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T_N Dependence on Hole Concentration in the $La_{2-x}Sr_xCuO_{4+\delta}$ System

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Hole concentration, h, was determined by using the coulometric titration technique for the powdered samples of $La_{2-x}Sr_xCuO_{4+\delta}$ $(0 \leq x \leq 0.02)$ annealed in flowing 1 atm N_2 and 1 atm O_2. From the temperature dependence of magnetic susceptibility we found that the Nêel temperature, T_N, decreases steeply with increasing h and that $T_N(h)$ can be fitted in the following expression $T_N(h)/T_N(0)=1-\{h/h_c\}^n$ where $T_N(0)$, h_c and n are constants. This power-law dependence might be explained by finite size scaling theory.

[2D antiferromagnet, Nêel temperature, hole concentration, finite size scaling, high-T_c superconductor]

§1. Introduction

One of the most interesting features of cuprate high-T_c superconductors is that the parent compounds are two-dimensional antiferromagnetic insulators.[1] The antiferromagnetic ordering vanishes steeply with doping holes and further doping causes superconductivity.[2] In order to reveal a correlation between antiferromagnetic ordering and doped holes, $La_{2-x}Sr_xCuO_{4+\delta}$ is one of the suitable systems, because the structure is most simple, i.e. the structure has only one CuO_2 sheet per a formula unit.[1]

The role of doped holes in antiferromagnetic ordering of this system has not been understood yet, since the precise measurement of hole concentration, $h=x+2\delta$, is technically difficult. In this paper, we report the experimental result of the measurement of h as functions of the Sr concentration, x, and annealing conditions leading to the different excess oxygen, δ. Here, the value of h has been determined by the coulometric titration method.[3] The relation between h and antiferromagnetic ordering temperature, T_N, which was determined by temperature dependence of dc magnetic susceptibility is discussed from a view point of size scaling law.

§2. Experimental

The samples of $La_{2-x}Sr_xCuO_{4+\delta}$ for $0 \leq x \leq 0.02$ were prepared from high purity La_2O_3 (99.99%), $SrCO_3$ (99.99%), and CuO (99.999%) powders. Starting materials were ground and pressed into pellets and preheated in air at 900°C for 24 hours. After heating, the products were quenched to room temperature, reground and pelletized again. They were annealed again to homogenize at 1050°C in air for 1 or 2 days. This process was repeated several times in order to obtain homogeneous samples. The powder sample was separated into two parts, one of which was annealed at 900°C in flowing N_2 ($P_{N_2}=1$ atm) with high purity of above 99.995% for 24 hours (N_2 treatment) and the other was done at 400°C in flowing O_2 ($P_{O_2}=1$ atm) with the same purity for 24 hours (O_2 treatment) and both were cooled to room temperature at the rate of 1~2°C/min. The X-ray powder diffraction (XRD) measurements were performed to check the samples and all samples prepared were confirmed to be single phases having the K_2NiF_4-type structures with orthorhombic symmetry.[4]

The value of h was determined by use of the coulometric titration technique using CuCl as a reducing reagent.[3,5] After the sample of $La_{2-x}Sr_xCuO_{4+\delta}$ was dissolved into the solution of 1 N-HCl containing excess CuCl, holes in the sample existing as a form of $[CuO]^+$ easily oxidized Cu^+ in CuCl to Cu^{2+}. The hole content was determined from the electric oxidation of the remaining Cu^+ by flowing constant current of 5 mA. We took sufficient care to remove O_2 from the solution before titration because it also oxidizes Cu^+.

The temperature dependence of the dc magnetic susceptibility $\chi(T)$ was measured at 0.6 Tesla using a torsion magnetic balance. T_N was assumed to be the peak temperature of $\chi(T)$ curve, at which the three-dimensional long range antiferromagnetic ordering occurs resulting from a weak interaction between adjacent CuO_2 planes.[1]

§3. Result and Discussion

The Sr concentration dependence of h determined from the coulometric titration analysis is shown in the upper part in Fig. 1. In the lower part of this figure, δ vs. x curve is also presented. It is to be noted that h can be directly determined by the coulometric titration and that δ can be determined from the equation, $\delta=(h-x)/2$ by taking the nominal Sr content as x. For $x=0$, the difference of the oxygen contents between the samples with the O_2 treatment and with the N_2 treatment is about 0.003, which is consistent with the result of our thermogravimetric analyses.

The value of δ obtained for each annealing condition gradually decreases with x. On the other hand, h increases with x. It is clear that the excess oxygen considerably contributes to the total hole concentration even in the samples with the N_2 treatment.

The x dependence of T_N determined from $\chi(T)$ is shown in the inset of Fig. 2 for each annealing condition. For the samples with the N_2 treatment, T_N decreases drastically with x and the long range antiferromagnetic ordering disappears for $x>0.02$. In the same way, for the samples with the O_2 treatment, T_N decreases drastically with x and goes down to 0 K around $x\sim0.015$. If we compare two samples having the same x value, T_N is always lower in the case of the O_2 treatment than in the case of the N_2 treatment, indicating T_N tends to

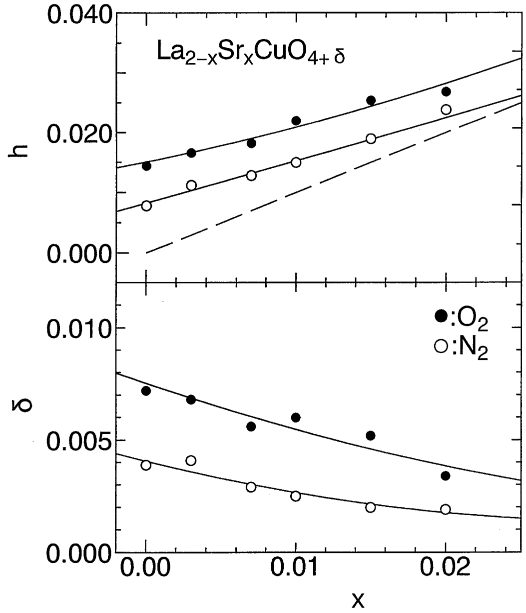

Fig. 1. (upper) Sr concentration, x, dependence of the hole concentration, h, determined from coulometric titration. (lower) Sr concentration, x, dependence of excess oxygen, δ. Closed circles: the O_2 treatment. Open circles: the N_2 treatment. The solid lines are guides for the eyes. The broken line indicates the relationship for the system with no oxygen vacancy or no excess oxygen, i.e. $h=x$.

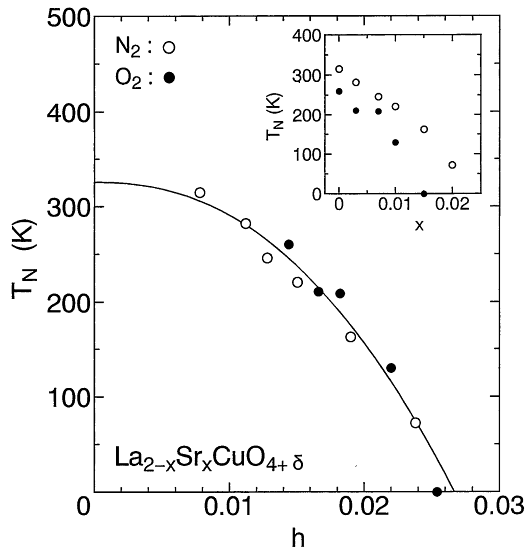

Fig. 2. The dependence of T_N on the hole concentration, h. The solid line is the fit by the function in the text. (inset) The dependence of T_N on the Sr concentration, x. Closed circles: the O_2 treatment. Open circles: the N_2 treatment.

decrease with introduction of the excess oxygen. Our T_N data are for the most part in agreement with the data of Cho *et al.*[6] and Saylor and Hohenemser.[7] However, we did not observe superconductivity down to 4 K in any samples of $x \leq 0.02$ with the O_2 treatment, which differs from the results by Cho *et al.* We suppose that this difference is caused from the differences in preparing conditions. For instance, if the magnetic measurement is done for a sintered specimen, rather than for a powdered one, superconducting volume fraction is sometimes overestimated due to the weak coupling. Superconductivity observed by Cho *et al.* might be ascribed to a trace of superconducting phase formed due to inhomogeneity in the sample, though we do not know whether they measured a sintered specimen or not.

Next, T_N is plotted as a function of h in Fig. 2. One can notice that the decrease of T_N correlates significantly with h. The sharp decrease of T_N by doping small amount of holes can not be explained by the simple dilution model. In the non superconducting system of $La_2Cu_{1-y}M_yO_4$ (M=Zn, Mg) and the n-type superconducting system of $Pr_{2-y}Ce_yCuO_4$, T_N decreases more slowly with y.[2,8)]

Cho *et al.* pointed out that the decrease of T_N with x (note that x is not equal to hole concentration in a strict sense as described above) showed power-law dependence.[6] They suggested a *microscopic* phase separation where the doped holes are concentrated in hole-rich walls separating undoped domains. The *microscopic* phase separation has been found in much highly doped region from our measurement of nuclear quadrupole resonance.[9]

The rapid collapse of the antiferromagnetic ordering can be explained from the finite size scaling theory.[10] $T_N(h)$ curve in Fig. 2 can be fitted by the least-square analysis in the following expression

$$\frac{T_N(h)}{T_N(0)}=1-\left\{\frac{h}{h_c}\right\}^n$$

where $T_N(0)=326$ K, $h_c=0.0268$ and $n=2.27$. This power-law dependence may be also explained by the finite size scaling theory. We suppose that there occurs the *microscopic* phase separation into antiferromagnetic and non-antiferromagnetic regions due to the hole distribution. In this case, the finite domain means the one with the three-dimensional antiferromagnetic correlation (3dAFC). The reason why the domain size is finite comes from the fact that the antiferromagnetic correlation between the adjacent CuO_2 planes is considerably weaker than the one in the CuO_2 plane.[11] Hole doping would reduce the size of the 3dAFC domain because, above T_N, the spin-spin antiferromagnetic correlation length, ξ, rapidly decreases with increasing both x and δ.[2,11,12] As far as the decrease of T_N is concerned, x and 2δ can be treated equivalently. The fitting in Fig. 2 leads the maximum value of T_N to be about 326 K with $h \rightarrow 0$. We conclude, therefore, that holes play a key role in disordering the quasi two-dimensional antiferromagnetic state in CuO_2 plane. Further study is desired in order to explain how doped holes destroy the antiferromagnetic ordering.

References

1) D. C. Johnston: J. Magn. Magn. Mater. **100** (1991) 218.
2) B. Keimer, N. Belk, R. J. Birgeneau, A. Cassanho, C. Y. Chen, M. Greven, M. A. Kastner, A. Aharony, Y. Endoh, R. W. Erwin and G. Shirane: Phys. Rev. B **46** (1992) 14034.
3) K. Kurusu, H. Takami and K. Shintomi: Analyst **114** (1989) 1341.
4) H. Takagi, T. Ido, S. Ishibashi, M. Uota and S. Uchida: Phys. Rev. B **40** (1989) 2254.
5) P. Podhâjecky and F. P. Dousek: Physica C **173** (1991) 99.
6) J. H. Cho, F. C. Chou and D. C. Johnston: Phys. Rev. Lett. **70** (1993) 222.
7) J. Saylor and C. Hohenemser: Phys. Rev. Lett. **65** (1990) 1824.
8) S-W. Cheong, A. S. Cooper, L. W. Rupp, Jr. and B. Batlogg: Phys. Rev. B **44** (1991) 9739.
9) K. Yoshimura, T. Uemura, M. Kato, T. Shibata, K. Kosuge, T. Imai and H. Yasuoka: *The Physics and Chemistry of Oxide Superconductors*, ed. Y. Iye and H. Yasuoka (Springer-Verlag, Tokyo, 1992) p.405.
10) M. E. Fisher and M. N. Barber: Phys. Rev. Lett. **28** (1972) 1516.
11) Y. Endoh, K. Yamada, R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. R. Thurston, J. M. Tranquada, G. Shirane, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki and T. Murakami: Phys. Rev. B **37** (1988) 7743.
12) T. Imai, C. P. Slichter, K. Yoshimura, M. Kato and K. Kosuge: Phys. Rev. Lett. **71** (1993) 1254.