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Powder Neutron Diffraction Study on $La_{1.8}Sr_{0.2}CuO_{4-x}S_x$(x=0, 0.05, 0.1)

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Abstract: Recent experimental results of transport properties on $La_{2-y}M_yCuO_{4-x}S_x$ (M=Sr and Ba) were found to be consistent with the idea that though the doping of every two S atoms, three O atoms are expelled from the LaO planes, which results in the creation of one oxygen vacancy site. Powder neutron diffraction experiments on $La_{1.8}Sr_{0.2}CuO_{4-x}S_x$ (x=0, 0.05, 0.1) were made to verify the idea: The S atoms were found to enter the oxygen sites in LaO planes. However the creation of oxygen vacancy in LaO planes was not detected with the present experimental error.

1. Introduction

Superconducting transition temperature T_c of high-T_c Cu oxides shows the very sensitive decrease with atomic substitution for Cu in the CuO_2 planes. Even in the case where atoms substituted for Cu do not have magnetic moments and do not change the carrier density, they show the large decrease in T_c. This is in clear contrast to the cases of ordinary superconductors. Drastic changes of various physical properties accompany this degradation of the superconductivity. The electrical resisitivity of the CuO_2 planes is increased pronouncedly, for example, which suggests an important role of the electron localization.

The T_c($\leq$36K) of $La_{2-y}Sr_yCuO_4$ is relatively low compared to other high-T_c Cu oxides. It has been often argued in relation to this T_c-suppression by the atomic substitution: The T_c of this system may be suppressed by the microscopic randomness introduced into the LaO planes by the Sr-substitution for La and/or the possible existence of O atom vacancies in the CuO_2 planes for relatively large y (>0.20). It is interesting to clarify whether the randomness introduced into the LaO planes or outside of the CuO_2 planes suppress T_c or not.

Recently we have measured the T_c and the Hall coefficients of $La_{2-y}M_yCuO_{4-x}S_x$ (M

=Sr and Ba) for various values of x and y.[1] The T_c versus $(y-x)$ curve of the system is found to be almost identical to the T_c versus y curve of $La_{2-y}M_yCuO_4$ system: The S-doping does not suppress the T_c values. It also causes the reduction of the hole concentration by x. These results are consistent with the idea that though the doping of every two S atoms, three O atoms are expelled from the LaO planes, which results in the creation of one oxygen vacancy site. The randomness introduced outside of the CuO_2 planes does not have an appreciable effect on the T_c values in the present system.

This paper reports the result of powder neutron diffraction study on $La_{1.8}Sr_{0.2}CuO_{4-x}S_x$ (x=0, 0.05, 0.1) to verify the idea. The S atoms were found to enter the oxygen sites in LaO planes. However the creation of oxygen vacancies in LaO planes were not detected with the present experimental error.

2. Experiment

Initial mixtures of proper amounts of La_2O_3, $SrCO_3$, CuO and CuS were fired at 930 ℃ for 10h. They were ground again and pressed into pellets. These pellets were sintered at 1050 ℃ in air for 2 days and cooled in furnace.

Neutron diffraction patterns were obtained using a high resolution powder diffractometer(HRPD) with 64 detectors installed at JRR-3M in JAERI. Incident neutron wave length was 1.823 Å. The collimation was 6'-20'-6'. A vanadium sample cell was used to avoid diffraction peaks from the cell. Powder specimen was rotated at room temperature during the measurement to prevent a preferred orientation effect. The intensity data were collected at about 0.05° step(2θ) and the data in the 2θ range of 27 -152.5° were used for analysis. A few weak impurity peaks were detected for samples with $x \neq 0$. They were excluded from the calculation.

The diffraction patterns were analyzed by the Rietveld method using a computer program RIETAN applied to multicountered system. The scattering lengths used in it were 8.240, 7.020, 7.718, 5.803 and 2.847x10 $^{-13}$ cm for La, Sr, Cu, O and S, respectively. The background level was also fitted by a polynomial expression through the analysis. We have calculated the R factors in two different ways: In defining $R_p = | y_i(obs) - y_i(cal) | / | y_i(obs) |$, for example, we use two kinds of $y_i(obs)$, raw counted number, $y_{i(S+BG)}$ and $y_{iS} = \{y_{i(S+BG)} - background\}$. These two kinds of R factors are distinguished by the subscripts S and (S+BG), where R_{pS} is always considerably larger than $R_{p(S+BG)}$.

A profile of powder neutron diffraction peak by a steady source is well known to be expressed by a Gaussian function. However the tail of profile presently obtained by HRPD showed a deviation from the Gaussian function, probably due to a high resolution of HRPD. Then a Lorentzian function was mixed with the Gaussian one, and the ratio γ of Gaussian fraction was refined also. The adoption of $\gamma \neq 1$ lowered $R_{wp(S+BG)}$ from about 13.5% to about 10%, and the γ obtained was ~ 0.6.

3. Results and Discussions

A crystal structure of $La_{2-y}Sr_yCuO_4$ at room temperature has already been reported by many authors.[2-7] A space group is tetragonal I4/mmm (No.139) and the atomic positions are as follows: La/Sr:4e (0,0,z), Cu:2a (0,0,0), O1:4c (0,0.5,0),O2:4e (0,0,z), where $z(La/Sr) \sim 0.36$ and $z(O2) \sim 0.18$. The structure is schematically shown in Fig. 1 by the circles with ionic radii corrected for their coordinations, where the ionic radii presented by Shannon [8] were used. We can notice that Cu and O atoms in CuO_2 planes are almost in touch with each other. Then S atoms are considered to enter the O site in LaO planes, because the ionic radius of S atom is much larger than that of oxygen atom.

In the case of neutron diffraction, it is impossible to determine independently the occupation of the different kinds of atoms with the same thermal vibrations in crystallographically equivalent sites. Then we analyzed the observed powder neutron diffraction pattern with the assumption that all of the S atoms enter the oxygen positions in LaO planes.

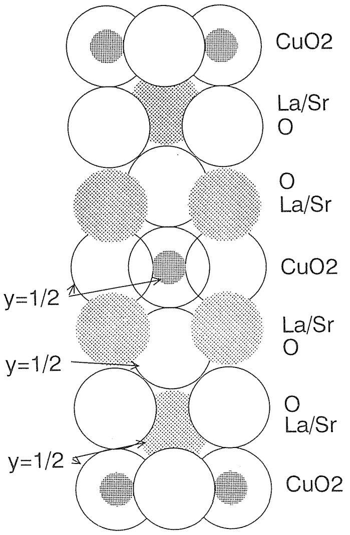

Fig. 1. The schematic structure of $La_{2-y}Sr_yCuO_4$ shown by the circles with ionic radii corrected for their coordinations. The small and the large hatched circles indicate Cu and La/Sr atoms, respectively. The white circles and the open circle indicates O atoms.

The results of the profile fits are shown in Fig.s 2, 3 and 4 for $La_{1.8}Sr_{0.2}CuO_{4-x}S_x$ (x=0, 0.05, 0.1), respectively. The lattice parameters a and c and the R factors were as follows: a=3.7717 (1) Å, c=13.2421 (2) Å, $R_{wp(S+BG)}$=9.7%, $R_{p(S+BG)}$=7.0% (R_{pS}=11.6%) and R_{IS}=3.5% for x=0; a=3.7755 (1) Å, c=13.2324 (2) Å, $R_{wp(S+BG)}$=9.5%, $R_{p(S+BG)}$= 7.0% (R_{pS}=11.8%) and R_{IS}=3.6% for x=0.05; a=3.7803 (1) Å, c=13.2163 (2) Å, $R_{wp(S+BG)}$=10.3%, $R_{p(S+BG)}$=7.6% (R_{pS}=12.6%) and R_{IS}=4.0% for x=0.1. The structural parameters obtained are listed in Table I.

The structure for x=0 and y=0.2 is consistent with the structures presented previously for x=0 and y=0.12, [6] 0.15, [2,3,4,5,7] 0.3. [7] Though the occupancy of oxygen site in CuO_2 planes by S atoms, $g(S1)$, was fixed to 0.0 for x=0.05 and 0.1, the occupancy of the site by oxygen atoms, $g(O1)$, showed no meaningful changes compared to the one for x=0. This result seems to indicate the correctness of the assumption. The occupancy of oxygen site in LaO planes by oxygen atoms, $g(O2)$, decreased with the increase of occupancy of the site by S atoms, $g(S2)$. Though the decrease was not so large as that expected from the transport experiments, this result does not give reliable verification because the expected values are very small

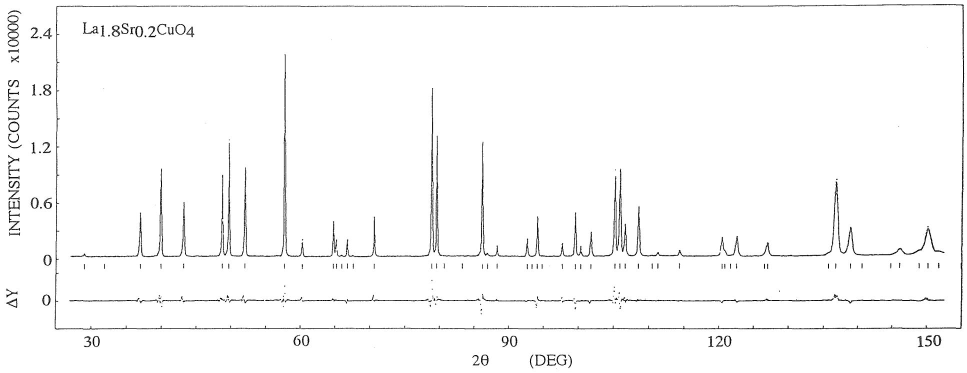

Fig. 2. Neutron Rietveld refinement pattern for $La_{1.8}Sr_{0.2}CuO_4$. The calculated pattern is shown as a line through the data points while the difference plot is shown in the lower portion.

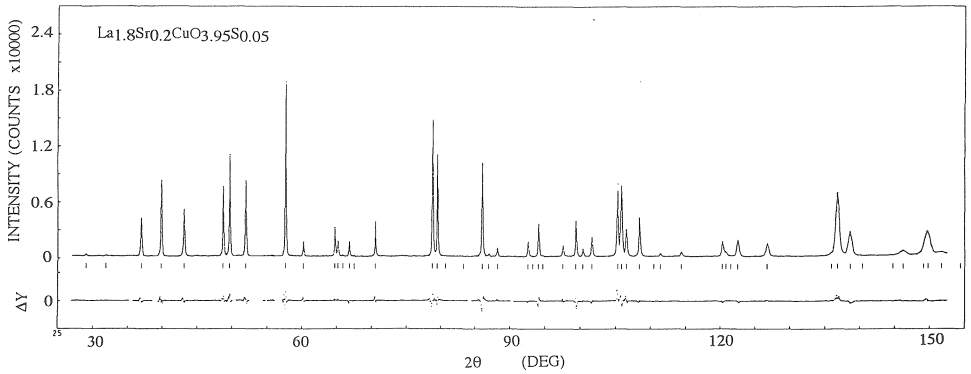

Fig. 3. Neutron Rietveld refinement pattern for $La_{1.8}Sr_{0.2}CuO_{3.95}S_{0.05}$.

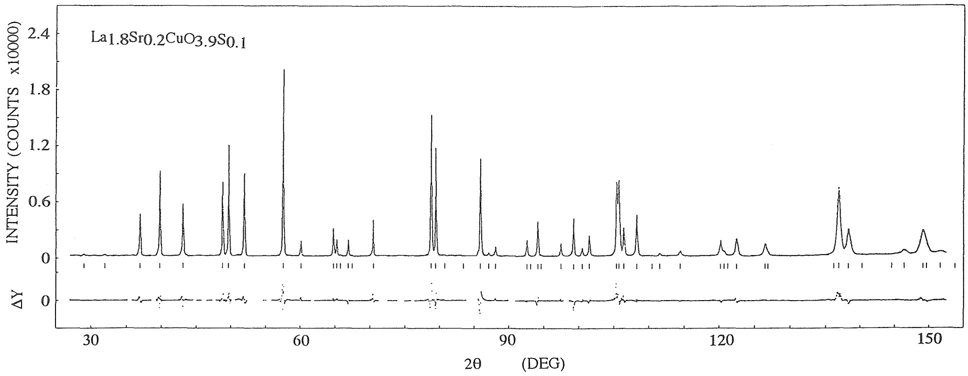

Fig. 4. Neutron Rietveld refinement pattern for $La_{1.8}Sr_{0.2}CuO_{3.9}S_{0.1}$.

compared to the estimated standard deviations: The expected values for occupancy of oxygen vacancies are 0.0125 and 0.025 for x=0.05 and 0.1, respectively.

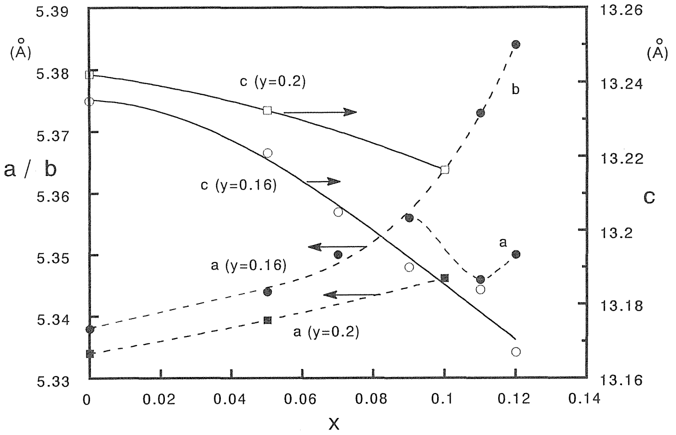

Fig. 5. Lattice parameters of $La_{2-y}Sr_yCuO_{4-x}S_x$. The data for y=0.16 are taken from ref.9. The a of tetragonal system is $\sqrt{2}$ times multiplied to compare that of orthorhombic system in higher x content.

The lattice parameters a and c are displayed by squares in Fig. 5 as a function of x in comparison with those for y=0.16 previously presented. [9] The a of tetragonal system is $\sqrt{2}$ times multiplied in the figure. The lattice parameter a increased and the c decreased with the substitution of oxygen by the large S atoms, which is consistent with the previous results for y=0.16 [9] and 0.15 [1]. The elongation and shrinkage are also observed in the $La_{2-y}Sr_yCuO_4$ system with decreasing content y of Sr atoms. On the basis of the results, S atoms were previously considered to be incorporated in the in-plane sites of the CuO_2 planes. [9] As stated in Section 1, the increasing Sr content y and the decreasing S content x cause the same effect on the value of T_c and the Hall coefficient of $La_{2-y}Sr_yCuO_{4-x}S_x$ system. [1] We may notice the same effect on the value of the lattice parameters in the tetragonal region in Fig.5. However the average ionic radius of La/Sr or O/S becomes larger with increasing y or x, respectively. Then it seems natural to consider that the elongation of the a-axis and the shrinkage of the c-axis with the substitution of oxygen by the large S atoms are caused by the decrease of average ionic radius of O/S resulting from the creation of oxygen vacancies outside of the CuO_2 planes, though the creation was not directly detected by the present structure analysis.

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References

1) T. Nishikawa, H. Harashina and M. Sato: Physica C **211** (1993) 127.

2) M. Onoda, S. Shamoto, M. Sato and S. Hosoya: Novel Sperconductivity (ed.s S.A. Wolf and V. Z. Kresin, 1987, Plenum Publishing Corpo.) p.919

3) M. Onoda, S. Shamoto, M. Sato and S. Hosoya: Jpn. J. Appl. Phys. **26** (1987) L363.

4) H. H. Wang, U. Geiser, R. J. Thorn, K. D. Carlson, M. A. Beno, M. R. Monaghan, T. J. Allen, R. B. Proksch, D. L. Stupka, W. K. Kwok, G. W. Crabtree and J. M. Williams: Inorg. Chem. **26** (1987) 1190.

5) R. J. Cava, A. Santro, D. W. Johnson, Jr. and W. W. Rhodes: Phys. Rev. B**35** (1987) 6716.

6) M. Francois, K. Yvon, P. Fischer and D. Decroux: Solid State Commun. **63** (1987) 35.

7) T. Kamiyama, F. Izumi, H. Asano, H. Takagi, S. Uchida, Y. Tokura, E. Takayama-Muromachi, M. Matsuda, K. Yamada, Y. Endoh and Y. Hidaka: Physica C **172** (1990) 120.

8) R. D. Shannon: Acta Cryst. A **32** (1976) 751.

9) H. Kozuka, S. Fujihara, T. Yoko and S. Sakka: Jpn. J. Appl. Phys. **29** (1990) L1608.

Table I Structural parameters of $La_{1.8}Sr_{0.2}CuO_{4-x}S_x$ at room temperature. Space group:I4/mmm (No.139); La/Sr:4e (0,0,z), Cu:2a (0,0,0), O1:4c (0,0.5,0), O2:4e (0,0,z). Unit of *B* is Å^2. Numbers in parentheses indicate the estimated standard deviations.

	x=0.0	*x*=0.05	*x*=0.1
z (La/Sr)	0.3603 (6)	0.3606 (6)	0.3610 (7)
B (La/Sr)	0.48 (18)	0.45 (17)	0.49 (20)
B (Cu)	0.34 (24)	0.30 (24)	0.41 (27)
g (O1)	1.004 (53)	1.002 (51)	1.009 (57)
g (S1)	---	0.00 (fixed)	0.00 (fixed)
B (O1)	0.84 (36)	0.81 (35)	0.94 (39)
g (O2)	0.984 (49)	0.975 (45)	0.960 (53)
g (S2)	---	0.025 (fixed)	0.05 (fixed)
z (O2)	0.1818 (10)	0.1823 (10)	0.1827 (11)
B (O2)	1.06 (31)	1.09 (31)	1.15 (35)