallic and magnetic (*e.g.*, oxygen[5]). The lanthanide series contains many of the last remaining hold-outs against pressure-induced superconductivity. The non-magnetic lanthanides with completely empty or filled $4f$ shells, La and Lu become superconducting at ambient and high pressure, respectively,[6,7] and in the remaining lanthanides, superconductivity is initially precluded by pair breaking effects due to the presence of strong local magnetic moments associated with partially filled $4f$-electron orbitals. However, Ce and Eu, both elements with unstable valences, have been demonstrated to become superconducting under pressure. The most recently discovered elemental superconductor, Eu, becomes superconducting above $\sim$80 GPa,[8] following a possible pressure-induced valence change from a strongly magnetic Eu^{2+} ($J = 7/2$) configuration to weak Van Vleck paramagnetism in Eu^{3+} ($J = 0$).

Cerium metal undergoes an isostructural phase transition from the fcc γ-phase, characterized by Curie-Weiss local magnetic moment behavior, to the α-phase when subjected to a pressure of approximately 0.7 GPa at room temperature. The transition to the α-phase results in a huge $\sim$16% collapse of the atomic volume, which appears to be accompanied by a valence change from $\sim$3 to $\sim$3.7 and the development of a large Pauli-like susceptibility.[9–11] Superconductivity appears in the α-phase at $P = 2$ GPa with $T_c = 20$ mK. Upon further application of pressure above 4 GPa, α-Ce transforms to α'-Ce, which has the same structure as α-U,[12] and T_c jumps from 50 mK to 1.9 K.[13,14]

Pr,[15] Gd,[16,17] Tb,[18] Dy,[19] and Ho[20] metals also exhibit volume collapse transitions under pressure, although cerium is the only case where the transition is isostructural. These phases are believed to derive from the increased participation of the $4f$-electrons in bonding[21–23] and result in low symmetry crystal structures that are similar or identical to those of the light actinide elements in which the $5f$-electrons are thought to be itinerant. The behavior of volume collapse transitions in rare earth metals has been interpreted in terms of either a Mott metallization of the f-states (Hubbard model) or Kondo screening of the f magnetic moment (periodic Anderson model), although it now appears that the two models may be closely related.[24] Similar low symmetry structures appear in Nd[25] and Sm[26,27] metals at high pressure without any significant volume collapse.

Studies of the these transitions in pure rare earth elements continue to be of fundamental interest since many materials which exhibit heavy fermion, quantum critical, non-Fermi liquid, and/or unconventional superconducting behaviors are based on rare earth ions with unstable valences. While the structural properties of most of the rare-earth metals have been investigated in some detail into the megabar pressure range, the corresponding low temperature transport and magnetic properties have yet to receive the same attention. The combination of structural, transport, and magnetic data on the $\gamma \rightarrow \alpha$ transition of Ce provided a crucial jumping-off point for much of the current theory regarding f-electron delocalization. Although a technical challenge, extending such studies to the remaining rare-earth elements at significantly higher pressures will likely provide further insights. We therefore undertook to extend the low temperature measurements of the electrical resistivity of Pr metal into the megabar pressure range.

At room temperature, following a series of crystallographic transformations at lower pressures, dhcp(Pr-I) $\rightarrow$ fcc(Pr-II) $\rightarrow$ d-fcc(Pr-III) $\rightarrow$ (Pr-VII), Pr transforms to the α-U structure (Pr-IV) with a $\sim$10% collapse of the volume per atom near 20 GPa.[15,17,28–31] After Ce, Pr exhibits the second largest volume collapse among the rare earth elements. Early searches for superconductivity in the collapsed phase of Pr were carried out by Wittig,[32] who found no evidence for superconductivity down to $\sim$1.2 K at pressures as high as $\sim$23 GPa. At ambient pressure, the electrical resistivity of Pr metal displays negative curvature over a broad range of temperatures, due either to crystalline electric field effects or to s-d scattering as described by Mott and Jones.[33] As pressure is increased towards the volume collapse transition, the resistivity becomes nearly temperature independent above $\sim$50 K, and drops rapidly at lower temperatures. This suggests that pressure strengthens the hybridization between the f-states and conduction electrons, resulting in increased scattering at higher temperatures and the formation of a coherent ground state as temperature is lowered. The ambient pressure resistivity and a sample of the data of Wittig are plotted in the upper panel of Figure 1. Upon increasing the pressure through the volume collapse transition, the resistance drops over the entire temperature range from room temperature down, and becomes approximately linear with temperature.[32] The disappearance of the nearly temperature independent part of the high temperature resistivity is consistent with the picture that the f-electrons delocalize, removing a source of scattering and adding charge carriers to the system. A recent investigation of the electrical resistivity of Pr metal at higher pressures ($P \leq 32$ GPa) and temperatures as low as 130 mK was carried out by Tateiwa *et al.*[34] showing no evidence for superconductivity. Room temperature resistivity measurements to pressures as high as 179 GPa using designer diamond anvils were carried out by Velisavljevic *et al.*[35] These measurements confirmed the $\sim$50% drop in resistance upon transforming to the α-U structure and found that the resistance remained roughly constant to much higher pressures, passing through a peak near 150 GPa. This peak in resistance coincides with a transition to a distorted α-U crystal structure (Pr-V).[36]

The diamond anvil cell employed was a mechanically loaded commercial model based on the design by Kyowa Seisakusho Ltd. One of the anvils was a "designer diamond anvil"[37] containing four symmetrically arranged, deposited tungsten microprobes encapsulated in high-quality homo-epitaxial diamond. The designer anvil was beveled with a flat diameter of 100 μm and a culet diameter of $\sim$300 μm. The distance between two opposite leads was $\sim$ 20μm. The gasket was made from a 200 μm thick hardened MP35N foil pre-indented to 30 μm with a 60 μm diameter hole electro-spark drilled through the center of the pre-indented region. High purity praseodymium metal obtained from Ames Laboratory was removed from storage in an evacuated

quartz ampoule. A thin sliver of shiny praseodymium metal was cut from the center of the rod with a razor blade and loaded into the sample chamber along with several pieces of either ruby (first experiment) or SrB_4O_7:Sm^{2+} (second experiment) manometer. The Pr was exposed to air for only several minutes and remained shiny with no visible oxidation at the time of sealing the sample chamber. No pressure medium was utilized and the sample was in direct contact with the gasket. Pressures were determined at room temperature from the fluorescence spectrum of ruby using the calibration of Chijioke *et al.*[38] or from SrB_4O_7:Sm^{2+} using the calibration of Datchi *et al.*[39] Pressure gradients in the sample are estimated to be as large as 20% from the full width at half maximum of the ruby line. The diamond cell was equipped with a Delrin spacer which serves to limit changes in the pressure upon cooling from room temperature. Pressure changes before and after cooling were minimal. The resistivity data were obtained using a Linear Research LR-700 AC resistance bridge. Low temperatures down to ~ 1.1 K were obtained with a home built pumped ^{4}He dewar while temperatures as low as $\sim$50 mK were generated with an Oxford Kelvinox ^{3}He-^{4}He dilution refrigerator.

Two separate sets of high pressure runs were performed. In the first set ("Run 1"), pressures of 41, 73, and 26 GPa were applied in that order. At each pressure, the cell was cooled to ~ 1.1 K and at 41 and 73 GPa measurements were also performed down to ~ 50 mK. In the second set of experiments ("Run 2"), we performed measurements down to ~ 140 mK at 22 GPa and $\sim$50 mK 104 GPa, followed by a measurement to ~ 1.1 K at 120 GPa. After the measurement at 120 GPa, we began to increase the pressure towards 160 GPa in order to perform a measurement in the Pr-V phase, but unfortunately the diamonds failed before reaching this pressure.

Figure 1 (left panel) presents the electrical resistivity over the entire temperature range and Figure 1 (inset) highlights the low temperature data. An estimate of the resistivity ρ is obtained from the resistance R using the equation $\rho = (\pi t R/\ln 2)$, where t is the thickness of the sample.[40] The sample thickness is determined from the previously measured equation of state for Pr,[41] assuming that all of the volume change occurs in the thickness of the sample, since the diameter of the sample chamber is observed to remain almost constant above 20 GPa. According to this estimate, the sample thickness varies from $\sim$15 μm near 20 GPa to $\sim$9 μm at 120 GPa. Because the sample thickness is comparable to the separation of the probes, the above equation provides an inexact estimate of the conversion from resistance to resistivity. On the basis of comparison with previous three-dimensional current flow simulations of the type described in Nellis *et al.*,[42] the error in our estimated resistivity could could be as large as $\pm 50\%$. However, this uncertainty does not effect our conclusions and the above equation results in resistivity values that are consistent with the previously published results at lower pressures. For comparison, we have plotted the ambient pressure resistivity of Pr (James *et al.*[43]) and the resistivity at 16 GPa as measured by Wittig.[32] Wittig's data were originally reported as resistance, so we have scaled the data according to the measured equation of state and the known ambient pressure resistivity.

The noise for the data at the lowest temperatures is somewhat higher due to the lower excitation current required to ensure that no spurious heating effects were present. The measurements at 22 and 26 GPa show behavior characteristic of the pre-collapsed phase, while all of the measurements at higher pressures show typical metallic behavior all the way to the lowest measured temperatures. We note that other authors have also found the precollapsed phase persisting to $\sim$25 GPa.[44] The measurement at 41 GPa shows a residual resistivity ratio (RRR) of $\sim$30; a value quite close to that observed by Wittig near 23 GPa.[32] These somewhat large RRR values under non-hydrostatic pressure could be related to a rather low shear strength of Pr. At the lowest temperatures, the resistivity becomes flat and exhibits no trace of superconductivity.

The right panel of Figure 1 presents the pressure dependence of the resistivity at 1 K (triangles) and 200 K (circles) for both Run 1 (filled symbols) and Run 2 (open symbols). The errors bars correspond to the 50% error in the conversion from resistance to resistivity described above. The initial pressure dependence of the resistivity in the precollapsed phases (P $\lesssim$ 25) GPa is difficult to resolve given the sparsity of data points and magnitude of the uncertainty. However our data are consistent with earlier reports[32,35] that found an initial increase in the resistivity within this low pressure region. This initial increase in resistivity may be attributed to enhanced scattering due to an increase in hybridization between the conduction and $4f$-electrons. The precipitous drop in resistivity over the entire temperature interval at the Pr III $\rightarrow$ Pr IV transition (P ~ 25 GPa) is discussed in the introduction. At still higher pressures, the resistivity at 200 K becomes only weakly pressure dependent. However, the resistivity at 1 K exhibits a strong increase with pressure beginning at 41 GPa. While some caution must be exercised in comparing data from Run 1 and Run 2, the increase in the residual resistivity above 41 GPa is substantial enough that it cannot be accounted for by measurement uncertainty. A simple explanation for this increase is growing defect scattering as the sample is cold-worked under non-hydrostatic pressure conditions, though a more profound explanation, such as scattering due to a still increasing hybridization between the conduction electrons and incompletely delocalized $4f$-electrons, can not be ruled out.

It is interesting to directly compare the behavior of Ce, Pr, and U, all of which adopt the same low symmetry α-U crystal structure at high pressure. Within the α-Ce structure, the room temperature magnetic susceptibility is known to drop steadily with pressure,[10] while the superconducting T_c exhibits a modest increase with pressure.[13,14] An extrapolation of the susceptibility to the pressure at which Ce completes its transition to α'-Ce (α-U structure) results in a value nearly the same as that observed for the tetravalent elements Hf and Th. Thus, by the time Ce transitions to α'-Ce, the $4f$ magnetic moment appears to be mostly destroyed. Upon transforming to α'-Ce, T_c jumps from 50 mK to 1.9 K, so the α-U structure seems to be comparatively favorable for superconductivity. However, within this phase, further pressure increases only lead to a gradual decline in T_c. The T_c of α-U metal itself is either low or vanishing at ambient pressure, and passes through a broad dome, reaching about 2.4 K at

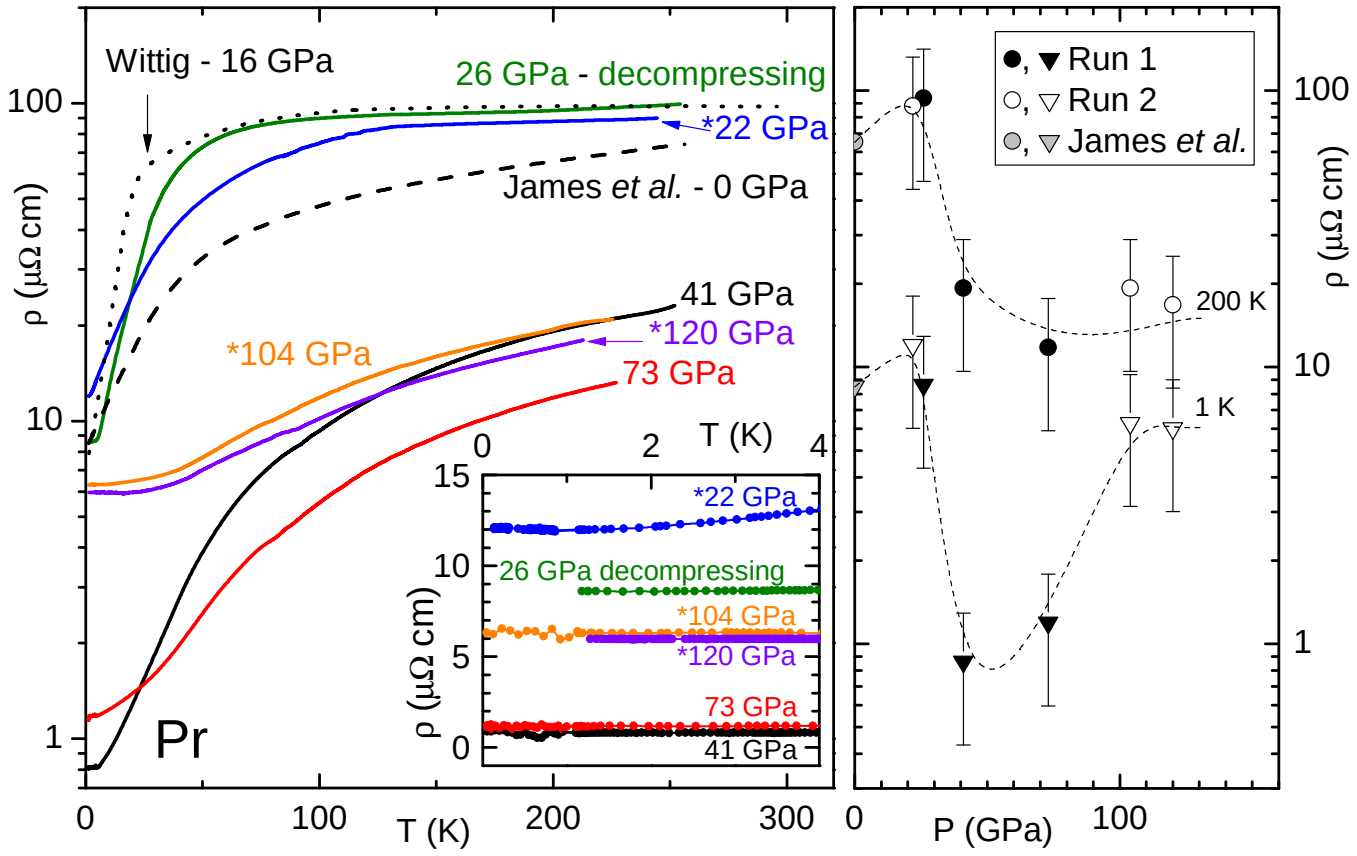

FIG. 1. *left*: Electrical resistivity ρ versus temperature T at several pressures for pure Pr metal. The dotted and dashed lines indicate data taken from Wittig[32] and James *et al.*[43] respectively. The resistance data of Wittig have been scaled by an arbitrary constant to facilitate comparison with our resistivity values. *inset*: Electrical resistivity in the low temperature region. The curves marked without (Run 1) and with asterisks (Run 2) indicate data from two different experiments. *right*: Pressure dependence of the resistivity at 200 K (circles) and 1 K (triangles). The dashed lines are guides to the eye.

1.2 GPa.[45,46] The increase in the T_c of U appears to be connected to the suppression of several charge density wave transitions which lead to a partial gapping of the Fermi surface. Within a Bilbro-McMillan[47] type interpretation, as the charge density wave transitions are suppressed, the fraction of the Fermi surface available to the superconducting state grows, leading to the increase in T_c. The maximum in T_c appears to roughly coincide with the pressure at which the final charge density wave transition has been destroyed. Further pressure increase then lowers T_c. Thus, for both Ce and U in the α-U structure, in the absence of other factors, pressure seems to depress superconductivity.

One possible explanation for the lack of pressure-induced superconductivity in Pr is that sufficiently strong magnetism persists throughout the region where superconductivity might otherwise develop. To date, little information about the magnetic properties of Pr at high pressure is available. X-ray emission spectroscopy (XES) measurements under pressures up to 42 GPa show no evidence for any change in the spectral parameters across the Pr III $\rightarrow$ Pr IV transition.[48] Similar XES results are found for the $\gamma \rightarrow \alpha$ transition of Ce, as well as for Nd which does not show a volume discontinuity.[48] These results are consistent with a Kondo-like scenario, in which the $4f$ moments become screened by conduction electrons. Within this scenario, there can be a continuum of behavior spanning the range from magnetic to non-magnetic. As mentioned in the introduction, this behavior can also be viewed as a delocalization of the f-electrons. Although the volume collapse transition seems to represent an abrupt increase in screening, the f state may continue to strongly impact the magnetic properties in the collapsed phase. Ce is a prime example of this behavior, where the susceptibility exhibits a large exchange enhancement in the α phase that probably contributes to the very low T_c.[10] A similar situation may occur in Pr under pressure, so that, after transforming to the α-U structure, the screening (or delocalization) of the f-state is still incomplete. The appearance of superconductivity in Pr would, therefore, hinge on whether the f moments become sufficiently screened before superconductivity is precluded by the "intrinsic" negative pressure dependence of T_c in the α-U structure discussed in the preceding paragraph.

In summary, we have carried out electrical resistivity measurements on Pr metal under high pressures and temperatures down to $\sim$50 mK using designer diamond anvils. Unlike Ce metal, Pr does not appear to exhibit superconductivity in the collapsed phase up to at least 120 GPa. A possible explanation is that superconductivity is precluded by incomplete screen-

ing/delocalization of the f state. Direct measurements of the magnetic susceptibility under pressure could help to clarify the situation.

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