

Neutralization of holes by hydrogen in $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$

N. M. Suleïmanov, H. Drulis,¹⁾ G. Chadzynski,¹⁾ A. D. Shengelaya, E. F. Kukovitskii, R. G. Mustafin, and J. Janchak¹⁾

Kazan' Physicotechnical Institute, Academy of Sciences of the USSR

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The effects of a saturation of lanthanum–strontium ceramics with hydrogen and the effects of hydrogen on the superconducting properties of these materials have been studied for the first time.

Hydrogen has an extremely simple electronic structure and a small mass but is nevertheless capable of causing substantial perturbations of the local electron density, with a comparatively slight distortion of the lattice. The introduction of hydrogen into a superconducting metal oxide might therefore provide important information about the properties of the material, including its superconducting properties. In this letter we are reporting a study of the effect of hydrogen on the $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ system. We have carried out an NMR study of the resulting samples.

Ceramic samples of the metal oxide were prepared by the standard procedure.¹ The interaction of hydrogen with $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ was studied by two independent methods: by a volumetric method, on the basis of the change in the pressure in the reaction cell of a Sieverts apparatus,² and by a thermogravimetric method, which made it possible to detect changes in the mass of a sample within 4×10^6 g as the sample interacted with hydrogen.³ In each case, after grinding, the powdered metal oxide was held in a vacuum of 10^{-2} torr at room temperature for several hours. Pure gaseous hydrogen, produced through the decomposition of the hydride of Ti, was then admitted into the cell. The hydrogen pressure was 600 torr. The sample was heated at a rate of 30 deg/h.

The volumetric measurements showed that the hydrogen pressure in the reaction cell begins to decrease at $T = 200^\circ\text{C}$ as during the absorption of hydrogen by metals. Figure 1 shows a gravimetric curve of the interaction of hydrogen with the lanthanum–strontium ceramic. It follows from this curve that the mass initially decreases slightly, apparently because of reduction of oxygen. The mass of the sample then begins to increase, indicating an absorption of hydrogen by the sample. Studies of the hydrogenated samples by x-ray structural analysis showed that the reflections characteristic of the tetragonal structure of the original sample persist, but their intensity decreases with increasing hydrogen concentration, and the noise increases. This “amorphization” of the x-ray diffraction patterns apparently results from the grinding of the samples, to dimensions smaller than a certain critical dimension in the region $\leq 0.1 \mu\text{m}$ (Ref. 4). We did not observe any other reflections which might have been caused by the formation of a new phase. In addition, an analysis of the x-ray diffraction patterns showed that the lattice constant along the tetragonal axis increases systematically with increasing hydrogen concentration (Table I). In this manner we produced samples of $\text{H}_x\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-\delta}$ with $x = 0, 0.02, 0.1, 0.3, \text{ and } 0.866$.

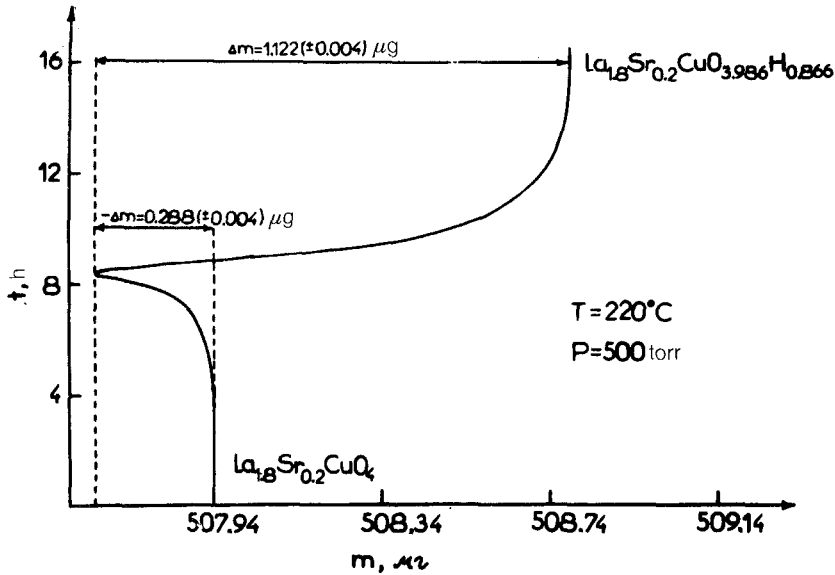


FIG. 1. Gravimetric curve of the interaction of hydrogen with $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$.

To determine the superconducting transition temperature, we measured the rf magnetic susceptibility. In samples with $x \geq 0.1$, the superconductivity was suppressed essentially completely. In the sample with $x = 0.02$, on the other hand (Fig. 2), the transition onset temperature T_{c0} , corresponding to the slope change in χ , remained the same as that of the original sample. The amount of superconducting phase, however, decreased by a factor of 1.5 (as we determined from the deviation of χ per unit mass of the sample at the transition to the superconducting state at $T < T_{c0}$). The absorption of hydrogen thus results in a decrease in the amount of superconducting phase in the metal oxide. In other words, the superconductivity is suppressed in certain parts of the sample. We do not observe the formation of a new phase, and, in fact, such an event would not be expected at such low hydrogen concentrations. On the other hand, the hydrogen concentration in the sample with $x = 0.1$, at which the superconductivity is

TABLE I. Lattice constants and unit-cell volume of $\text{H}_x\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-\delta}$.

$\text{H}_x\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-\delta}$	H content x	Lattice constants		Cell volume (Å^3)
		$a(\text{Å})$	$c(\text{Å})$	
$\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$	0	3.774	13.232	188.43
$\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{3.99}$	0.02	3.776	13.237	188.74
$\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{3.98}$	0.10	3.774	13.267	188.94
$\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{3.99}$	0.30	3.774	13.322	189.72

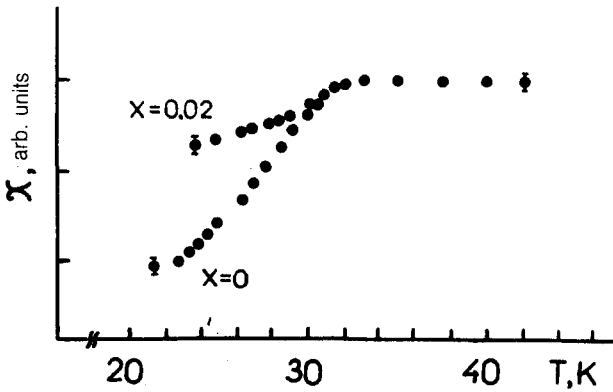


FIG. 2. Temperature dependence of the magnetic susceptibility of $H_xLa_{1.8}Sr_{0.2}CuO_{4-\delta}$ samples.

suppressed, is approximately equal to the concentration of the Sr dopant atoms in this ceramic. In this concentration, we suggest that the mechanism for the suppression of the superconductivity by hydrogen in the lanthanum–strontium ceramic is probably associated with a neutralization of holes as hydrogen localizes in a copper–oxygen plane. That hydrogen can localize in this plane, in the positions with the coordinates $(1/2, 1/2, 0)$ and $(0, 0, 1/2)$, is confirmed by an analysis of the sizes of the interstices based on crystallographic data and the ionic radii of the elements. These positions are

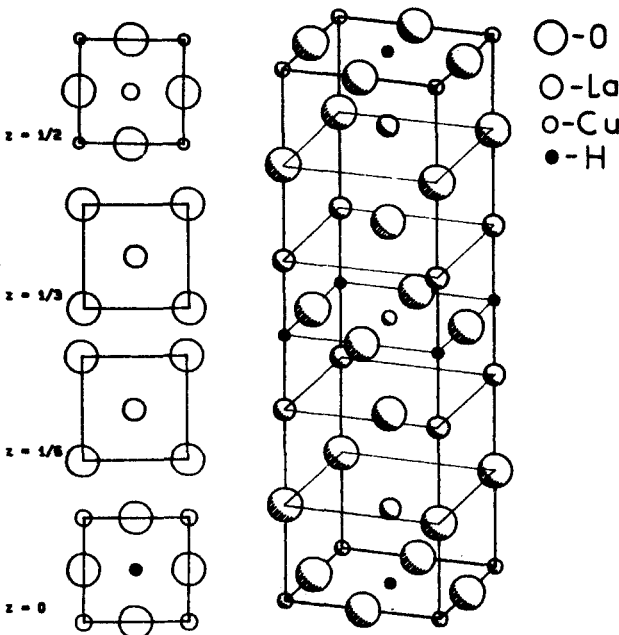


FIG. 3. Localization of hydrogen atoms in the unit cell of $La_{1.8}Sr_{0.2}CuO_4$.

equivalent, and each has four O^{2-} ions (with an ionic radius of 1.40 \AA) in its neighborhood. These oxygen ions form interstices with the size of about 1 \AA —the optimum size for being filled by a hydrogen atom. Along the tetragonal axis, these positions lie between two La^{3+} cations, whose interaction with the hydrogen cation (proton) is apparently the reason for the increase in the lattice constant c (Fig. 3). There are several other considerations which speak in favor of this model for the position of hydrogen in the lattice. A hole may be thought of as a ruptured bond, and hydrogen plays an important role in specifically the neutralization of ruptured bonds in amorphous silicon ($a\text{-Si:H}$).⁵ In this process, the hydrogen localizes near a ruptured bond, and its electron neutralizes the hole, thereby “healing” the bond. In our opinion, the neutralization of holes by hydrogen in this ceramic occurs in a similar way. In addition, NMR measurements at a frequency of 60 MHz on an SKhR-100 pulsed spectrometer, for a sample with $x = 0.866$, showed that the proton-resonance signal is a single symmetric line of Gaussian shape with a width of 63 kHz, which is essentially independent of the temperature. We estimated the width of the NMR line caused by the dipole interaction of a proton with nearest La and Cu nuclei and protons, with oxygen occupying the positions under consideration. For a powdered sample, the mean square width (the second moment) is given by⁶

$$\Delta \overline{H_g^2} = \frac{3}{5} \gamma_{I_1} \hbar^2 I_1 (I_1 + 1) \sum_n r_{mn}^{-6} + \frac{4}{15} \gamma_{I_2} \hbar^2 I_2 (I_2 + 1) \sum_{n'} r_{mn'}^{-6}, \dots$$

The sum $\sum_n r_{mn}^{-6}$ is over all hydrogen positions n among all possible positions m , while the sum $\sum_{n'} r_{mn'}^{-6}$ is over all metal positions n' with a nuclear spin I_2 .

For a Gaussian line, the width is related to the second moment by

$$\Delta H = 2,35 \sqrt{\Delta \overline{H_g^2}}.$$

From these formulas we find the linewidth to be $\approx 30 \text{ kHz}$, or comparable to the width found experimentally. Finally, there is yet another circumstance: If hydrogen does occupy these positions, the composition of the resulting samples will be $H_{1.0}La_{1.8}Sr_{0.2}CuO_4$. This composition is close to the composition with the maximum hydrogen content found in our experiments, from the saturation of the lanthanum-strontium ceramic with hydrogen.

Opinion is divided on the particular oxygen orbital (P_σ or P_π) of the holes. It follows from our results that hydrogen occupies positions in the center of the Cu–O planes of the unit cell. These positions are in a region of a distribution of the electron density of oxygen P_π orbitals, and they are extremely characteristic of the hydrogen atom in compounds of oxygen (e.g., in the structure of ice). Under the assumption that the suppression of superconductivity observed here is indeed due to a neutralization of holes by hydrogen, the circumstance above would apparently indicate that the holes have a P_π symmetry.

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¹Institute of Low Temperatures and Structural Research of the Polish Academy of Sciences, Wrocław

¹D. Vaknin *et al.*, *Phys. Rev. Lett.* **58**, 2802 (1987).

²*Hydrogen in Metals* [Russian translation], Mir, Moscow, 1981.

³H. Kubicka and G. Chadzynski, *Polish J. of Chem.* **55**, 1563 (1981).

⁴Ya. S. Umanskiĭ *et al.*, *x-Ray Diffraction*, Nauka, Moscow, 1951.

⁵*Physics of Hydrogenized Amorphous Silicon* [Russian translation], Mir, Moscow, 1987.

⁶J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

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