

Phase separation of hydrogenated $\text{La}_{2-x}\text{Sr}_x\text{Cu}(\text{Fe})\text{O}_4$

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Hydrogenated powdered $\text{H}_2\text{La}_{2-x}\text{Sr}_x\text{Cu}(\text{Fe})\text{O}_4$ was studied by means of Mössbauer spectroscopy, magnetic ac susceptibility, and x-ray powder diffraction. We have shown that hydrogenation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ leads to a decrease of charge carrier concentration. Low-temperature ($T < 280$ K) Mössbauer spectra of highly hydrogenated $\text{H}_2\text{La}_{2-x}\text{Sr}_x\text{Cu}(\text{Fe})\text{O}_4$ samples exhibit the presence of magnetic and nonmagnetic parts. We interpret this as being due to phase separation into magnetic insulating and metallic regions, taking place slightly below room temperature.

INTRODUCTION

It is a well known fact that charge doping of La_2CuO_4 by means of $\text{Sr}^{2+} \rightarrow \text{La}^{3+}$ substitution changes its properties from antiferromagnetic insulator to a superconducting metal.¹ The simplest explanation of such behavior could be the shift of Fermi level induced by charge (hole) doping. The picture emerging from spectroscopic data² is however different: it seems that increased Sr concentration induces electronic states transfer into a gap between valence and conduction bands. Hall constant R_H does not follow¹ the simple $1/x$ proportionality suggested by "chemical" doping, but at higher values of x it decreases anomalously, rather excluding simple one-band description of the electronic structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

The dependence of the critical temperature of superconducting transition T_c of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ on strontium index x forms a parabolalike curve with a maximum at $x \approx 0.15$. When x is increased above 0.15, T_c falls down, although the charge carrier concentration increases and the compound becomes better conducting. Doping with Sr also induces structural transformation increasing the room-temperature symmetry of the unit cell from orthorhombic to tetragonal.^{1,3}

The above-mentioned facts provoke experiments aimed at changing the properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ by means of electron doping in the reverse direction, i.e., towards lower hole concentration, with x set at a given level. Hydrogen H^+ doping of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ should essentially be equivalent to electron doping. A lot of work has been devoted to the studies of another hydrogenated hole-type high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.⁴⁻⁶ In the case of $\text{H}_2\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ it was shown^{5,6} that increasing hydrogen concentration leads to the similar effects as reducing oxygen index. An interesting phenomenon of phase separation of the material into magnetic and nonmagnetic regions was also observed at high values of z .⁶

Hence we decided to check the possibility of electron doping of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ by means of hydrogenation. To get more insight into the properties of the studied compound at the microscopic level taking advantage of such powerful tool as Mössbauer spectroscopy (MS), we have investigated lightly ^{57}Fe -doped $\text{La}_{2-x}\text{Sr}_x(\text{Cu}_{1-y}\text{Fe}_y)\text{O}_4$ ($y = 0.005$). As it is known from data published so far,^{7,8} doped iron occupies copper position in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and reflects the magnetic properties of Cu.

EXPERIMENTAL

Ceramic samples of $\text{La}_{2-x}\text{Sr}_x(\text{Cu}_{1-y}\text{Fe}_y)\text{O}_4$ ($y = 0.005$) were prepared using standard solid-state reaction method, with La_2O_3 , SrCO_3 , CuO , and Fe_2O_3 (enriched to 95% ^{57}Fe) taken as starting materials. The hydrogenation of $\text{La}_{2-x}\text{Sr}_x\text{Cu}(\text{Fe})\text{O}_4$ samples was carried out by means of volumetric method in a sealed reaction cell at the constant temperature of 157°C . The hydrogen concentration was determined from the overall decrease of the hydrogen pressure in the reaction cell.

Ac susceptibility was measured using Lake Shore 7000 susceptometer in the ac fields of 10 Oe. Mössbauer absorption spectra were taken in standard transmission geometry in the temperature range 30–300 K in a gas-flow cryostat, with $^{57}\text{Co}(\text{Rh})$ source kept at room temperature. All isomer shifts are given in respect to metallic iron.

In the case of magnetically measured transitions to the superconducting state two criteria for determination of the critical temperature T_c were used: onset of diamagnetism (T_c^{on}), and the midpoint of the transition defined as the temperature at which $d\chi'/dT$ peaks (T_c^{md}).

RESULTS AND DISCUSSION

We have chosen two Sr concentrations $x = 0.11$ and 0.20, i.e., belonging to the underdoped and overdoped re-

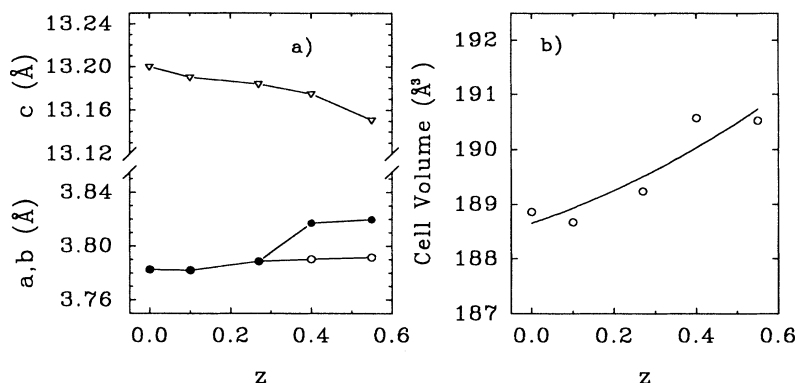


FIG. 1. Unit-cell parameters and cell volume of $H_zLa_{1.89}Sr_{0.11}Cu(Fe)O_4$ plotted vs hydrogen content z . For the sake of clarity a and b lattice constants of samples with low-temperature tetragonal structure were divided by $\sqrt{2}$.

gimes. Such a choice eliminated also the possible uncertainties connected with $T_c(x)$ anomaly around $x = 0.12$.

X-ray powder diffractograms proved all samples discussed in this work to be single phase with K_2NiF_4 structure of $La_{2-x}Sr_xCuO_4$. Only the diffractogram of ($x = 0.11, z = 0.55$) sample showed traces (less than 8%) of an unknown phase. Room-temperature lattice parameters of $x = 0.11$ series are presented in Fig. 1 versus hydrogen content z . Unit-cell volume increases with increasing z and the symmetry changes from tetragonal to orthorhombic.

The observed changes of lattice constants with increas-

ing hydrogen index suggests that hydrogen entered the samples homogeneously. The change of the room-temperature symmetry of the unit cell indicates the increase of the temperature T_0 at which the orthorhombic distortion of the tetragonal symmetry of $La_{2-x}Sr_xCuO_4$ occurs. T_0 is governed by the bond-length mismatch between LaO and CuO₂ layers.³ This mismatch is a function of both the Sr content x and the temperature. Increasing hole concentration leads to removal of electrons from antibonding orbitals. Changing the temperature causes changes of the equilibrium La-O bond length. T_0 falls down from above 500 to 0 K when x is increased from 0 to 0.23 (see Ref. 3 and references therein). From the observed increase of T_0 with increasing hydrogen index z for $x = 0.11$ we can draw the conclusion that hydrogenation corresponds to the decrease of charge-carrier concentration.

Room temperature (RT) Mössbauer spectra of all the samples studied were similar to the RT spectrum presented in Fig. 2(a) and were fitted assuming a unique doublet, i.e., iron in one crystallographic position. Isomer shift δIS values for $x = 0.11$ series extracted from RT spectra are presented in Fig. 3 vs the hydrogen index z . We observe an increase of isomer shift δIS upon increase of z . In the case of nonhydrogenated $La_{2-x}Sr_xCu(Fe)O_4$, the $\delta IS(x)$ dependence is governed by the number of delocalized holes in Cu-O planes.⁷ Decrease of Sr concentration x leads to an increase of δIS . Hence the observed here $\delta IS(z)$ dependence could be explained as being due to the decrease of charge-carrier concentration.

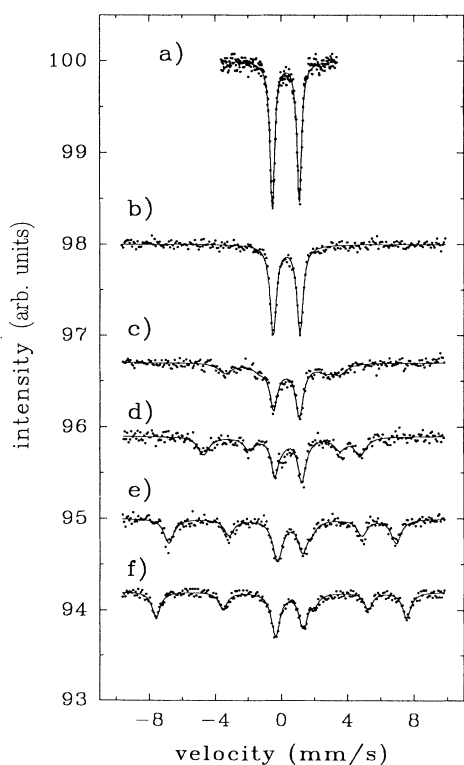


FIG. 2. Mössbauer absorption spectra of $H_zLa_{1.89}Sr_{0.11}Cu(Fe)O_4$ taken at temperatures: (a) $T = 292$ K ($z = 0$); (b) $T = 292$ K ($z = 0.55$); (c) $T = 260$ K ($z = 0.55$); (d) $T = 210$ K ($z = 0.55$); (e) $T = 105$ K ($z = 0.55$); (f) $T = 33$ K ($z = 0.55$).

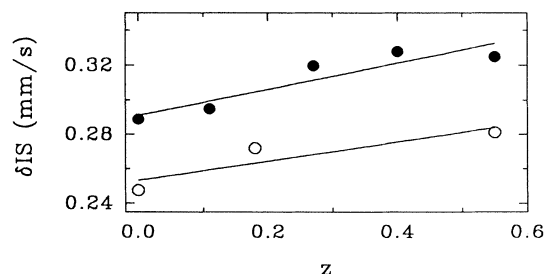


FIG. 3. Isomer shift δIS obtained from room-temperature Mössbauer spectra of $H_zLa_{2-x}Sr_xCu(Fe)O_4$ samples with $x = 0.11$ (closed symbols) and $x = 0.20$ (open symbols) plotted vs hydrogen index z .

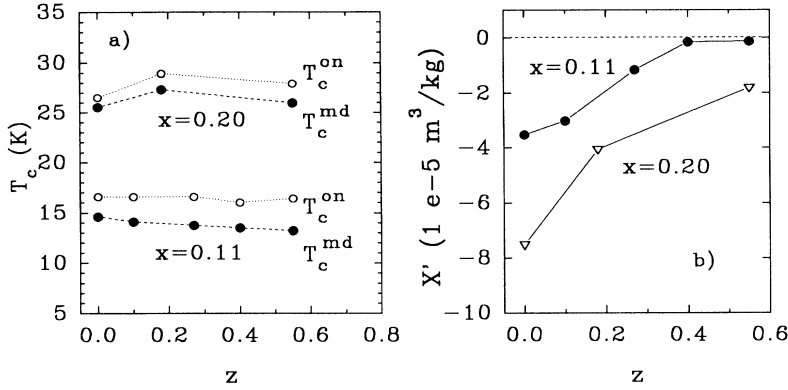


FIG. 4. Critical temperatures of superconducting transitions T_c^{md} and T_c^{on} (a) and real part of magnetic ac susceptibility χ' measured at 5 K (b) plotted vs hydrogen content for $x=0.11$ and 0.20 samples.

The hydrogen concentration ascribed to a particular sample was estimated on the basis of the volumetric method. Therefore the question arises whether hydrogenation leads to deoxygenation of the samples. Deoxygenation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ was thoroughly studied in Ref. 9 and, according to that work, decreasing the oxygen index below 4.0 results in strong decrease of T_c , because of the randomness introduced to Cu-O planes by oxygen vacancies. Since the hydrogenation did not significantly lower T_c (in the case of $x=0.20$ series it even increased T_c), we deduce that we did not alter the oxygen content of our samples. The above presented room-temperature Mössbauer and structural data suggest that hydrogenation most probably decreases overall charge-carrier concentration without lowering the oxygen content of the samples.

We are aware of the fact, that the nominal hydrogen content z is generally not equal to the amount of hydrogen in the structure z_B : a certain amount could be absorbed in voids or in other imperfections of the polycrystalline material used. Also the already mentioned occurrence of additional broad peaks in the diffractogram of ($x=0.11$, $z=0.55$) sample suggests that hydrogenation could result in the destruction of rather small amounts of the hydrogenated material. The observed small decrease of the normalized MS line intensity S/B_0 with increasing z supports such a view: ^{57}Fe atoms in random positions could give rise to a variety of spectra of small intensity but with different quadrupole splittings, hidden hence in the background. Decrease of S/B_0 could also be caused by the decrease of Debye temperature θ_D . However, using the temperature dependence of the isomer shift $\delta\text{IS}(T)$, we found θ_D of nonhydrogenated ($x=0.11$, $z=0$) and hydrogenated ($x=0.11$, $z=0.27$) samples to be the same within the experimental error (460 ± 5 K). We assume that there exists a proportionality between nominal hydrogen index z and the amount of hydrogen effectively bound in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ z_B , i.e., $z_B \sim z$.

The influence of hydrogenation on superconducting properties of $\text{La}_{2-x}\text{Sr}_x\text{Cu}(\text{Fe})\text{O}_4$ is similar to that reported in Ref. 10. Hydrogenation slightly increases the critical temperature of $x=0.20$ series [Fig. 4(a)]. The decrease of T_c of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ for $x > 0.15$ is usually connected with exceeding the “optimal” for superconductivity hole concentration at $x=0.15$ (overdoping). Then the

slight increase of T_c of hydrogenated overdoped $x=0.20$ samples could be explained as being due to the decrease of charge-carrier concentration. A simple London formula for the magnetic penetration depth λ gives $\lambda^2 \propto 1/n_s$, where n_s is the concentration of superconducting charge carriers. A decrease of n_s caused by hydrogenation should then correspond to the decrease of diamagnetic susceptibility $-\chi'$ (5 K), as it was observed [Fig. 4(b)].

Problems arise in the interpretation of the $T_c(z)$ curve for $x=0.11$ series [Fig. 4(a)]. According to Ref. 11, T_c of all high- T_c superconducting cuprates seems to be determined by charge-carrier concentration. If hydrogen reduces hole concentration of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, it should be followed by a decrease of T_c , what is not observed. However, in our work we have to do with double doping (i.e., supposed electron doping by means of hydrogen H^+ and hole doping through $\text{Sr}^{2+} \rightarrow \text{La}^{3+}$ substitution) and one should be cautious when interpreting the results of experiments like this. We can recall here the results of another double-doping experiment presented in Ref. 12: a partial substitution of trivalent lanthanum with tetravalent cerium in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ shifted the position of the minimum of $T_c(x)$ dependence at $x \approx 0.12$ towards higher Ba concentrations, but it did not change T_c at lower (i.e., below 0.10) values of x .

There exists an alternative explanation of the superconducting properties of $\text{H}_z\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ proposed in Ref. 10. According to that hypothesis, hydrogen atom locally suppresses superconductivity in small volume V_H around its position. The charge concentration in the rest of the material (i.e., outside of V_H) remains essentially unchanged. This model explains the unchanged T_c of hydrogenated underdoped $x=0.11$ series.

In this context we would like to discuss the occurrence of magnetic splitting visible in the low-temperature Mössbauer (MS) spectra of our highly hydrogenated samples, i.e., $x=0.11$, $z=0.40, 0.55$ and $x=0.20$, $z=0.55$ (see Fig. 2). Room-temperature spectra of these samples consist of unique quadrupole doublets, but below $T_s \approx 280$ K these spectra split into magnetic and nonmagnetic parts. T_s seems to be the same for $z=0.40$ and $z=0.55$ samples. The relative intensities of magnetic (M) and nonmagnetic (NM) subspectra I_M and I_{NM} are depicted in Fig. 5. I_M and I_{NM} do not change significantly

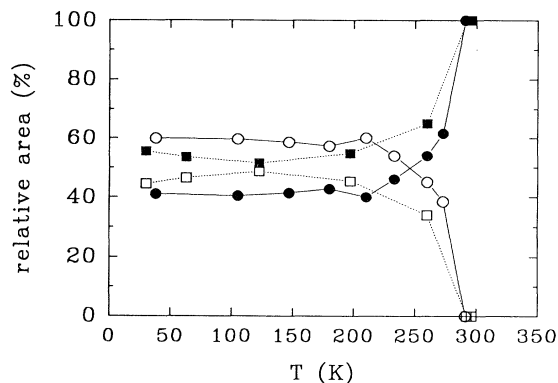


FIG. 5. Relative intensities of magnetic (open symbols) and nonmagnetic (closed symbols) parts of MS spectra of $\text{H}_2\text{La}_{1.89}\text{Sr}_{0.11}\text{Cu(Fe)O}_4$ samples with $z=0.40$ (squares) and $z=0.55$ (circles). Lines are drawn as guides for the eye.

below 200 K. This fact rather excludes the possibility that the NM subspectrum comes from small particles of the magnetic phase through superparamagnetic effect.

The temperature dependence of the hyperfine magnetic field at ^{57}Fe nucleus H_{hf} of the magnetic subspectrum was similar to that reported for antiferromagnetic La_2CuO_4 compound.^{7,8} We successfully fitted to it (over the range 30–230 K) the integral form of the formula proposed in Ref. 13. According to Ref. 13 the reduction in magnetization $M(T)$ —and correspondingly in $H_{\text{hf}}(T)$ —is caused by the excitation of spin waves in the anisotropic antiferromagnet, in which the planar interaction is much stronger than the interplanar one. The values of the parameters: planar exchange energy J and the ratio of the interplanar to planar hopping strengths r obtained in this work ($J=1220$ K and $r=0.022$) are similar to those obtained in Refs. 7 and 8 for La_2CuO_4

($J=1600$ K and $r=0.011$).

The occurrence of both magnetic and nonmagnetic parts in the MS spectra of highly hydrogenated samples could be explained as being due to

(i) “static” sample inhomogeneity [there are hydrogen-rich regions, which are insulating and antiferromagnetic (AF) at lower temperatures, and metallic regions, with small—if any—hydrogen content, which at low temperatures becomes superconducting]. Such nonhomogeneity could occur at higher temperatures during hydrogenation

(ii) phase separation of homogeneously hydrogenated material, when temperature is lowered slightly below RT, into antiferromagnetic and nonmagnetic regions.

As case (i) means sample nonhomogeneity at room temperature, it does not find support in the already discussed crystallographic and MS data. Therefore we rather support the second explanation (ii), i.e., the phase separation taking place slightly below RT. A similar phenomenon can be recalled here. It is the phase separation of oxygenated $\text{La}_2\text{CuO}_{4+\delta}$ ($\delta>0$) which takes place in the temperature interval 180–280 K.¹⁴ $\text{La}_2\text{CuO}_{4+\delta}$ separates into domains of stoichiometric (insulating and AF) La_2CuO_4 and oxygen-rich (metallic, nonmagnetic and superconducting below 35 K) $\text{La}_2\text{CuO}_{4.05}$. Separation occurs through oxygen diffusion.

In summary we have shown that hydrogenation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ leads to the decrease of charge-carrier concentration. Hence the hydrogenation seems to be a useful tool in studying the properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compound. We interpret the observed complex MS spectra of highly hydrogenated samples as being due to phase separation into magnetic insulating and nonmagnetic metallic regions taking place slightly below room temperature.

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