Pressure Dependence of T_c in $L_{2-x}M_x\mathrm{CuO}_{4-y}$ (L = Pr,Nd,Sm,Eu; M = Ce,Th): Antisymmetric Behavior of Electron- versus Hole-Doped Copper-Oxide Superconductors

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Measurements of the superconducting transition temperature T_c in the electron-doped copper-oxide compounds $L_{2-x}M_x\mathrm{CuO}_{4-y}$ under pressure P to ~20 kbar reveal that, in general, T_c decreases with P, in contrast to the behavior of hole-doped copper-oxide compounds. The quantity $d\ln T_c/d\ln V$ exhibits a dependence on T_c similar to that of hole-doped compounds, but opposite in sign, and can be as large as ~24. Correlation of structural and transport properties indicates competition between interlayer and intralayer effects in these materials.

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The recent discovery[1] of superconductivity in electron-doped copper oxides of the form $L_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-y}$ (L = Pr,Nd,Sm; $x \approx 0.15$) has stimulated appreciable interest. As indicated by Hall-effect[1,2] and thermopower[2,3] measurements, the charge carriers are apparently electrons, in contrast to the hole conduction observed in other copper-oxide superconductors.[4] Additional $\mathrm{Nd_2CuO_4}$-type structure superconductors have been discovered either by alternate cation substitution ($L_{2-x}\mathrm{Th}_x\mathrm{CuO}_{4-y}$, L = Pr,[5] Nd,[6] and Sm[7]), by rare-earth substitution[5] ($\mathrm{Eu}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-y}$), or by anion doping[8] ($\mathrm{Nd_2CuO}_{4-z-y}\mathrm{F}_z$). The excess electrons provided by doping apparently induce an insulator-metal transition accompanied in a narrow range, near $x=0.15$ for cation doping, by superconductivity. Although the symmetry of electron and hole doping is obvious and appealing, it is apparent that the electron-doped compounds are more complicated than their hole-doped counterparts in several ways. A reduction anneal is necessary to induce metallic behavior; the reason for the required oxygen deficiency is unclear, but defect-assisted quantum percolation has been suggested.[9] Muon-spin-relaxation experiments[10] have shown that Cu antiferromagnetic order persists over a much wider range of dopant concentration than in the $\mathrm{La}_{2-x}M_x\mathrm{CuO}_{4-y}$ hole-doped compounds. X-ray-photoemission[11,12] (XPS) and x-ray-absorption[13] (XAS) spectroscopies indicate an increase in Cu^{1+} concentration with doping, although another XAS study[14] finds a lack of monovalent Cu. Other XPS measurements[15] and electron-energy-loss spectroscopy[16] suggest the presence of oxygen holes.

In the hole-doped superconductors, an increase of the superconducting transition temperature T_c with nearly hydrostatic pressure below ~20 kbar has generally been reported.[17-22] A composition-dependent study[18] of $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_{4-y}$ yielded increasingly positive $d\ln T_c/dP$ for compositions departing from $x=0.15$. For the electron-doped system, both an absence of a pressure effect[22] and, at most, a small, positive pressure effect[5] on T_c have been reported for $\mathrm{Nd}_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_{4-y}$, while a small, negative pressure derivative[23] has been observed for $\mathrm{Nd}_{1.85}\mathrm{Th}_{0.15}\mathrm{CuO}_{4-y}$. In this Letter, we report the results of an extensive investigation of the pressure dependence of T_c for all seven known cation-substituted electron-doped superconductors, $L_{2-x}M_x\mathrm{CuO}_{4-y}$ (L = Pr,Nd,Sm,Eu; M = Ce; and L = Pr,Nd,Sm; M = Th). The data, primarily for $x=0.15$ specimens, indicate a generally negative $d\ln T_c/dP$, opposite to the behavior of the hole-doped copper-oxide materials. We observe, however, that the magnitude of $d\ln T_c/dP$ as a function of T_c is similar for both electron- and hole-doped materials: The magnitude is large for low-T_c samples. We also provide an overview of the lattice parameters and transition temperatures for the various electron-doped compounds; together with the pressure data, these reveal a competition between interlayer and intralayer coupling in these materials.

Polycrystalline samples of $L_{2-x}M_x\mathrm{CuO}_{4-y}$ were prepared by a solid-state reaction as described in Refs. 5-7. For each host-dopant combination, the temperature of the final reduction anneal was varied (5-10 values) to identify the maximum T_c and diamagnetic fraction; the corresponding optimal oxygen deficiencies, determined by iodometric titration, were in the range $y=0.01$-0.03, with uncertainty $\Delta y=0.02$. Electrical resistivity measurements under nearly hydrostatic pressure were performed utilizing a beryllium-copper self-clamping device containing a Teflon cell, a lead manometer, and a 1:1 mixture of isoamyl alcohol and n-pentane as a pressure-transmitting medium. X-ray diffraction measurements were performed using a GE model XRD-6 diffractometer, Cu $K\alpha$ radiation, and an internal Si standard; lattice-refinement calculations were performed upon indexing the twelve intense peaks occurring in the range $2\theta = 20°$-$60°$.

In Fig. 1 are shown representative electrical resistivity data for $\mathrm{Pr}_{1.85}\mathrm{Th}_{0.15}\mathrm{CuO}_{4-y}$, for temperatures near T_c and at several applied pressures. The normal-state resistivity decreases with increasing pressure at an approximately temperature-independent rate $(1/\rho)(d\rho/dP)$

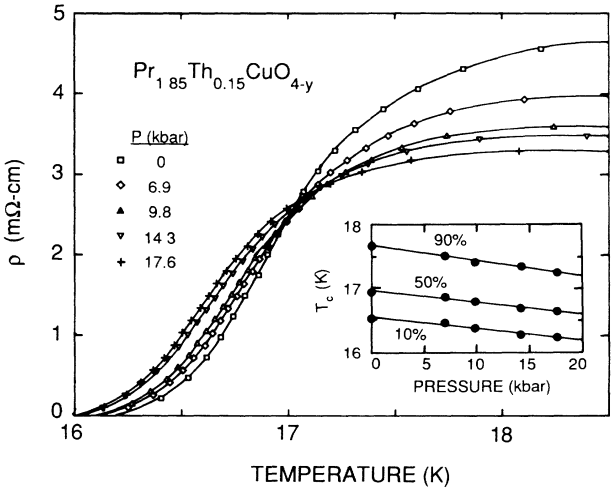

FIG. 1. Electrical resistivity ρ vs temperature for $Pr_{1.85}Th_{0.15}CuO_{4-y}$ for various applied pressures. Inset: The 10%, 50%, and 90% transition points vs pressure.

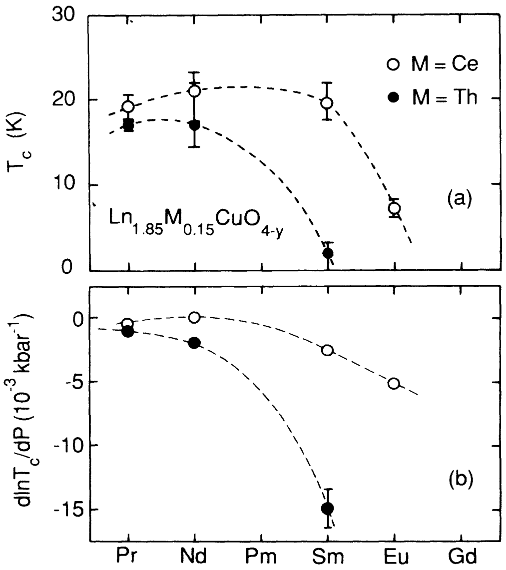

FIG. 2. (a) The resistive superconducting transition midpoints (symbols) and 10%-90% widths (bars) for $L_{1.85}M_{0.15}CuO_{4-y}$ for M = Ce (open symbols) and M = Th (solid symbols), and (b) relative rate of change of T_c (90% point) with applied pressure P, $d\ln T_c/dP$, as functions of the host lanthanide element.

≈ -0.016 kbar^{-1}, similar to other electron-doped polycrystalline specimens.[5,22,23] Presumably, such a large effect is primarily due to improved intergranular contact; however, a single-crystal uniaxial pressure study[24] of $YBa_2Cu_3O_7$ has revealed an intragranular contribution to the decrease in ρ. A clear decrease in T_c with increasing pressure is evident in the inset of Fig. 1, where the pressure dependence of the 10%, 50%, and 90% transition points, defined as percent of the maximum normal-state resistance, is depicted. A pressure derivative of $dT_c/dP \approx -0.020$ K/kbar may be deduced from the 90% transition points. We believe that the 90% points are a better indication of the intrinsic behavior of T_c under pressure than the 50% and 10% points since for $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ and $Nd_{1.85}Th_{0.15}CuO_{4-y}$, the lower part of the transition curve narrowed under pressure, an effect also assumed to be associated with enhanced granular contact.

The superconducting transition temperatures T_c at atmospheric pressure for the various electron-doped $L_{1.85}M_{0.15}CuO_{4-y}$ specimens are shown in Fig. 2(a) as a function of the lanthanide host element; the symbols denote the resistive transition midpoint, and the bars indicate the 10%-90% transition widths. For M = Ce, T_c evidently peaks for an intermediate size of the lanthanide element. For M = Th, a similar trend occurs, although the peak has shifted to larger host-ion size. The relative rate of change of T_c (T_c is hereafter defined as the 90% resistive transition point) with pressure, $d\ln T_c/dP$, is plotted as a function of the lanthanide host in Fig. 2(b) for the various host-dopant combinations. Similar to the T_c behavior of Fig. 2(a), $d\ln T_c/dP$ is evidently a peaked function of host-ion size, with a somewhat different scale for the Ce- and Th-doped series. It is noteworthy that while the pressure derivatives for the $x = 0.15$ series remain in the range $|dT_c/dP| < 0.05$ K/kbar, such values represent large *relative* pressure effects for low-T_c specimens, particularly for $Eu_{1.85}Ce_{0.15}CuO_{4-y}$ and $Sm_{1.85}Th_{0.15}CuO_{4-y}$. Except, perhaps, for the highest-T_c specimen, dT_c/dP is negative, in sharp contrast to the positive values of dT_c/dP generally observed for the hole-doped copper-oxide superconductors. We have also observed negative dT_c/dP values for specimens which depart from the optimal $x = 0.15$ stoichiometry: In the $Sm_{2-x}Ce_xCuO_{4-y}$ system, for example, we find $dT_c/dP = -0.062$ and -0.019 K/kbar for $x = 0.12$ ($T_c = 3.9$ K) and 0.18 ($T_c = 14.7$ K), respectively.

The lattice parameters a_0 and c_0 and the unit-cell volume V_0 for the various tetragonal Nd_2CuO_4-type structure materials are presented in Fig. 3 as a function of the lanthanide host element. Several unusual trends should be noted. For each lanthanide host element, a_0 increases upon doping, while c_0 decreases. This feature has been reported previously for the $Nd_{2-x}Ce_xCuO_{4-y}$ system.[2] The increase in a_0 is surprising in light of the fact that the usual eightfold-coordinated ionic radii[25] for the tetravalent Ce and Th dopant ions (0.97 and 1.05 Å, respectively) are smaller than those of the trivalent host ions Pr (1.13 Å) through Eu (1.07 Å). Another feature of interest, which is consistent with the sizes of the Ce and Th ions, is the opposing magnitude of the a_0 expansion (c_0 contraction) afforded by Ce vs Th doping; i.e., the a_0 expansion is greater for Th doping, while the c_0 contraction is greater for Ce doping. Finally, we point out that in all cases except for $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ and $Nd_{1.85}Ce_{0.15}CuO_{4-y}$, the unit-cell volume increases upon doping; these two exceptions also have the lowest

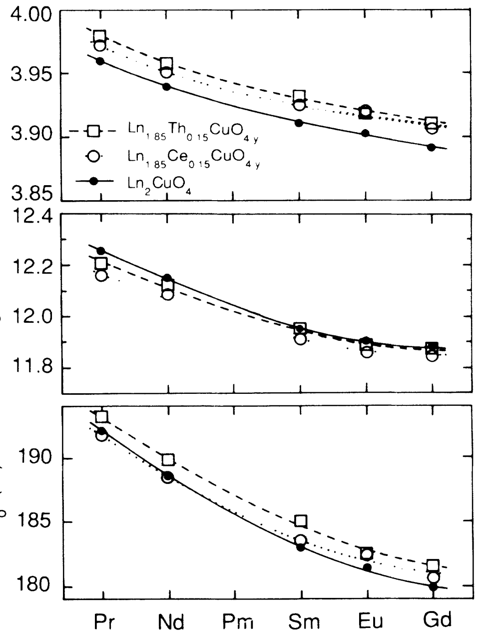

FIG. 3. Tetragonal unit-cell parameters a_0 and c_0 and unit-cell volume V_0 for the various undoped (solid circles), Ce-doped (open circles), and Th-doped (open squares) Nd_2CuO_4-type structure compounds.

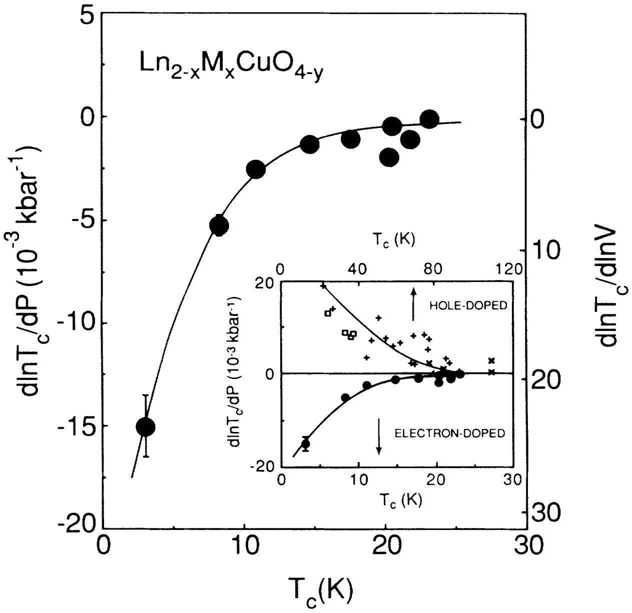

FIG. 4. Relative rate of change of T_c (90% point) with applied pressure P, $d\ln T_c/dP$, as a function of T_c for the electron-doped superconductors. Inset: Same data plotted together with similar data for hole-doped superconductors from Ref. 22. (□: La-based "2:1:4;" +: R-based "1:2:3;" and ×: Bi-Sr- and Tl-Ba-Ca-Cu-O materials.)

values of $|dT_c/dP|$. Again, for the smaller tetravalent dopants, the increase in V_0 is unexpected.

The increase in a_0 (while c_0 decreases) upon doping may reflect a predominantly two-dimensional nature of the internal pressure induced by a change in electronic structure upon delocalization; i.e., populating the presumed in-plane Cu-O antibonding $dp\sigma$ band[26] would lengthen the Cu-O-Cu distance. It is noteworthy that T_c does not vary systematically with the lanthanide magnetic moment (e.g., T_c is very low for Eu, which has a $J=0$ ground state); such behavior, as well as the coexistence of superconductivity and magnetic order for the Sm and Nd compounds,[23,27] implies that paramagnetic pair-breaking contributions are probably negligible. Similarly, no universal variation of T_c or dT_c/dP with a_0, c_0, or V_0 alone is observable; plots of such dependencies yield two-family curves similar to those in Fig. 2. The most general observation that can be made regarding T_c variation is that for a given host, Th doping results in a lower T_c than Ce doping. It is unlikely that the observed trend arises from differences in the dopant electronic structure (e.g., intermediate-valent Ce), since a comparative compositional study[28] finds equivalent concentration dependences of the diamagnetic fraction and normalized T_c for the two dopants. Because of the smaller size of the Ce^{4+} ion compared to Th^{4+}, evident in Fig. 3 by the smaller values of a_0 and c_0, one might conclude that increased intralayer or interlayer coupling, or both, is responsible for the higher-T_c values of the Ce-doped compounds. Many theoretical models[17] favor intralayer coupling as being of predominant importance; in particular, T_c has been predicted[29] to increase with nearest-neighbor transfer integral t. However, decreasing a_0 and c_0 cannot both increase T_c, since T_c generally decreases with pressure, as seen in Fig. 2(b). Thus we are led to conclude that the two types of coupling have a competitive effect on T_c. It may be that the relatively two-dimensional electronic structure results in a sufficiently anisotropic compressibility so that external pressure predominantly decreases c_0; in that case, it would be concluded that increasing interlayer coupling reduces T_c, while increasing intralayer coupling increases T_c.

Examination of the data of Figs. 2(a) and 2(b) leads immediately to the observation that both T_c and $d\ln T_c/dP$ display the same qualitative dependence on the various combinations of host and dopant ions, suggestive of a smooth variation of $d\ln T_c/dP$ with T_c. We plot in Fig. 4 $d\ln T_c/dP$ as a function of T_c; the right scale of the figure expresses the results in terms of $d\ln T_c/d\ln V$, which is more accessible to theoretical models,[17] under the assumption that the bulk modulus is lanthanide independent with value[30] $B \approx 1600$ kbar, as for La_2CuO_4. Several important points warrant mention. Most notably, the $d\ln T_c/d\ln V$ data are predominantly positive, in contradistinction to the general trend for the hole-doped copper-oxide superconductors. Shown in the inset of Fig. 4 are similar data for hole-doped materials. The magnitude of $d\ln T_c/d\ln V$ is small for samples with T_c near the maximum value observed for the electron-doped materials ($T_c \approx 24$ K); however, for low-T_c values, $|d\ln T_c/d\ln V|$ can be quite large, similar to the maximum magnitude observed in the hole-doped compounds. Such large values cannot be explained in the framework of the BCS theory with electron-phonon interaction.[17] The shape of $d\ln T_c/d\ln V$ is similar for both systems, although the maximum T_c attained in the two cases differs by about a factor of 5. The fact that $d\ln T_c/d\ln V$ becomes very small near the highest T_c so far obtained in each case may indicate that electron-doped materials have a maximum $T_c \approx 25$ K. It is difficult to determine if the negative pressure dependence is an inherent characteristic of electron doping in copper oxides; structural differences, e.g., the lack of apical oxygen atoms, are no doubt important, although the electronic and structural aspects are apparently intimately related. For a successful theory of superconductivity in the copper oxides to encompass both systems, this antisymmetric pressure dependence of T_c must be accommodated.

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