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# Effect of spin substitution on stripe order in $La_{1.875}Ba_{0.125}Cu_{1-y}M_yO_4$ ($M$=Zn or Ni)

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The destruction of stripe order by Zn ($S=0$) and the formation of a new phase by Ni ($S=1$) are demonstrated directly from the substitution dependence of the electronic coefficient of specific heat $\gamma$ in $La_{1.875}Ba_{0.125}Cu_{1-y}M_yO_4$ ($M$=Zn or Ni). In the Zn-substitution case, $\gamma$, which is strongly suppressed by stripe phase formation, increases to a value that corresponds to the state where there is no stripe order. In the Ni-substitution case, $\gamma$ saturates at nearly half the value of the Zn-substitution case. The difference can be explained by a difference in the spin interactions between the substituent atom and the nearest neighbor Cu atoms, indicating that spin interaction plays an important role in the formation of charge stripes.

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Many insulating cuprate oxides with strong two dimensionality exhibit high temperature superconductivity by the doping of holes. The transition temperature $T_c$'s have a single maximum at a certain hole concentration. However, in $La_{2-x}Ba_xCuO_4$ and rare earth substituted $La_{2-x}Sr_xCuO_4$, superconductivity is suppressed near hole concentrations of 1/8 and $T_c$ exhibits two maxima.[1,2] In the same concentration range, these compounds also exhibit a structural transition from a low temperature orthorhombic (LTO) phase to a low temperature tetragonal (LTT) phase.[3,4] Nuclear quadrupole resonance (NQR) and muon-spin-relaxation ($\mu$SR) experiments have revealed the existence of some magnetic ordering below the structural transition temperature.[5,6] The structural transition, the strong suppression of superconductivity, and magnetic ordering have been observed in both $La_{2-x}Ba_xCuO_4$ and $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ at $x\sim1/8$. Tranquada *et al.* detected several satellite peaks in elastic neutron diffraction for single-crystal $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ ($x\sim1/8$).[7,8] The position of these satellite peaks indicates that the periods of charge and spin modulation are equal to four and eight times the lattice constant, respectively. Stripe order was proposed in order to explain the state in which the densities of charge and spin are not uniform in real space. In this stripe phase, there are periodically arranged lines where holes are segregated, termed charge stripes, and the regions in between, where antiferromagnetic order is formed, are termed spin stripes. In $La_{2-x}Ba_xCuO_4$ ($x\sim1/8$), it is difficult to observe the satellite peaks, if they exist, because of difficulties in preparing a single crystal. However, it is widely accepted that a stripe phase will also exist in $La_{2-x}Ba_xCuO_4$ ($x\sim1/8$) because the compound exhibits the anomalies mentioned above.

Stripe order has also been observed in nickel oxides, and a related phenomenon—static charge stripes—has been observed in manganese oxides.[9,10] So, such a stripe structure may be a common phenomenon in transition-metal oxides. Whereas certain features of stripe phase, such as transition temperature and the structure of charge and spin orders, have been studied well,[7,8] it is yet to be clarified why stripe order forms. As stripe order is the state where spins and charges become ordered simultaneously, it is important to investigate how charge stripes vary when spin stripes are changed and vice versa. As an approach to this issue, we focus on two points in $La_{2-x}Ba_xCuO_4$; partial substitution of Zn or Ni atoms for Cu atoms, and measurement of the electronic specific heat coefficient. The spin moment of the Cu sites in Zn or Ni substitution is changed from $S=1/2$ to $S=0$ or $S=1$, respectively. Such spin substitutions will have a direct effect on spin stripes,[11] leading to a variation of the charge stripes. The electronic specific heat coefficient $\gamma$ is proportional to the electronic density of states and is sensitive to changes in electronic structure. In fact, a significant suppression of $\gamma$ has been observed in a narrow range of hole concentrations around $x=1/8$ in $La_{2-x}Ba_xCuO_4$ where the charge stripes are formed.[12] Therefore, the measurement of $\gamma$ will be suitable for investigating the variation of charge stripes due to changes of spin stripes.

In this paper, we report the experimental results of the change in $\gamma$ when Zn and Ni atoms are partially substituted into the Cu site in $La_{2-x}Ba_xCuO_4$ with $x=1/8$. The spin moment on the substituent Cu site is changed from $S=1/2$ to $S=0$ or $S=1$. The results reveal the destruction of stripe order by Zn ($S=0$) and the formation of a new phase by Ni ($S=1$). The different behaviors can be explained by differences in the spin interaction between the substituted atom and the nearest neighbor Cu atoms, indicating that spin interaction plays an important role in the formation of charge stripes.

Polycrystalline samples of $La_{1.875}Ba_{0.125}Cu_{1-y}M_yO_4$ ($M$=Zn,Ni) were prepared from $La_2O_3$, $BaCO_3$, CuO, ZnO, and NiO powders of 5N purity by solid state reaction. The primary materials, with the desired stoichiometry, were mixed well and ground in an agate mortar. The powder was heated in a furnace with an initial temperature increase of 200 °C/h, and reacted at 950 °C in air for 30 h. The material was quenched by dropping it into liquid nitrogen. The reacted material was then reground in an agate mortar. The ground material was pressed into cylindrical pellets, which were then reacted at 1050 °C in air for 10 h and quenched. Finally, the pellets were annealed at 500 °C in an $O_2$ atmosphere. Each sample was confirmed to be single phase by x-ray diffraction analysis. The specific heat of the samples was measured by the thermal relaxation method in a temperature region of 1.5 to 7 K. The typical weight of samples used in specific heat measurements was about 30 mg.

The temperature dependence of the specific heat of the $La_{1.875}Ba_{0.125}Cu_{1-y}M_yO_4$ ($M$=Zn or Ni) systems is shown

 

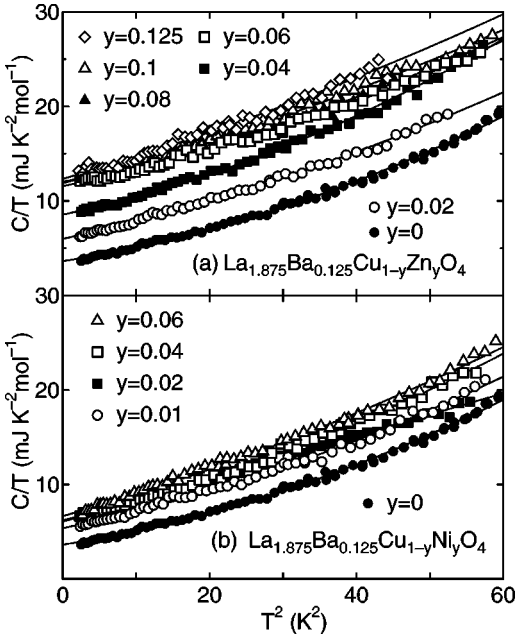


FIG. 1. Temperature dependence of the specific heat of $La_{1.875}Ba_{0.125}Cu_{1-y}M_yO_4$. (a) $M=$Zn (b) $M=$Ni. Horizontal axis is the square of temperature $T^2$, vertical axis is the specific heat divided by temperature $C/T$, solid lines represent $C=\gamma T+\beta T^3+\alpha T^5$.

in Fig. 1, where $C/T$ is plotted as a function of $T^2$. For all samples examined, $C/T$ increases linearly with increasing $T^2$ below $T^2=25$ K$^2$ ($T=5$ K), and exhibits an upward curvature with increasing temperature above $T=5$ K. The most striking feature of this relationship is that the value of $C/T$ shifts to larger values with increasing $y$. However, the rate of shift decreases at larger $y$. In the Zn substitution case, the rate becomes small above $y=0.06$, whereas in the Ni substitution case, the rate becomes small above $y=0.02$. The temperature dependence of specific heat at low temperatures is usually represented by the fitting function $C=\gamma T+\beta T^3$, where the first term is the contribution of electrons and the second term is that of phonons. The specific heat of phonons follows a $T^3$ law when the temperature is lower than one-fiftieth of the Debye temperature $\theta_D$, which is estimated by $\theta_D^3 \sim 12\pi^4 N k_B/(5\beta)$, where $N$ is the total number of all atoms. The $\theta_D$ of the present samples is estimated to be about 240 K. The $T^3$ law is an adequate approximation below 5 K, however, it does not hold above 5 K, as shown in Fig. 1. Above 5 K, a function $C=\gamma T+\beta T^3+\alpha T^5$ was found to fit the data well. The results are indicated by the solid lines in Fig. 1. A $T^5$ term is needed in the fitting function, representing the contribution from anharmonic lattice vibration or low lying optical phonons. The value of $\gamma$ is obtained from this fitting function. The slopes of $C/T$ with $T^2$ are nearly identical for all samples regardless of the nature of the substitution (Zn or Ni), indicating that the lattice contribution to $C$ remains almost unchanged.

Figure 2 shows values of $\gamma$ plotted as a function of $y$ for the Zn substitution case. The $\gamma$ value for the unsubstituted sample is 3.6 (mJ/mol K$^2$), which is in agreement with the value reported by Okajima *et al.*[12] From the figure it can be

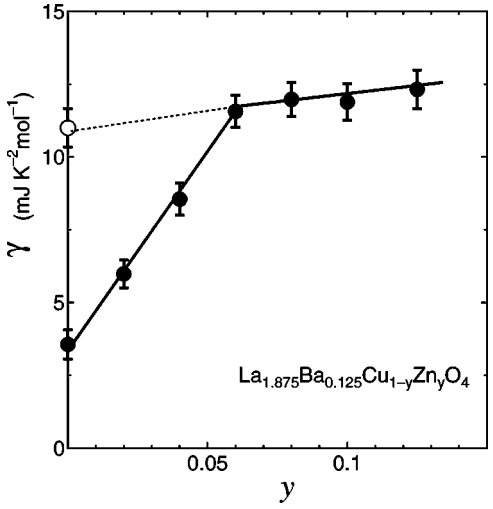


FIG. 2. Dependence of $\gamma$ on $y$ for $La_{1.875}Ba_{0.125}Cu_{1-y}Zn_yO_4$. Open circle is the value extrapolated from above $y=y_0^{Zn}$, solid lines are guides to the eye.

seen that $\gamma$ increases rapidly with increasing Zn content up to $y=0.06$. Above $y=0.06$, the rate of increase drops by a factor of 10. Thus, there is a characteristic concentration of Zn; $y_0^{Zn}=0.06$, which suggests that the electronic state in the region above $y_0^{Zn}$ is different from that at $y=0$ where stripe order is formed. By extrapolating the $y$ dependence of $\gamma$ above $y_0^{Zn}$ to $y=0$, we can estimate $\gamma_0$ which is expected when the state above $y_0^{Zn}$ is realized at $y=0$. The value of $\gamma_0$ obtained is 11 (mJ/mol K$^2$), which is about three times larger than that of the unsubstituted sample in which a stripe phase is formed.

The estimated value of $\gamma_0$ from Fig. 2 is shown in Fig. 3 together with the $\gamma$ dependence on $x$ of $La_{2-x}Ba_xCuO_4$ measured by Okajima *et al.*[12,13] Okajima *et al.* observed a large suppression of $\gamma$ near $x=0.125$ in $La_{2-x}Ba_xCuO_4$,[12,13] whereas Momono *et al.* investigated in detail $\gamma$ as a function of $x$ in $La_{2-x}Sr_xCuO_4$ for which stripe

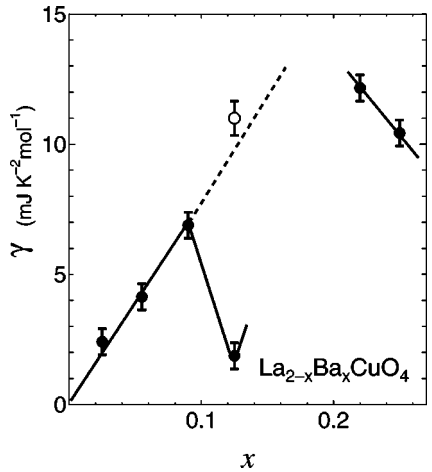


FIG. 3. Dependence of $\gamma$ on $x$ for $La_{1.875}Ba_{0.125}CuO_4$. Closed circles are values measured by Y. Okajima *et al.* (Ref. 12 and 13), open circle is $\gamma_0$, solid lines are guides to the eye.

order was not formed, and found that $\gamma$ increases monotonically with increasing $x$.[14] It is suggested that if the stripe phase is not formed at $x=0.125$ in $La_{2-x}Ba_xCuO_4$, then $\gamma$ would increase monotonically with increasing $x$ similar to the $La_{2-x}Sr_xCuO_4$ case, which is indicated by a broken line in Fig. 3. The value of $\gamma_0$ estimated from Fig. 2 coincides well with the broken line in Fig. 3, and hence we can conclude that stripe order is not formed in the region above $y_0^{Zn}$. Below $y=y_0^{Zn}$, stripe order may be destroyed gradually because $\gamma$ increases continuously with $y$.

The destruction process of the stripe phase by Zn substitution can be understood as follows: The stripe phase consists of charge and spin stripes. In the charge stripes, there is no spin order and holes exist, whereas in spin stripes, there is antiferromagnetic order and no holes. When a Zn atom is substituted into the spin stripe, spin interactions between the Zn atom and the nearest neighbor Cu atoms cease because the Zn atom has no spin. As a result, holes in neighboring charge stripes may transfer to the Cu sites around the Zn atom and, at the same time, the spins in the site area fluctuate. As the Zn content increases, holes may exist uniformly over the entire $CuO_2$ plane, leading to the full destruction of spin stripes. Therefore, the $\gamma$ value that is strongly suppressed by the formation of the charge stripe will return to its original value as a result of Zn substitution. The existence of holes over the entire $CuO_2$ plane does not result in metallic conduction, rather, the temperature dependence of the resistivity of $La_{1.875}Ba_{0.125}CuO_4$ reveals that the material after Zn substitution exhibits insulating behavior due to the localization of holes.[15] The value of $\gamma$ obtained in this study may not be significantly influenced by the localization effects.[16]

The effect of Zn doping has been extensively examined in $La_{2-x}Sr_xCuO_4$ system. The $La_{2-x}Sr_xCuO_4$ system shows inelastic incommensurate magnetic peaks, which are observed in neutron scattering experiments.[17] Around $x=1/8$, a small amount of Zn doping shifts the spectral weight of spin fluctuations from the inelastic to the quasi-elastic region.[18] This fact shows that static magnetic ordering appears in Zn-doped $La_{2-x}Sr_xCuO_4$ around $x=1/8$. It has been considered that dynamical stripe correlations exist in the $La_{2-x}Sr_xCuO_4$ system and they are pinned by a small amount of Zn doping. This idea was first proposed by Tranquada *et al.*, although they pinned the dynamical stripe correlations by the structural deformations in the low-temperature-tetragonal structure of $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$.[7] Many experimental evidences of the former pinning have been accumulated for the last five years.[18,19] It should be noted that, in all these works, Zn is doped to the samples without the static stripe order, and the Zn content is smaller than or equal to 0.02. In the present work, on the other hand, Zn is doped to the samples with the static stripe order, and the Zn content is up to 0.125, which is six times larger. Since the stripe order is already pinned by the lattice deformations in $La_{2-x}Ba_xCuO_4$ with $x=1/8$, the pinning effect by Zn doping is never observed. Alternatively, the destruction process by Zn is observed, as in the present work.

Figure 4 shows values of $\gamma$ plotted as a function of $y$ for the Ni substitution case. $\gamma$ increases linearly as Ni content $y$ increases for $y\leqslant 0.02$. Above $y=0.02$, $\gamma$ remains almost constant, although the data only extend to $y=0.06$. Thus, there is also a characteristic Ni content, $y_0^{Ni}=0.02$, demonstrating that different electronic states exist above and below $y_0^{Ni}$, similar to the Zn substitution case. The slope of $\gamma/y$ below $y=0.02$ is similar to that for Zn, however, $\gamma$ at $y_0^{Ni}$ is almost a half that at $y_0^{Zn}$. The smallness of this value indicates that the stripe phase is not fully destroyed by Ni substitution above $y=y_0^{Ni}$.

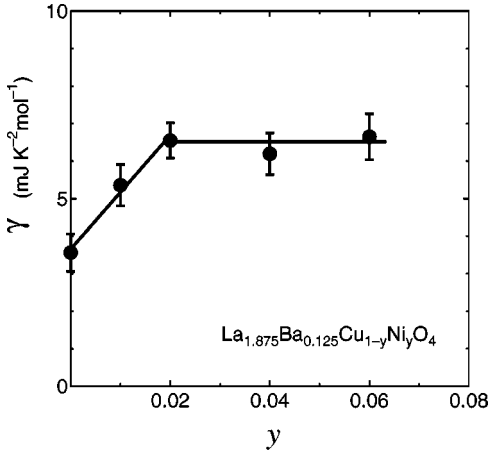


FIG. 4. Dependence of $\gamma$ on $y$ for $La_{1.875}Ba_{0.125}Cu_{1-y}Ni_yO_4$. Solid lines are guides to the eye.

It is noted that $\gamma$ increases with $y$ below $y=0.02$ in the Ni substitution case, in the same way as in the Zn substitution case. This indicates that there are several regions in which spins fluctuate and to which holes can transfer from the charge stripes, as mentioned in the Zn substitution case. The spin moment of a Ni atom is 1 ($S=1$), which means that spin interactions between the Ni atom and the nearest neighbor Cu atoms are effectively enhanced. When a single Ni atom is substituted into the $CuO_2$ plane, the stripe order is formed in such a way that the center of the spin stripe is fixed on the Ni site. The stripe order is not changed markedly and only an excess spin moment appears at the Ni site. When several Ni atoms are substituted, stripe orders form independently around each Ni site, resulting in the emergence of several sections with stripe order in the $CuO_2$ plane. The stripe order is not always connected smoothly at the boundary between the sections. Therefore, spins fluctuate in the boundary region and holes can exist, leading to an increase in $\gamma$.

Above $y=0.02$, on the other hand, $\gamma$ remains constant with increasing Ni content. This invariance indicates that the boundary region where holes can exist ceases to grow, that is, the section with stripe order does not divide any further. Excess Ni atoms are not always placed at the center of the spin stripe. In the Ni content region, the spin stripe may be swollen around the Ni atom and the next spin stripe may narrow in accommodation, resulting in the charge stripe being bent around the Ni atom in each section. A single charge stripe may be bent several times around Ni atoms. Thus, the charge stripe can be envisaged as a meandering river of charge, which characterizes the ''meandering'' stripe phase,

in contrast to a ''straight'' stripe phase. Recently, Kivelson *et al*. theoretically proposed that the stripe phase is an electronic quantum liquid-crystal phase in which transverse fluctuations of the charge stripe occur and the meandering rivers of charge move dynamically.[20] The meandering stripe phase mentioned here is not dynamic, however is very similar to the liquid-crystal phase.

The partial substitution of Zn or Ni atoms for Cu atoms changes the spin moment on the substituted Cu sites from $S=1/2$ to $S=0$ or $S=1$, respectively. The spin interactions between the substituted atom and the nearest neighbor Cu atoms differs for between Zn and Ni atoms. Such differences are brought about by the marked difference in the dependence of $\gamma$ on the substituent, as mentioned above. Charge stripes are completely destroyed by Zn substitution, whereas they become ''meandering'' rivers of charge with Ni substitution. This demonstrates experimentally and directly that spin interactions not only create antiferromagnetic order in spin stripes, but also play an important role in the formation of charge stripes. This will also be true for other systems with stripe order, such as nickel oxides. In order to clarify the relationship between spin interaction and the formation of stripe order, the investigation of spin-substitution effects in nickel oxides is meaningful.

In summary, it was found that substitutions that induce changes in spin from $S=1/2$ to either $S=0$ or $S=1$ have different effects on the stripe phase of $La_{1.875}Ba_{0.125}CuO_4$. Charge stripes are completely destroyed by substitutions resulting in a change from $S=1/2$ to $S=0$ (Zn substitution), whereas the substitution producing $S=1$ (Ni substitution) changes charge stripes to a meandering phase. Based on these facts, we claim that spin interactions not only create antiferromagnetic order in spin stripes, but also play an important role in the formation of charge stripes.

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