High-pressure effects on single crystals of electron-doped $Pr_{2-x}Ce_xCuO_4$

C. R. Rotundu,[1,2,*] V. V. Struzhkin,[3] M. S. Somayazulu,[3] S. Sinogeikin,[4] Russell J. Hemley,[3] and R. L. Greene[1]
[1]*Center for Nanophysics & Advanced Materials and Department of Physics, University of Maryland, College Park, Maryland 20742, USA*
[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[3]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA*
[4]*HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

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We present high-pressure diamond-anvil cell synchrotron x-ray, resistivity, and ac-susceptibility measurements on the electron-doped cuprate $Pr_{2-x}Ce_xCuO_4$ to much higher pressures than previously reported. At 2.72 GPa between 88 and 98% of the superconducting T' phase of the optimally doped $Pr_{1.85}Ce_{0.15}CuO_4$ transforms into the insulating phase T. With application of pressure, the T phase becomes more insulating, so we present here an example of electron doping in the T structure. The results have implications for the search for ambipolar high-T_c cuprate superconductors. The T_c of the remaining 2–12% T' phase is suppressed continuously from 22 to 18.5 K at about 14 GPa. Remarkably, the T_c of the overdoped $Pr_{1.83}Ce_{0.17}CuO_4$ remains practically unchanged even at 32 GPa.

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I. INTRODUCTION

Although hole-doped cuprates are the most studied class of high-T_c materials, attention has been drawn recently to the electron-doped cuprates[1,2] in the effort to achieve a unified understanding of the high-temperature superconducting mechanism in cuprates. High-pressure experiments are important for understanding the superconductivity and to help identify ways for increasing T_c. Experiments on hole-doped cuprates showed an increase of T_c when pressure is applied, with the record belonging to $HgBa_2Ca_2Cu_3O_{8+\delta}$,[3] for which the T_c is enhanced from 133 to 164 K when compressed to 30 GPa. Pressures up to 2.5 GPa showed no (or extremely small) changes in structural[4] and other physical properties[5,6] of electron-doped cuprates. We present here a high-pressure study of the structural and other physical properties of single crystals of electron-doped $Pr_{2-x}Ce_xCuO_4$. We explain the close relation between the structural and superconducting properties. To our best knowledge, there are no high-pressure (>2.5 GPa) studies of the superconducting properties of electron-doped cuprates, except for the resistivity study on polycrystalline $Ln_{1.85}Ce_{0.15}CuO_{4-y}$ to 10 GPa by Beille *et al.*[7]

II. EXPERIMENTAL METHODS

Single crystals of $Pr_{2-x}Ce_xCuO_4$, $x = 0.15$ (optimally doped) and 0.17 (over-doped) were synthesized via a flux method refined by Peng *et al.*[8] The $x = 0.15$ crystal had $T_c = 21$ K under normal pressure conditions as determined from magnetization measurement in 20 Oe, in agreement with literature values.[8] Diamond-anvil cell (DAC) high-pressure resistivity measurements were run on a small sample of approximately $40 \times 40 \times 10$ μm^3 cleaved from a-few-mm size crystal. The measurements were performed using a standard four-probe Van der Pauw configuration, and the schematic of the setup is shown in Fig. 1(a).

Pressure was achieved using a lever-arm system with two 300-μm culet diamonds mounted on tungsten carbide supports. On the culet of one of the diamonds four radial platinum-based polymer conductive leads were deposited using focused ion beam (FIB) lithography.[9] The inner end of these leads passed over the sample, thereby assuring electrical contact and mechanical attachment of the sample to the diamond [Fig. 1(b)]. A stainless-steel gasket was indented first to 40 μm thickness and a centered $\sim$100-μm hole in the indentation was drilled. Cubic boron nitride (BN) powder was indented in the hole and on the conical side of the gasket, creating a thin insulating layer. Four electrodes 5 μm made of thin platinum foil were indented in a radial position to assure electrical contact with the FIB depositions [Fig. 1(d)]. The BN was drilled in the center to match the gasket's hole, and the space created formed the sample chamber. Before closing the DAC, ruby spheres were placed next to the sample for *in situ* pressure determination based on a calibrated fluorescence shift.[10] Finally, the DAC was closed in precompressed Ne gas at about 0.2 GPa, which served as a pressure-transmitting medium. During the course of the experiment, it was essential that the diamond anvils do not press directly on the sample. Thus, the thicknesses of the indented gasket and sample were 40 and 10 μm, respectively. Measurements were stopped on compression when the gasket thinned down such that the sample was in direct contact with the diamonds. We note that the material under study cannot withstand a uniaxial pressure larger than 0.5 GPa.[11] In the present resistivity measurement the pressure corresponding to gasket collapse was larger than 43 GPa.

DAC magnetic ac-susceptibility measurements were carried out using a double-frequency modulation method with details given elsewhere.[12–14] The DAC consisted of two pairs of diamonds inside a larger primary coil, a secondary signal coil (encircling the pair of the diamonds with the sample), and secondary compensating coil—identical to the secondary signal coil but with no sample. The gasket, made of a NiCrAl nonmagnetic alloy, was preindented by the two pairs of diamonds and then drilled in the center of the indentations. The crystal was cut to approximately $50 \times 50 \times 20$ μm^3 and placed inside one of the drilled holes, and the other was left blank intentionally.

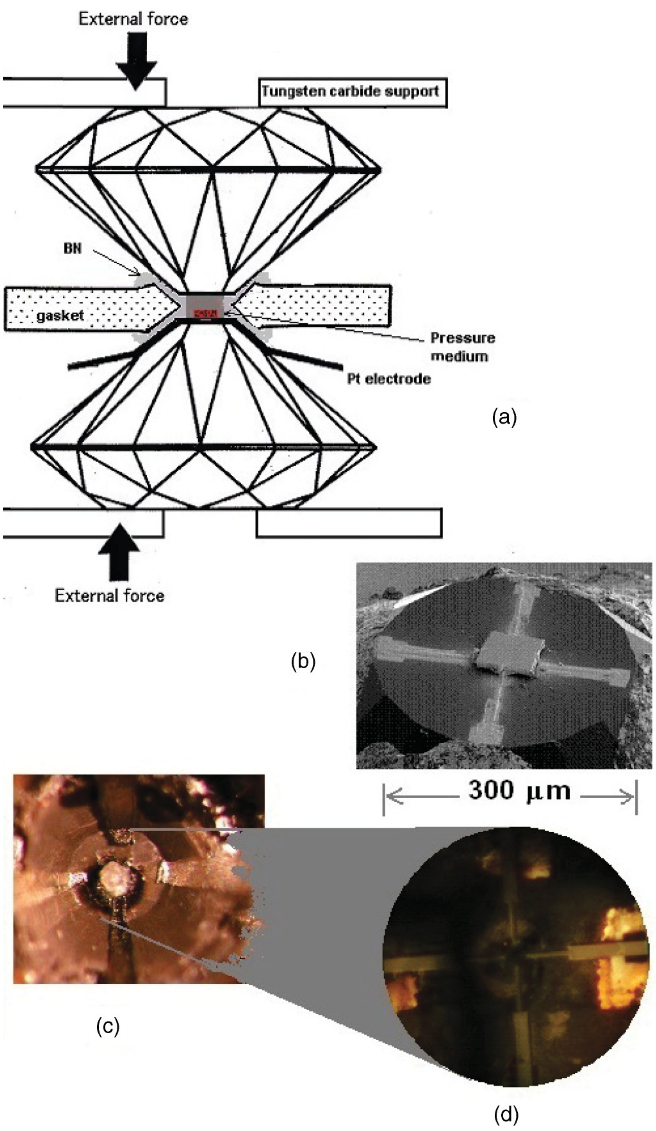

FIG. 1. (Color online) (a) Schematic of the diamond-anvil cell resistivity high-pressure setup. (b) The diamond culet with the platinum-based polymer contacts on the sample. (c) Indented boron nitride with platinum-foil made leads. The center hole becomes the sample space. (d) View of the sample with the electrical contacts after DAC assembly was closed under compressed neon gas and ready for the experiment (details in the text).

High-pressure x-ray diffraction was performed on powder from crushed crystals at HPCAT (Sector 16) at the Advanced Photon Source (APS), Argonne National Laboratory. In these experiments, a DAC with 400-μm culet diamonds with a sample chamber having a 50 mm diameter was used. As for the resistivity and ac-susceptibility measurements, Ne was used as the pressure medium. Ne provides a quasihydrostatic environment for pressures up to about 15 GPa; above this value, the pressure gradients remain very small: at 50 GPa the standard deviation of pressure is less than 1%.[15]

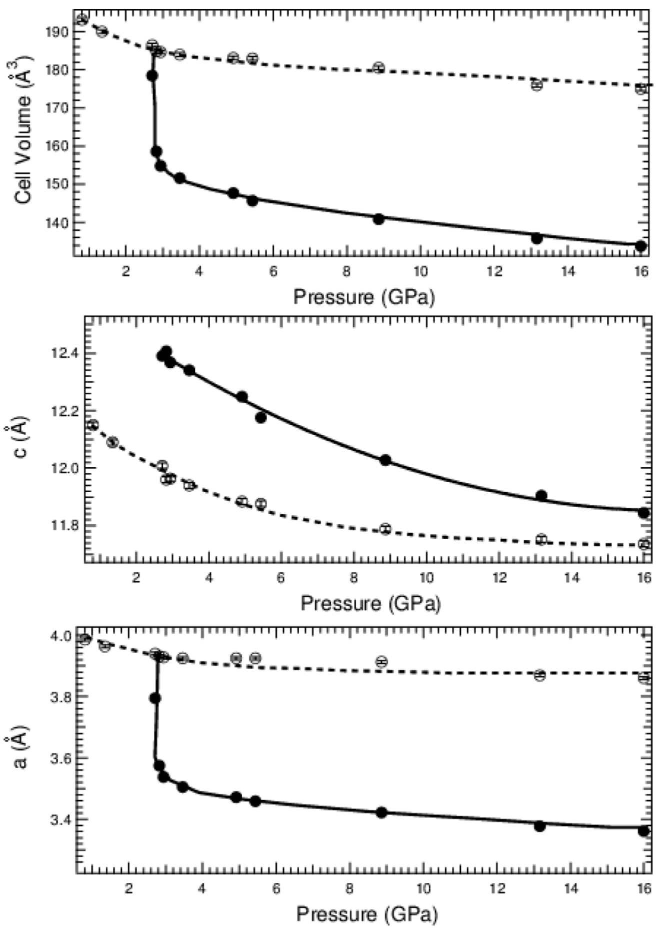

FIG. 2. Lattice parameters versus pressure of $Pr_{1.85}Ce_{0.15}CuO_4$. From top to bottom: Volume cell versus pressure (P), c axis versus P, and a axis versus P. Solid symbols are for the T phase, hollow for the T', and the lines are a guide to the eye. At 2.72 GPa between 88 and 98% of the T' phase transforms to the T phase.

III. RESULTS AND DISCUSSION

An early high-pressure x-ray (to 0.6 GPa) study by Kamiyama *et al.*[4] showed a very small but clear decrease of the lattice parameters with pressure of the undoped Nd_2CuO_4 and optimally doped $Nd_{1.835}Ce_{0.165}CuO_4$. Higher pressure experiments showed that in the parent Nd_2CuO_4 a T' (Ref. 16) to T structural transition takes place at 21.5 GPa,[17] but the transition is found to take place at 15.1 GPa in the parent Pr_2CuO_4.[18] Here we show x-ray data for an electron-doped cuprate to a pressure higher than 0.6 GPa. Figure 2 shows the lattice parameters a and c and volume cell versus pressure of the optimally doped $Pr_{1.85}Ce_{0.15}CuO_4$. Our first pressure data point is 0.8 GPa. Interestingly, the T' to T transition takes place at a much lower pressure, 2.72 GPa, when 88–98% of the T' phase transforms to the T phase (Fig. 3). This is of interest because for the case of the undoped Pr_2CuO_4 at 37.2 GPa there is still 50% of the T' phase surviving.[18] While we believe the differences are mostly intrinsic, the different pressure media used (N2 gas in Wilhelm *et al.*[17,18] vs the more hydrostatic Ne gas in the present study) may have a sizable influence. The standard deviation of pressure is about 3–4% in N2 gas at 25 GPa, while for the case of Ne it is less than 1% even

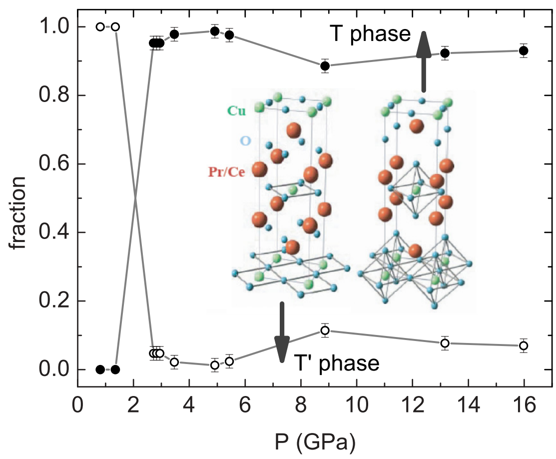

FIG. 3. (Color online) Fractions of phases T' and T versus pressure for $Pr_{1.85}Ce_{0.15}CuO_4$. Inset shows representations of both T' and T structures (Ref. 19).

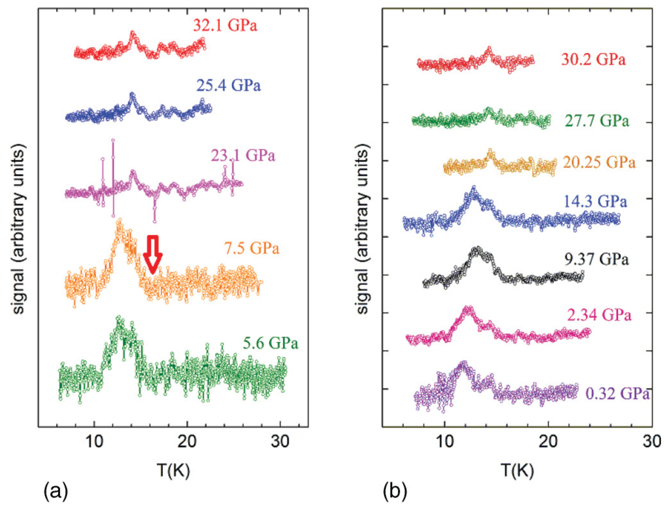

FIG. 5. (Color online) Real component of the ac susceptibility versus temperature of the overdoped $Pr_{1.83}Ce_{0.17}CuO_4$ at various pressures during (a) compression and (b) decompression. Data are vertically displaced for clarity. The arrow (shown for the 7.5-GPa data) points to the T_c.

at 50 GPa.[15] One question remaining to be addressed is up to what pressure the phase T' coexists with T in the optimally doped cuprate. In Pr_2CuO_4 both T' and T are present in a 50% ratio up to 37.2 GPa. In Nd_2CuO_4 the phases coexist for the [21.5, 29.5] GPa pressure interval[17] and shorten further to [11.4, 15] GPa for $LaNdCuO_4$.[18] Upon applying pressure, the lattice constants of the T' phase of $Pr_{1.85}Ce_{0.15}CuO_4$ are continuously suppressed through the phase transition as seen in Fig. 2. One other observation is that 16 GPa pressure produces a more drastic shrinkage of the lattice parameters of the T' phase than a 23% Ce substitution of Pr.[20] In fact, the 23% Ce doping (maximal solubility[8]) produces lattices changes equivalent to about 2 GPa of pressure.

Figure 4 shows resistivity versus temperature of $Pr_{1.85}Ce_{0.15}CuO_4$ at 4.5, 7.0, 13.7, 34, and 43 GPa. The attempt to compress the DAC to the next higher pressure resulted in the collapse of the metallic gasket and therefore end of the resistivity experiment. At relatively low pressure the resistivity versus temperature curves show what resembles a superconducting transition (but with nonzero resistivity below

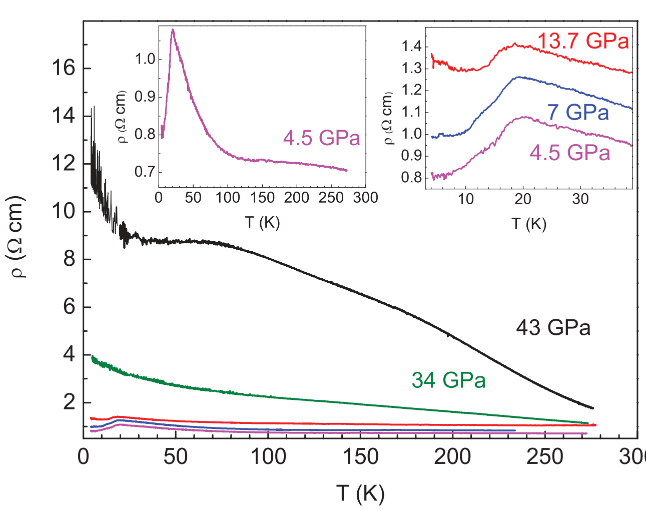

FIG. 4. (Color online) Resistivity ρ versus temperature of $Pr_{1.85}Ce_{0.15}CuO_4$ at 4.5, 7, 13.7, 34, and 43 GPa.

T_c) and enhancement of resistivity close to T_c (left inset of Fig. 4). This enhancement of the resistivity near T_c is due in part to a slight inclination of the sample cleaved face from the CuO_2 planes[21] and in part to granular effects within the crystal.[22] It is unlikely that this resistivity enhancement near T_c is due to inhomogeneities in Ce doping (as proposed by Klimczuk *et al.*[23]) given that the enhancement in the $x = 0.15$ crystal (as seen in resistivity data at 4.5 GPa) is measured on a 10-μm-thick crystal while the inhomogeneities in Ce were found to appear more in crystals of thickness greater than 300 μm.[24,25]

The nonzero resistivity below T_c for pressures greater than the 2.72 GPa of the $T' \longrightarrow T$ transition can be explained based on the 88–98% insulating T phase. This is consistent with the magnitude of resistivity at 4.5 GPa that is of an order of a fraction of a Ω cm, while typical resistivity above T_c at normal pressure (where the material is in the T' phase) is a fraction of m Ω cm.[8] The same mechanism most likely is responsible for the high-pressure nonzero resistivity data of Beille *et al.*[7] below the superconducting transition in $Ln_{1.85}Ce_{0.15}CuO_{4-y}$ (Ln = Nd, Sm, Eu), although no high-pressure x ray is available for these compositions.

T_c is suppressed by pressure and at 34 GPa we cannot detect any sign of superconducting transition in the resistivity data, and the shape of the resistivity versus temperature curves are consistent with an insulating behavior. At higher pressure (43 GPa), the resistivity versus temperature curve shows two broad peaks. These mysterious features are perhaps due to the complicated effect of the pressure on the magnetic ordering (spin orientation),[26,27] and a better understanding of this will require a careful high-pressure neutron-scattering study.

Figure 5 shows DAC ac-susceptibility data (real component) for the overdoped $Pr_{1.83}Ce_{0.17}CuO_4$ at compression [Fig. 5(a)] and decompression [Fig. 5(b)], with maximum pressure of 32.1 GPa. The arrow points to the T_c. The shape of susceptibility data and how T_c is determined when a double-frequency modulation technique is used have been discussed in detail in a review paper by

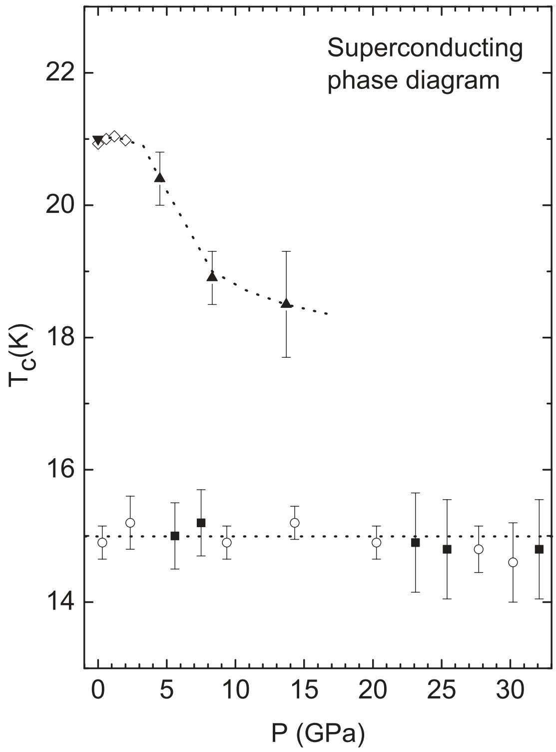

FIG. 6. T_c versus pressure for $Pr_{1.85}Ce_{0.15}CuO_4$ [▼: onset of diamagnetism from χ under normal pressure; ◇: adapted from resistivity on crystal by Crusellas *et al.* (Ref. 29); ▲: ρ during compression] and $Pr_{1.83}Ce_{0.17}CuO_4$ (●: χ during compression; ○: χ during decompression). The dotted lines are a guide to the eye.

Struzhkin *et al.*[12] and are based on the Hao-Clemm theory for reversible magnetization in type-II superconductors.[28] Basically, T_c in the ac-susceptibility data for $Pr_{1.83}Ce_{0.17}CuO_4$ is marked by the higher temperature "end" of the peak as shown in Fig. 5. The extremely sensitive ac-susceptibility proved to be an excellent probe for detecting and monitoring the evolution of T_c versus pressure given the small fraction of the T' superconducting phase beyond the structural transition. Remarkably, for the overdoped $Pr_{1.83}Ce_{0.17}CuO_4$, T_c remains unaltered all the way up to 32.1 GPa.

Finally, the phase diagram T_c versus pressure is drawn in Fig. 6, for both $Pr_{1.85}Ce_{0.15}CuO_4$ and $Pr_{1.83}Ce_{0.17}CuO_4$. T_c for the optimally doped $Pr_{1.85}Ce_{0.15}CuO_4$ is given by the temperature at the peak of resistivity versus T, and T_c for the overdoped $Pr_{1.83}Ce_{0.17}CuO_4$ from the ac-susceptibility versus T as described earlier. We also included in the superconducting phase diagram T_c versus pressure for 0–2 GPa as determined from resistivity measurements by Crusellas *et al.*[29] on an optimally doped $Pr_{1.85}Ce_{0.5}CuO_4$ (PCCO) crystal. It should be noted here that the high-pressure data points of Crusellas *et al.*[29] were obtained from data using 1:1 isoamyl and n-pentane alcohol, that is, a completely different pressure medium than the neon gas used in the present study. Therefore, lower pressures resistivity measurements using the same Ne gas pressure media will be needed to settle if T_c is monotonically suppressed with applying pressure or if that beyond 2.7 GPa (corresponding to the $T' \longrightarrow T$ transition) T_c is suppressed at a higher rate. Regardless, the rate of suppression of T_c for the optimally doped sample decreases beyond a pressure that is somewhere between 7 and 13 GPa showing a "saturation" to certain T_c.

Last we discuss the significance of the resistivity of the optimally doped (Fig. 4) "moving" into a more insulating regime with application of pressure in the context of search for ambipolar[30–32] high-T_c cuprate superconductors. One such example of an ambipolar high-T_c cuprate superconductors has been reported recently by Segawa and Ando.[30] They reported successful doping of n-type carriers by La substitution for Ba in $YBa_2Cu_3O_y$, such that $Y_{0.38}La_{0.62}Ba_{1.74}La_{0.26}Cu_3O_y$ is 2% electron doped. It has been known for a long time that the T-structure can be only easily hole doped, while the T' structure can be easily only electron doped.[33] In the present study, since 88–98% of the normal pressure T' phase (that is electron doped) transforms into the T phase, it is natural to assume that excess electrons were doped in the T phase. We believe the significance of the resistivity of the T phase becoming more insulating with application of pressure is that we successfully doped n-type carriers in the T structure. From the x-ray data it can be seen that the T structure is stable up to 16 GPa, so one question is if the structure is stable at much higher pressures.

IV. SUMMARY

We studied the evolution of superconductivity and structure (and the relationship between) with pressure of electron-doped $Pr_{2-x}Ce_xCuO_4$. At 2.72 GPa between 88 and 98% of the superconducting T' phase of the optimally doped $Pr_{1.85}Ce_{0.15}CuO_4$ transforms into the insulating T phase. T_c of the remaining 2–12% T' phase is suppressed from 22 to 18.5 K at a pressure of about 14 GPa. The nonzero resistivity below T_c can be explained based on the 88–98% insulating T phase for pressures beyond 2.72 GPa. This is in accord with the high magnitude (order of Ω cm) of resistivity at 4.5 GPa, while the typical resistivity above T_c at normal pressure (at which the material is in the T' phase) is a fraction of m Ω cm.[8] T_c of the overdoped $Pr_{1.83}Ce_{0.17}CuO_4$ remains practically unchanged even at 32.1 GPa.

One very interesting and surprising result is that with application of pressure, the T phase becomes more insulating, and so we present here an example of electron doping in the T structure. One of the most important questions is if by applying even larger pressure can the T phase be driven to electron-doped superconductivity. Most certainly the present study will spark interest and further experiments on the affect of high pressure on the electron-doped cuprates.

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*On leave from Lawrence Berkeley National Laboratory; corresponding author: costelrrotundu@gmail.com

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