Systematic Cation Disorder Effects in $L_{1.85}M_{0.15}CuO_4$ Superconductors

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The properties of three series of $(La, Nd)_{1.85}(Ca,Sr,Ba)_{0.15}CuO_4$ samples have been investigated. In each series the mean A-site cation radius is fixed, but the size variance σ^2 changes. Susceptibility and transport measurements show that this leads to hole trapping within the CuO_2 planes which rapidly suppresses superconductivity in the same manner as the substitution of diamagnetic elements such as Zn for Cu. Cation size disorder also stabilizes low temperature distorted superstructures of the basic tetragonal La_2CuO_4-type structure. The superconducting critical temperature and the orthorhombic-to-tetragonal structural transition both show a strong linear dependence on σ^2.

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Doping of La_2CuO_4 with other lanthanides (L) or alkaline earth metals (M) at the A-type (La) sites enables structural and superconducting properties to be studied. The dependence of the critical temperature, T_c, on the doping level in the Sr-substituted material has been extensively studied [1] and is believed to reflect the common behavior of cuprate superconductors. The structural dependence of T_c is still not fully understood; it was proposed that only the orthorhombic phase is superconducting [2], but later experiments have shown that the tetragonal phase of $La_{2-x}Sr_xCuO_4$ also exhibits superconductivity [3]. Distortions of the average structure of the CuO_2 layers from planarity due to lattice instabilities are known to suppress T_c [4]. Transitions from high temperature tetragonal (HTT, space group $I4/mmm$), to low temperature orthorhombic (LTO1, space group *Abma*) [5] symmetry are often observed. Additional transitions to another orthorhombic structure (LTO2, *Pccn* symmetry) and a low temperature tetragonal (LTT, space group $P4_2/ncm$ symmetry) are also observed in some samples [6,7].

Structural disorder is always present in these layered perovskites because of the size mismatch of the cations at the A-type sites. By varying the La/Nd and Ca/Sr/Ba ratios in compositions $(La, Nd)_{2-x}(Ca,Sr,Ba)_xCuO_4$ it is possible to fix the hole doping level x and the mean A cation radius $\langle r_A \rangle$ while changing the amount of structural disorder in a systematic way. Disorder is quantified by the variance in the distribution of the A cation radii [8], $\sigma^2 = \langle r_A^2 \rangle - \langle r_A \rangle^2$, calculated using standard 9-coordinate ionic radii [9]. Recent studies have shown that the ferromagnetic metal to paramagnetic insulator transition temperature in magnetoresistive manganese perovskites and T_c in superconducting copper oxides both show a strong linear decrease with σ^2 [8,10] at a fixed mean cation radius and doping level. In the latter study, the T_c vs σ^2 data were given for three $(La, Nd)_{1.85}(Ca,Sr,Ba)_{0.15}CuO_4$ series with $\langle r_A \rangle = 1.212$, 1.223, and 1.232 Å [10]. In this Letter we report further results on the superconducting properties and structural transitions in these materials.

Two of the series from the previous study were examined further, however, the T_c values in the initial $\langle r_A \rangle = 1.223$ Å series suggested that these materials were underdoped so a fresh set of 10 g samples has been prepared for characterization including neutron diffraction. Sample details are given in Table I. The oxygen contents of all the samples were determined by iodometric titration, and no significant change in stoichiometry was observed across any of the series. ac susceptibility measurements were performed on zero-field cooled powders in an applied field of 1 G. Susceptibility curves for the $\langle r_A \rangle = 1.223$ Å samples are shown in Fig. 1; similar changes are observed in the other two series. T_c values are shown in Table I and Fig. 2. The last sample in the $\langle r_A \rangle = 1.223$ Å series is anomalous as no superconducting transition was observed. The T_c values for the new $\langle r_A \rangle = 1.223$ Å series are ~5 K higher than those obtained previously and the value of 36.0 K for the first sample, $La_{1.85}Sr_{0.15}CuO_4$, compares well with the highest magnetically measured literature value [11], showing that the new samples are optimally doped. The linear variation of T_c with σ^2 has slope $\partial T_c/\partial\sigma^2 = -6900(300)$ K Å^{-2} and $T_c^0 = 40.5(2)$ K by extrapolation to $\sigma^2 = 0$, whereas the previously studied underdoped series gave $T_c^0 = 35.8(2)$ K and $\partial T_c/\partial\sigma^2 = -6100(100)$ K Å^{-2}. An approximately linear decrease in the diamagnetic fractions is also found in the three series (Fig. 3). The rates of decrease with σ^2 are essentially identical, suggesting that the penetration depth increases with σ^2.

Electronic transport measurements have been performed on sintered bars of the first seven samples in the $\langle r_A \rangle = 1.223$ Å series. Resistivities measured by a standard four probe ac method are shown in Fig. 4. The zero resistance T_c's (Table I) diverge slightly from the susceptibility values with increasing σ^2, and a linear fit gives $\partial T_c/\partial\sigma^2 = -8600(700)$ K Å^{-2} and $T_c^0 = 41(1)$ K. As σ^2 increases, the increase in the residual resistivity, extrapolated

TABLE I. Chemical data, cell parameters and volume (×0.5 for orthorhombic samples), T_c's from susceptibility/resistance measurements, and A_{2u} mode frequencies for the three series of $(L_{0.925}M_{0.075})_2CuO_4$ superconductors with mean A-site radii $\langle r_A \rangle$ as shown.

A-site composition	$\sigma^2/Å^2$	Oxygen content	$a/Å$	$b/Å$	$c/Å$	$V/Å^3$	T_c/K	ν/cm^{-1}
$\langle r_A \rangle = 1.232$ Å								
$La_{0.925}Sr_{0.019}Ba_{0.056}$	0.0035	4.00(1)	3.78905(3)	⋯	13.2979(1)	190.919(5)	32.0	503.9
$La_{0.921}Nd_{0.004}Sr_{0.018}Ba_{0.057}$	0.0036	3.98(1)	3.78524(3)	⋯	13.2829(1)	190.304(5)	31.7	503.1
$La_{0.906}Nd_{0.019}Sr_{0.013}Ba_{0.062}$	0.0039	4.00(1)	3.78607(3)	⋯	13.2868(1)	190.456(5)	31.1	502.8
$La_{0.888}Nd_{0.037}Sr_{0.007}Ba_{0.068}$	0.0043	4.03(1)	3.78627(3)	⋯	13.2817(1)	190.404(2)	30.0	503.3
$La_{0.868}Nd_{0.058}Ba_{0.075}$	0.0047	4.03(1)	3.78601(3)	⋯	13.2800(1)	190.353(5)	29.0	503.1
$\langle r_A \rangle = 1.223$ Å								
$La_{0.925}Sr_{0.075}$	0.0006	4.01(1)	3.7773(2)	⋯	13.2378(8)	188.88(3)	36.0/35.4	503.4
$La_{0.925}Sr_{0.060}Ca_{0.008}Ba_{0.007}$	0.0009	3.99(1)	3.7780(2)	⋯	13.2357(6)	188.91(2)	34.1/31.5	504.0
$La_{0.925}Sr_{0.045}Ca_{0.017}Ba_{0.013}$	0.0012	3.99(1)	3.7783(2)	⋯	13.2302(8)	188.86(3)	32.2/31.3	505.8
$La_{0.925}Sr_{0.030}Ca_{0.025}Ba_{0.020}$	0.0015	3.99(1)	3.7796(2)	⋯	13.2272(7)	188.95(3)	30.0/26.2	504.4
$La_{0.925}Sr_{0.008}Ca_{0.037}Ba_{0.030}$	0.0020	4.01(1)	3.7838(1)	⋯	13.2390(6)	189.55(2)	25.4/24.9	503.5
$La_{0.900}Nd_{0.025}Ca_{0.037}Ba_{0.038}$	0.0025	4.01(1)	3.7821(2)	⋯	13.2242(6)	189.16(2)	23.7/17.3	504.5
$La_{0.875}Nd_{0.050}Ca_{0.032}Ba_{0.043}$	0.0029	4.03(1)	5.3531(4)	5.3440(4)	13.2158(7)	189.04(3)	20.6/16.0	505.6
$La_{0.850}Nd_{0.075}Ca_{0.028}Ba_{0.047}$	0.0033	4.02(1)	5.3565(3)	5.3440(4)	13.2141(8)	189.13(3)	⋯	505.6
$\langle r_A \rangle = 1.212$ Å								
$La_{0.899}Nd_{0.026}Ca_{0.075}$	0	3.96(1)	5.34472(9)	5.33694(9)	13.1778(1)	187.946(9)	31.6	509.7
$La_{0.868}Nd_{0.057}Ca_{0.069}Ba_{0.006}$	0.0006	4.02(1)	5.34730(9)	5.33649(9)	13.1708(2)	187.921(9)	29.4	508.6
$La_{0.825}Nd_{0.100}Ca_{0.061}Ba_{0.014}$	0.0012	3.99(1)	5.35276(8)	5.33529(8)	13.1597(1)	187.910(10)	27.1	509.2
$La_{0.781}Nd_{0.144}Ca_{0.053}Ba_{0.022}$	0.0019	3.98(1)	5.35706(8)	5.33389(8)	13.1492(1)	187.955(10)	23.0	512.0

from high temperatures to $T = 0$ (Fig. 5), and the development of an upturn in resistivity on cooling towards T_c both suggest that the samples are becoming progressively underdoped. This is confirmed by thermoelectric power (S) measurements at 290 K (Fig. 5) which, unlike resistivities, are insensitive to grain boundary effects. The variation of S(290 K) with free hole concentration p in cuprates is well established [12], and the variation shown in Fig. 5 is equivalent to a fall from $p = 0.14$ to 0.12 across the series by comparison with data for $La_{2-x}Sr_xCuO_4$ [13]. The observed $\Delta p = -0.02$ would be consistent with a loss of 0.01 oxygen atoms across the $\langle r_A \rangle = 1.223$ Å series, which is below the sensitivity of the chemical analysis (Table I). However, this is inconsistent with the accompanying decrease in T_c by a factor of 2, which would require a much larger drop in the hole concentration of $\Delta p \approx -0.08$ (Ref. [14]). An alternative explanation is that the decrease in p results from hole trapping at local lattice distortions in the normal state (Anderson localization) which scales with σ^2. The trapped holes suppress superconductivity through pair breaking analogous to that caused by the substitution of diamagnetic ions such as Zn within the CuO_2 planes. The similarity between the susceptibility and resistivity variations in this study (Figs. 1 and 4) and those in the $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$ series [15] support this view. Furthermore, the T_c of $La_{1.85}Sr_{0.15}CuO_4$ is halved by the substitution of $x = 0.02$ Zn atoms in the latter system, [15] and by the trapping of 0.02 holes per Cu atom through A-site disorder in our $\langle r_A \rangle = 1.223$ Å series.

The effects of σ^2 upon the $L_{1.85}M_{0.15}CuO_4$ lattice have been investigated by powder diffraction and infrared spectroscopy measurements. The cell parameters and volume from fits to high-resolution powder x-ray patterns are given in Table I. The behavior of the unit cell volumes is as might be expected, increasing with increasing $\langle r_A \rangle$, but showing no systematic variations with σ^2 at a constant $\langle r_A \rangle$. However, systematic trends in lattice parameters are observed with σ^2. In the $\langle r_A \rangle = 1.223$ Å series, a increases and c decreases up to $\sigma^2 = 0.0025$ Å^2, above which there is a transition from HTT to LTO1 symmetry.

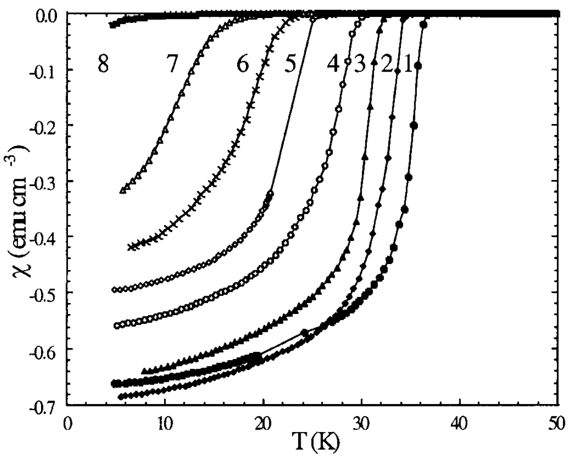

FIG. 1. Volume susceptibility data for the eight compositions in the $\langle r_A \rangle = 1.223$ Å series of $(L_{0.925}M_{0.075})_2CuO_4$ superconductors (see Table I) labeled 1–8 in ascending order of σ^2.

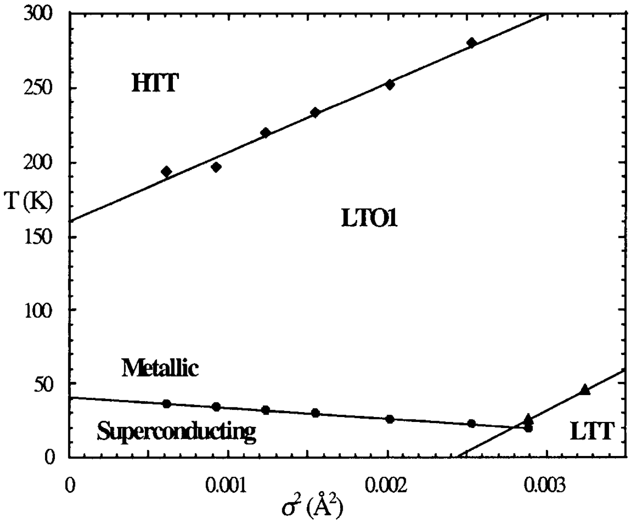

FIG. 2. Structural and electronic phase diagram as a function of σ^2 for $(L_{0.925}M_{0.075})_2CuO_4$ with $\langle r_A \rangle = 1.223$ Å showing the variations of T_c and the two structural transitions.

A variable temperature powder neutron diffraction study of the $\langle r_A \rangle = 1.223$ Å samples has been performed on the high-flux diffractometer D20 at the Institut Laue-Langevin, Grenoble, to examine the σ^2 dependence of the structural transitions. Patterns were collected in 1 K intervals from 5 to 300 K. HTT to LTO1 transitions were observed at $T_{OT} < 300$ K for the first six samples, in agreement with the room temperature x-ray diffraction results. T_{OT} shows a linear increase with σ^2 (Fig. 2), described by the parameters $T^0_{OT} = 158(5)$ K and $\partial T_{OT}/\partial\sigma^2 = 48000(3000)$ K Å^{-2}. A second structural transition, from LTO1 to LTT symmetry is seen at T_{TO} for the two samples with $\sigma^2 > 0.0029$ Å^2. This change of symmetry accounts for the disappearance of superconductivity in the final sample, as LTT symmetry is known to suppress superconductivity [6]. T_{TO} is almost coincident with T_c for the $\sigma^2 = 0.0029$ sample, and a mixture of LTO1 and LTT phases is observed down to 4 K. The presence of the former phase is consistent with the superconducting properties of this sample which follow the trends of the lower σ^2 materials (see Figs. 1 and 2). The two observed LTO1 to LTT transitions give a value of $\partial T_{TO}/\partial\sigma^2 = 55000(5000)$, equal, within error, to the above $\partial T_{OT}/\partial\sigma^2$ showing a general sensitivity of the structural transitions to A-site disorder. The composite structural and electronic phase diagram is shown in Fig. 2.

The transmitted infrared spectra of all the samples were recorded between 1000 and 350 cm^{-1} at room temperature. The only phonon band that is clearly identified

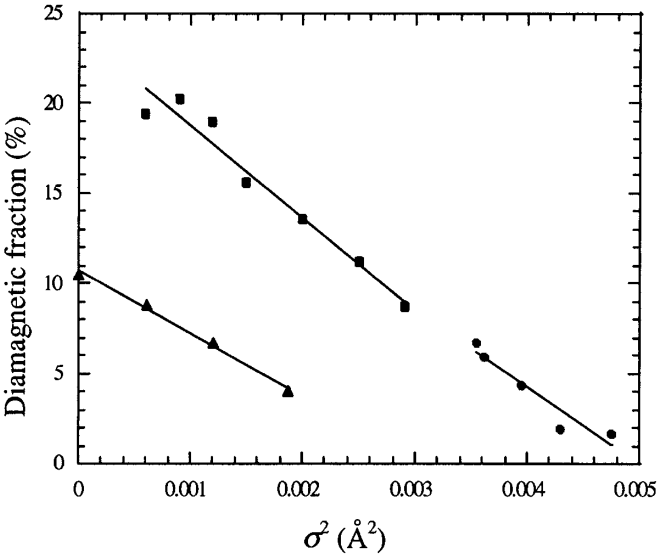

FIG. 3. Diamagnetic fractions plotted against σ^2 for the series with mean A-site radii $\langle r_A \rangle = 1.212$ Å (triangles), 1.223 Å (squares), and 1.232 Å (circles).

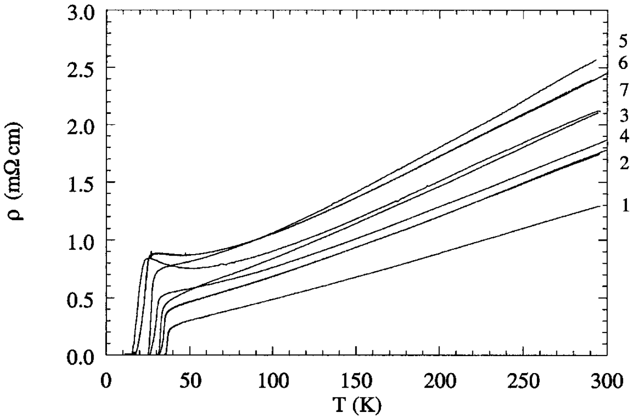

FIG. 4. Resistivity data for the seven superconducting compositions in the $\langle r_A \rangle = 1.223$ Å $(L_{0.925}M_{0.075})_2CuO_4$ series labeled 1–7 in ascending order of σ^2.

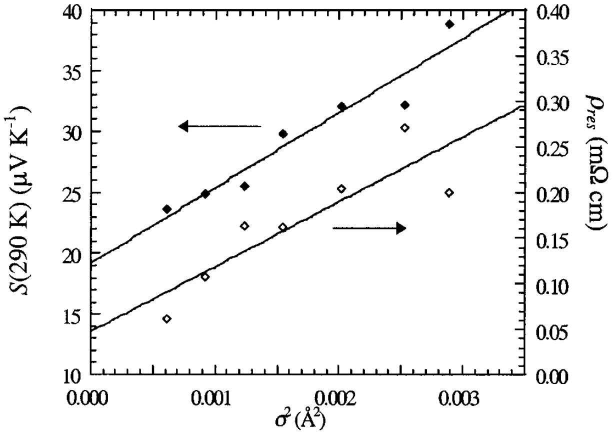

FIG. 5. Plot of thermoelectric powers at 290 K (closed points) and residual resistivities (open points) against σ^2 for the $\langle r_A \rangle = 1.223$ Å series.

is the A_{2u} vibration which occurs at 500–515 cm^{-1} and involves atomic motions parallel to c. The frequency of this vibration (Table I) increases with increasing $\langle r_A \rangle$ but there is no systematic dependence on σ^2. No peak broadening of the band with σ^2 was observed, although the observed peak widths of ~80 cm^{-1} are much greater than the intrinsic widths due to screening by the conduction electrons and polycrystalline averaging.

In conclusion, it has been shown that mean A cation radius alone is insufficient to describe lattice effects in $(L_{2-x}M_x)\mathrm{CuO}_4$ superconductors at a fixed doping level, and the cation size disorder, quantified by the variance σ^2 is required to give a clearer description of the effects of the adjacent insulating layers on superconducting and structural properties. The transport results show that a concentration of trapped holes within the CuO_2 planes increases in proportion to σ^2 leading to a rapid suppression of superconductivity analogous to that caused by Zn substitution. This may reflect local breaking of d-wave pairing symmetry. Cation disorder also stabilizes the low temperature distorted superstructures of the basic HTT arrangement. A full electronic and structural phase diagram of the $(L_{2-x}M_x)\mathrm{CuO}_4$ system will thus require at least four dimensions ($T, x, \langle r_A \rangle$, and σ^2). Figure 2 shows one section through this space which illustrates the simple linear dependences of both the superconducting and structural transitions upon σ^2. These results also provide a clear demonstration that the change from LTO1 to LTT structure type suppresses superconductivity even at the $x = 0.15$ nominal doping level.

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