

Structural, magnetic, and transport properties of $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$

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Li substitutes for Cu in La_2CuO_4 up to the limiting stoichiometry $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$, which has superstructure order. The effects of this in-plane hole doping on the structural and magnetic properties of La_2CuO_4 are very similar to those due to Sr substitution. The tetragonal-orthorhombic structural phase transition occurs, for a given amount of Sr or Li, at nearly the same temperature, and the in-plane lattice constant of $\text{La}_{2-y}\text{Sr}_y\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ at room temperature depends only on the combined hole count ($x+y$) and not on the individual Sr or Li concentration. Long-range magnetic order is destroyed upon substituting 3% Li for Cu, analogous to the effect of Sr substitution on $T_{\text{Néel}}$. However, the holes introduced by Li substitution are bound. The resistivity as a function of temperature is nonmetallic for all Li concentrations. [S0163-1829(96)07541-8]

Extensive work exists on the effect of chemical substitution on the properties of La_2CuO_4 . The original work, of course, involved Ba and other alkaline earth substitutions for La, leading to superconductivity.^{1,2} Later, it was found that interstitial oxygen could introduce hole conductivity into the CuO_2 planes and lead to superconductivity as well.³ On the other hand, for those compositions which are superconducting, in-plane substitutions were found to have strong negative effects on T_c as well as on conductivity. Quite generally, such substitutions were found to decrease T_c rapidly, independent of whether or not the substitutions carried a magnetic moment.⁴ Zn substitution in particular was found to be deleterious to T_c , 3 at. % Zn substitution for Cu being sufficient to completely suppress T_c in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.⁴ The conclusion from this and similar in-plane substitution studies was that disturbing the CuO_2 planes was very hostile to the superconductivity.

A particularly interesting in-plane substitution is that of Li (which has no magnetic moment) for Cu (which has $S=1/2$). Li^{1+} has an ionic radius essentially the same as that of Cu^{2+} [0.74 Å vs 0.73 Å (Ref. 5)] and brings a hole with it to the plane. This hole appears to be localized, and it is interesting to compare in-plane substituted holes with the mobile ones introduced by out-of-plane substitutions. Most simply, the question is whether Li is more like Zn (in that it is an in-plane dopant) or like Sr (in that it is a hole donor) as a substitutional element in La_2CuO_4 . There has been considerable experimental work already reported on Li substitution in La_2CuO_4 .⁶⁻¹⁰ Our aim has been to understand the apparent loss of Cu magnetic moment due to Li substitution and its relationship to the effect of Li substitution on the superconducting properties of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. We,^{9,10} following and expanding on the earlier work,⁶⁻⁸ have shown that Li is more like Sr than like Zn and that the "hole physics" appears to be the dominant effect in this substitution. Here, we present a more complete analysis of the similarities and differences

between Li and Sr as dopants in La_2CuO_4 , comparing our Li-substitution work with what is known from the literature about $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

Although it has been possible to grow single crystals over a limited range of Li concentrations,¹¹ all of the data reported here were taken with polycrystalline samples. The sintered specimens were synthesized using standard ceramic preparation techniques. The appropriate stoichiometric amounts of La_2O_3 , SrCO_3 , CuO , and Li_2CO_3 were mixed and fired at 900 °C over a multiday period with several intermediate regrindings. The rather low sintering temperature was dictated by the volatility of Li_2O ; however, no appreciable Li losses were observed in our specimens. x-ray powder diffraction revealed the samples to be essentially single phase, and structural refinements based on neutron powder diffraction data indicated that all of the Li was incorporated in a given sample (i.e., the refined occupation of the Li sites was consistent with the nominal Li concentration). Li has a negative scattering length for neutrons whereas Cu's is positive so good concentration resolution is possible in the refinements. In all cases where comparisons could be made, the properties of the polycrystalline samples were consistent with those obtained with single crystals.

The phase purity of all samples was verified using x-ray powder diffraction, and the lattice constants of a given sample were refined using a least-squares minimization from the observed hkl 's, with Si used as an internal standard. Electrical resistivity measurements were made in the four-probe van der Pauw configuration using dc excitation. Magnetic susceptibility measurements were made using a Quantum Design superconducting quantum interference device magnetometer.

Neutron powder diffraction data were collected using the HB4 high-resolution powder diffractometer at the High-Flux Isotope Reactor at ORNL. This instrument has a Ge (115) monochromator which selects an incident neutron wave-

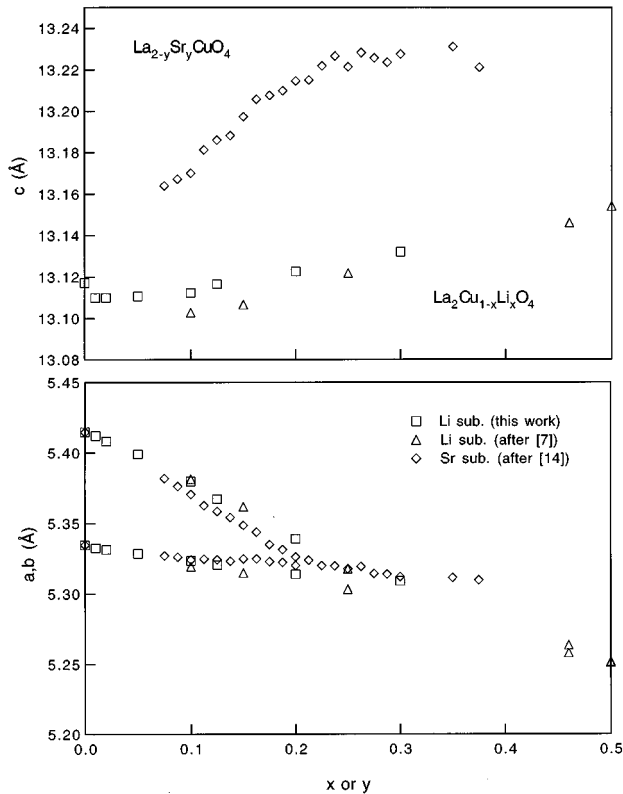


FIG. 1. Out-of-plane (upper panel) and in-plane (lower panel) lattice constants at low temperature for $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ [squares ($T=15$ K), this work; triangles ($T=5$ K), after Ref. 7] and $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ [diamonds ($T=10$ K), after Ref. 14].

length of 1.5 \AA . The neutron wavelength was determined more precisely to be $1.4993(2) \text{ \AA}$ on the basis of unit cell refinements for the NIST Standard Reference Material Si 640b. The samples were placed in vanadium cans and cooled in a displax refrigerator for data collection at temperatures between 15 and 295 K over the 2θ range of 11° to 135° . Input for the Rietveld refinement program was prepared by interpolating a constant step-size data set from the raw data, and the software package GSAS (Ref. 12) was used for the structural refinements. Further details of the structural refinements will be presented elsewhere;¹³ here, we focus only on the evolution of the lattice constants with temperature and Li concentration and note that the full structural refinements are consistent with the earlier work of Atfield and Ferey.⁷

In Fig. 1 we show the lattice constants of $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ for various x refined from our neutron powder diffraction data at low temperature together with the earlier data of Atfield and Ferey.⁷ The data for the two studies are in excellent agreement. The orthorhombic-tetragonal transition (indicated by the merging of the two distinct in-plane lattice constants) occurs near $x=0.3$, and the c -axis lattice constant shows very little change over the full range of Li concentrations. We see no evidence for the short-range order (as indicated by broad superlattice peaks in the diffraction pattern) at intermediate Li concentrations reported by Rykov *et al.*⁶ For comparison similar data for $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ by Radaelli *et al.*¹⁴ are shown. The in-plane lattice constants are essentially identical in the two cases, whereas the c -axis behavior is qualitatively different.

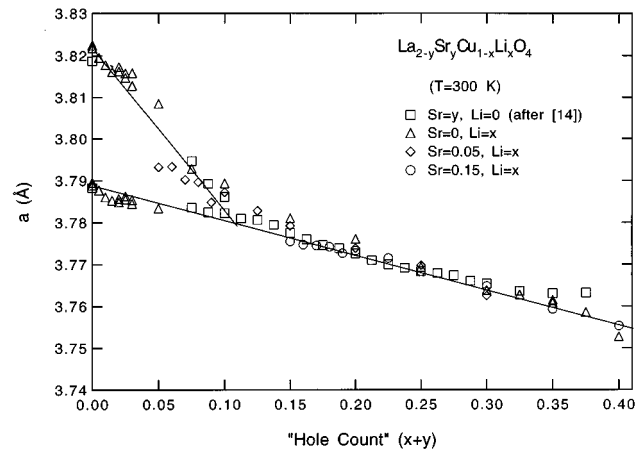


FIG. 2. In-plane lattice constant, a , of $\text{La}_{2-y}\text{Sr}_y\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ at room temperature. Data for $x=0$ are after Radaelli *et al.* (Ref. 14). The lines are guides to the eye.

The behavior of the c -axis lattice parameter, c , with Sr and Li substitution may explain the different solubility limits for the two dopants. The maximum Sr concentration which can be accommodated is near 0.35 (Ref. 14) and samples with $y>0.20$ are rather difficult to synthesize cleanly.¹⁵ For Sr substitution c appears to saturate near $y=0.25$, suggesting a solubility problem. On the other hand, the variation of c with Li is small and essentially linear up to and including the point ($x=0.5, y=0$) at which Cu and Li form an ordered superlattice. Thus, it would appear that the structural effects in the out-of-plane direction limit solubility rather than an in-plane hole-concentration effect.

The similarity in the in-plane lattice constants for $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ and $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ is rather surprising. The La ion is located away from the CuO_2 plane, and the replacement of La with Sr introduces an appreciable size mismatch [Sr^{2+} is approximately 10% larger than La^{3+} (Ref. 5)]. When Li replaces Cu in the CuO_2 plane, the size difference is negligible (the mismatch is 5 times smaller than in the La/Sr case). Thus, it would appear that the in-plane lattice constant(s) are determined not by size and/or tolerance factor effects but rather by the net hole concentration in the plane. The small difference in in-plane lattice constant between Sr and Li at a given concentration presumably represents the ionic size effect.

The scaling of the in-plane lattice constant with hole count can be seen most clearly in Fig. 2. Several series of samples were synthesized with varying Sr and/or Li concentration, and their in-plane lattice constants were determined using x-ray powder diffraction. (The Sr-only data are again the neutron results of Radaelli *et al.*¹⁴) The data for the in-plane lattice parameters collapse onto one plot versus hole count: the effect of Sr or Li addition is essentially identical structurally. It appears that the introduced hole has a particular size independent of its origin or whether or not the hole is mobile. Perhaps the way to think about the contraction of the in-plane lattice parameter with hole addition is as a relaxation about the hole in the highly negatively charged CuO_2 background. This may also provide a framework within which to understand the asymptotic behavior of superconducting T_c when plotted against in-plane lattice constant for

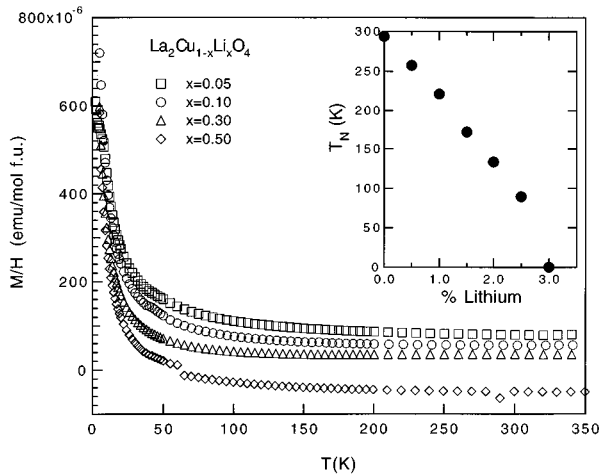


FIG. 3. Magnetic susceptibility (in units of emu/mole-formula unit) as a function of temperature for $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ for various values of x . The inset shows the suppression of T_{Neel} with Li substitution.

various cuprate superconductors.¹⁶

In the inset of Fig. 3, we show the suppression of the antiferromagnetic ordering temperature, T_N , as determined by the peak in magnetic susceptibility. Sr and Li have nearly identical effects on the magnetic phase diagram of La_2CuO_4 : the long-range magnetic order of the Cu moments is lost when the hole count in the CuO_2 plane reaches 0.03.⁶ Similar to the Sr case, one must be careful to remove any excess oxygen from these samples in order to accurately determine T_N . Excess oxygen, because it too introduces holes to the CuO_2 planes, reduces T_N at the same rate as Sr or Li.¹⁷ The suppression of T_N with Li substitution contrasts strongly with the effect of the in-plane isovalent dopants Zn or Mg. For both of these substitutions, the three-dimensional magnetic ordering temperature is depressed at nearly but less than the percolation rate, with roughly 30% substitution finally suppressing T_N completely.¹⁸ Muon spin rotation experiments also suggest that microscopically the magnetism in $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ is closer to that of Sr-doped La_2CuO_4 than that of Zn-doped La_2CuO_4 .¹⁹

The evolution of the temperature-dependent magnetic susceptibility at intermediate and high Li concentrations is shown in Fig. 3. Our data are qualitatively and quantitatively similar to that of Rykov *et al.*⁶ The susceptibility evolves with increasing Li concentration from Curie-Weiss-like to, aside from a small and sample-dependent extrinsic Curie tail, temperature-independent diamagnetism for $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$. The magnitude of the diamagnetism at room temperature (-60×10^{-6} emu/mol) is consistent with the expected core diamagnetism and van Vleck paramagnetism,^{6,20} so that, despite the presence of a Cu^{2+} ($S = \frac{1}{2}$) sublattice, no spin susceptibility is observed. Although the Cu is formally trivalent here, the stability of the material suggests that the diamagnetism is unlikely to be a property of Cu^{3+} . Furthermore, Yoshinari *et al.*²¹ have reported, using Cu NQR relaxation measurements, the observation of a magnetic excitation with an activation energy near 1500 K. These data are more easily understood by assuming that Cu possesses a spin (i.e., is Cu^{2+}) that is compensated in some sort of singlet rather than by assuming a trivalent Cu configuration.

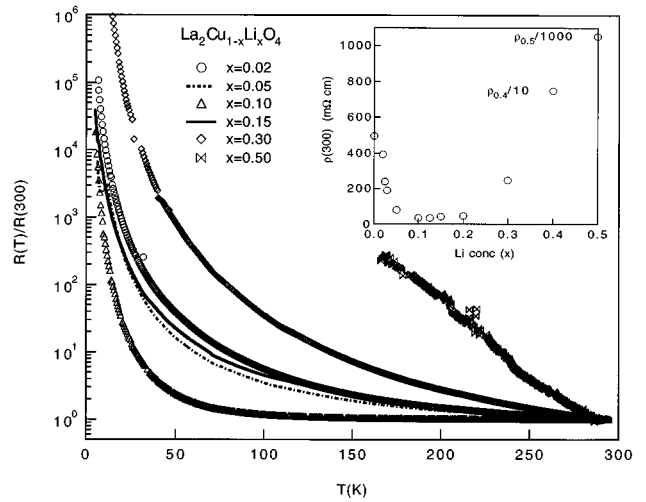


FIG. 4. Normalized resistance as a function of temperature for $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ for various values of x . The inset shows the room temperature resistivity as a function of Li concentration. Note that the values for $x=0.4$ and $x=0.5$ have been reduced by a factor of 10 and 1000, respectively, to bring them on scale.

The evolution of the magnetic susceptibility of $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ for intermediate and high Sr concentrations (i.e., $y \geq 0.05$) is qualitatively different.²² The susceptibility in pure and Sr-doped La_2CuO_4 is characterized by a broad peak as a function of temperature which moves to lower temperature as the Sr concentration is increased. By normalizing the data for various y with respect to a scaling temperature T_{max} , proportional to the intralayer Cu-Cu coupling constant J , the susceptibilities can be made to overlap and are in good agreement with calculation.²² Thus, the dominant effect of the Sr-produced holes is to reduce J and thereby shift the peak in susceptibility to lower temperature. No such peak is observed in our Li-doped La_2CuO_4 data. Although we do not have a quantitative understanding of these differences, it seems probable that the differences are due to the defects in the CuO_2 planes which Li introduces—the effect of which may be to mask the above-mentioned peak and to the finite screening length of the bound Li holes.

The room temperature and temperature-dependent resistivity as a function of Li concentration is shown in Fig. 4. $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ is extremely resistive [$\rho(300 \text{ K}) = 1 \text{ k}\Omega \text{ cm}$] and we were thus able to accurately measure the resistivity over only a limited temperature range; no decrease in resistivity, however, is observed to 5 K. These results confirm the earlier data of Kastner *et al.*⁸ The resistance of the samples increases substantially with decreasing temperature for all Li concentrations. Because the temperature dependence of the resistance is neither simply activated nor that appropriate to variable range hopping, a quantitative interpretation of the data is not obvious. It is clear, however, that, unlike the case of Sr substitution,²³ Li-doped La_2CuO_4 is neither metallic nor superconducting.

The evolution of the room-temperature resistivity with Li concentration is remarkable. We observe a drop in resistivity of more than one order of magnitude from $x=0$ to $x=0.15$, a broad minimum in resistivity from $x=0.15$ to $x=0.30$, and a rapid divergence in resistivity for higher Li concentrations. The concentration dependence of the room-temperature re-

sistivity for Sr-doped La_2CuO_4 is qualitatively similar. Initially, the resistivity drops even more rapidly, reaching $1.2 \text{ m}\Omega \text{ cm}$ for $\text{Sr}=0.15$, but then remains relatively constant for higher Sr concentrations $\rho(\text{Sr}=0.30)=0.7 \text{ m}\Omega \text{ cm}$.²³ Qualitatively, these results can be understood as a competition between increased carrier concentration and CuO_2 -plane disorder, with the conductivity in the Li case roughly tracking the Sr case until a percolation network of Li ions is formed, leading to a divergence in resistivity. Measurements of the thermopower and/or Hall effect for $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ would be useful in determining if a change in the sign of the carriers, as happens for high Sr concentrations, also occurs for Li substitution.

Because the suppression of T_c in optimally doped $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ with Li substitution is rather slow ($dT_c/dx=4 \text{ K}/\%$ Li) and is more similar to the effect of over-doping with Sr than to the effect of doping with Zn,^{9,10} we have also studied the resistivity of samples with a combined Sr+Li hole concentration of 0.15 in the hopes of “freeing” the bound Li holes with Sr. As Li replaces Sr, the room-temperature resistivity increases and a smooth crossover from T -linear resistance to semiconducting behavior is observed. Superconductivity occurs only in those samples which have sufficient Sr to be superconducting according to the well-known $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ phase diagram. Although the effects of Li on T_c for optimum doping are not very dele-

rious, the addition of Li does not have a positive effect as regards superconductivity in the underdoped regime. Thus, despite their relative similarity in most physical properties, the holes due to Li and those due to Sr cannot be made to act collectively (see also Ref. 6).

We have performed a detailed study of the structural, magnetic, and transport properties of Li-doped La_2CuO_4 . Although the holes produced by Li substitution are bound, they have an effect on the structure and magnetism in La_2CuO_4 that is remarkably similar to that due to Sr substitution. The principal differences between Sr and Li substitution are the temperature dependence of the magnetic susceptibility at intermediate doping levels and, of course, the absence of superconductivity in the Li case. These differences may be due solely to the disorder which Li introduces into the two-dimensional CuO_2 plane, but further theoretical study is warranted to ensure that the physics is that simple.

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fluxes, and Li concentrations of $0.1 \leq x \leq 0.2$ have been achieved with $\text{Li}_2\text{O-B}_2\text{O}_3$ fluxes.

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