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Impurity effect on the diagonal incommensurate spin correlations in $La_{2-x}Sr_xCuO_4$

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Neutron-scattering experiments were performed on Zn and Ni doped $La_{1.95}Sr_{0.05}CuO_4$ to study the impurity effect on the diagonal incommensurate spin correlations. Zn doping reduces the incommensurability and enhances the correlation length just slightly. On the other hand, Ni doping quickly destroys the incommensurability and restores Néel ordering, indicating a strong effect on hole localization. This suggests that Ni is doped as Ni^{3+} or that doped Ni^{2+} and a hole form a strongly bound state with the Zhang-Rice character. On the basis of the experimental results, the validity of the stripe and spiral models is discussed.

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One of the interesting aspects of the study of high-T_c superconductivity is the problem of clarifying the relation between transport properties and magnetism at the boundary of the metal-to-insulator transition. Extensive neutron-scattering studies on lightly doped $La_{2-x}Sr_xCuO_4$ have revealed that a diagonal spin modulation, which is a one-dimensional modulation rotated away by 45 deg from that in the superconducting phase, occurs universally throughout the spin-glass phase in $La_{2-x}Sr_xCuO_4$ $(0<x\leqslant 0.055)$.[1–5] It is now established that the static magnetic spin modulation changes from being diagonal to parallel at $x=0.055\pm0.005$, coincident with the insulator-to-superconductor transition.

One possibility to explain the diagonal incommensurate spin correlations is the stripe model.[6–11] The stripe phase has been experimentally observed in $La_{2-x-y}Nd_ySr_xCuO_4$,[12] $La_{2-x}Ba_xCuO_4$ $(x\sim\frac{1}{8})$,[13] and $La_{2-x}Sr_xNiO_4$.[14,15] The parallel stripe phase in $La_{2-x-y}Nd_ySr_xCuO_4$ and $La_{2-x}Ba_xCuO_4$ is stabilized by the structural distortion, namely, the low temperature tetragonal (LTT) structure, which is strongly coupled to the charge ordering. It has been suggested that the diagonal stripe in $La_{2-x}Sr_xNiO_4$ originates from the orbital ordering.[16] In lightly doped $La_{2-x}Sr_xCuO_4$, which has no LTT phase and no orbital degree of freedom, no evidence has been found that the stripe phase is realized. Most importantly, structural distortion, originating from the charge ordering, has not been observed, even though this can be due to disorder in periodicity and direction of the stripe.

Recently, Hasselman *et al.* reported that the diagonal incommensurate spin correlations in lightly doped $La_{2-x}Sr_xCuO_4$ are explained using the spiral model, originating from magnetic frustration caused by the localized hole spins.[17,18] In this model the incommensurate magnetic peaks are purely magnetic in origin and have nothing to do with charge ordering, in contrast to the stripe model. They also suggested neutron-scattering experiments to determine if the incommensurate magnetic peaks originate from the stripe or the spiral phase. According to them, the codoped sample $La_{2-x}Sr_xCu_{1-z}Zn_zO_4$ gives important information on this. Since Zn impurity is expected to reduce frustration caused by the hole spin, the magnetic correlation length should increase and the incommensurability should decrease by a factor of $1-\gamma z$ with $\gamma\sim 2$.

In order to clarify the origin of the diagonal incommensurate magnetic peaks, we performed neutron-scattering experiments on the Zn doped $La_{2-x}Sr_xCuO_4$. Ni doped $La_{2-x}Sr_xCuO_4$ also was measured to study the impurity dependence. Although we cannot distinguish whether the stripe or the spiral model is more appropriate from the results regarding Zn doping dependence, the results regarding Ni doping dependence tend to support the existence of the diagonal stripe state in lightly doped $La_{2-x}Sr_xCuO_4$. Furthermore, we find a drastic change in magnetism with a small amount of Ni doping, namely, reduction of incommensurability and stabilization of the Néel ordering. This suggests that Ni is doped as Ni^{3+} or that doped Ni^{2+} and a hole form a strongly bound state with the Zhang-Rice character, as previously reported in the case of doped La_2NiO_4.[19,20]

The single crystals of $La_{1.95}Sr_{0.05}Cu_{1-z}Zn_zO_4$ (z=0.03 and 0.05) and $La_{1.95}Sr_{0.05}Cu_{1-z}Ni_zO_4$ (z=0.01, 0.03, and 0.05) are grown by the traveling solvent floating zone method. Typical dimensions of the rod shaped crystals are $\sim 6\Phi\times 25$ mm^3. Structures of all the crystals except $La_{1.95}Sr_{0.05}Cu_{0.95}Ni_{0.05}O_4$ are almost all single domain structures. The $La_{1.95}Sr_{0.05}Cu_{0.95}Ni_{0.05}O_4$ crystal has two twin domain structures, which are estimated to be equally distributed.

The neutron elastic scattering experiments are carried out on the cold neutron three-axis spectrometer LTAS and the thermal neutron three-axis spectrometer TAS2 installed in the guide hall of JRR-3 at Japan Atomic Energy Agency. The fixed final neutron energies are 5 and 14.7 meV on LTAS and TAS2, respectively. The typical horizontal collimator sequences are guide-80′-S-80′-80′ on LTAS and guide-80′-S-40′-80′ on TAS2, respectively. The single crystal is oriented in the $(HK0)$ scattering plane in the orthorhombic ($Bmab$) phase notation, which corresponds to the CuO_2 plane, and is mounted in a closed cycle He gas refrigerator.

Figure 1 shows the typical magnetic diffuse scattering spectra in Zn and Ni doped $La_{1.95}Sr_{0.05}CuO_4$. As reported in $La_{2-x}Sr_xCuO_4$ ($x<0.055$), the diagonal incommensurate peaks are observed at $(1,\pm\epsilon,0)$ in $La_{1.95}Sr_{0.05}Cu_{1-z}Zn_zO_4$ (z=0.03, and 0.05) and $La_{1.95}Sr_{0.05}Cu_{1-z}Ni_zO_4$ (z=0.01). On the other hand, an almost commensurate peak is observed in $La_{1.95}Sr_{0.05}Cu_{0.97}Ni_{0.03}O_4$. The solid lines in Fig. 1 are the results of fits of a convolution of the resolution function with

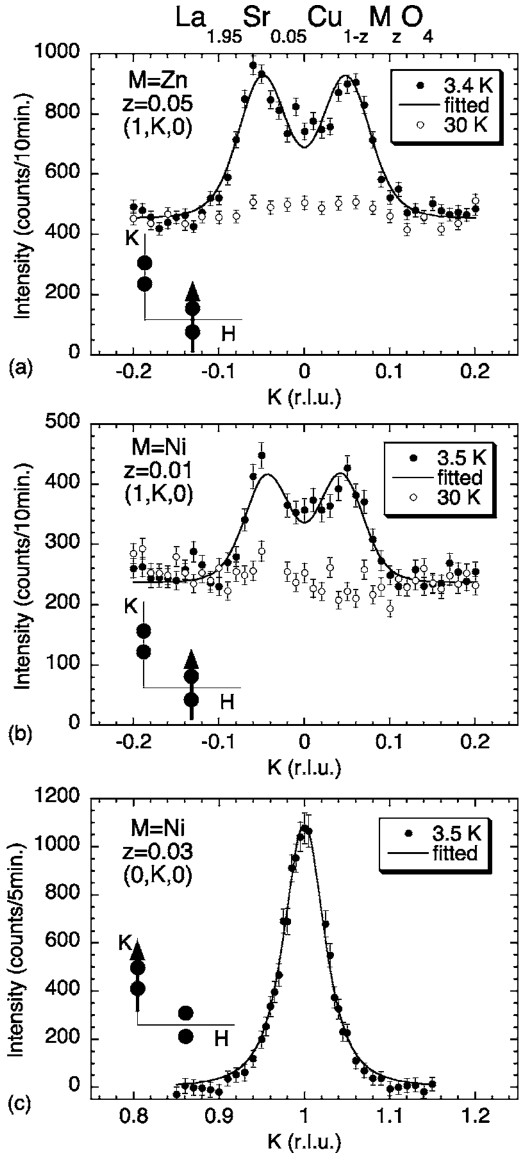

FIG. 1. Elastic scans along $(1,K,0)$ in $La_{1.95}Sr_{0.05}Cu_{0.95}Zn_{0.05}O_4$ (a) and $La_{1.95}Sr_{0.05}Cu_{0.99}Ni_{0.01}O_4$ (b) and along $(0,K,0)$ in $La_{1.95}Sr_{0.05}Cu_{0.97}Ni_{0.03}O_4$ (c). The solid lines are the results of fits of a convolution of the resolution function with 2D squared Lorentzians with the parameters shown in Table I. Background intensities measured at a high temperature have been subtracted in (c). Insets show the scan trajectories.

two-dimensional (2D) squared Lorentzians with the parameters shown in Table I.

The temperature dependences of the peak intensity in Zn doped samples and lightly Ni doped sample (z=0.01) are shown in Fig. 2(a). These three samples show almost the same temperature dependence as that in $La_{1.95}Sr_{0.05}CuO_4$. $La_{1.95}Sr_{0.05}Cu_{0.95}Ni_{0.05}O_4$ does not show magnetic diffuse peaks but rather sharp magnetic Bragg peaks, originating from a long-range magnetic order as in La_2CuO_4. $La_{1.95}Sr_{0.05}Cu_{0.97}Ni_{0.03}O_4$ shows both sharp magnetic Bragg peaks and diffuse magnetic peaks. The temperature dependences of the peak intensity in Ni doped samples (z=0.03 and 0.05) are shown in Figs. 2(b) and 2(c), respectively.

TABLE I. The inverse peak widths along a (ξ_a) and b (ξ_b) and incommensurabilities (ϵ) in $La_{1.95}Sr_{0.05}CuO_4$ and $La_{1.95}Sr_{0.05}Cu_{1-z}M_zO_4$ (M=Zn and Ni). The parameters in $La_{1.95}Sr_{0.05}CuO_4$ are obtained from a fit using the data in Ref. 2. Two sets of parameters from two different fits are obtained in $La_{1.95}Sr_{0.05}Cu_{0.97}Ni_{0.03}O_4$ as explained in the text. ϵ is shown in reciprocal-lattice units (r.l.u.).

	z	ξ_a (Å)	ξ_b (Å)	ϵ (r.l.u.)
	0	15.6(9)	22(1)	0.0605(8)
Zn	0.03	19.1(8)	31(1)	0.0543(6)
	0.05	21(1)	24(1)	0.0489(7)
Ni	0.01	22(2)	22(2)	0.043(1)
	0.03	>500	34(2)	0.0134(6)
	0.03	>500	24.5(6)	0(fixed)

These results indicate that the Zn and Ni doping affect magnetic correlations quite differently.

We first describe the Zn doping dependence of the diagonal incommensurate magnetic correlations. As shown in Table I and Fig. 3, the incommensurability ϵ decreases systematically with Zn doping. The inverse peak width ξ_b, which corresponds to the effective magnetic correlation length along b, increases with 3% Zn doping but ξ_b in the z=0.05 sample becomes similar to that in $La_{1.95}Sr_{0.05}CuO_4$. This behavior probably originates from the combined effects of increase in correlation length and randomness due to the impurity doping. In the z=0.03 sample, the increase in correlation length is dominant. On the other hand, following impurity doping, randomness affects the peak width more dominantly. ξ_a, which corresponds to the effective magnetic correlation length along a, does not change much with Zn doping. The increase in ξ_b and the decrease in ϵ are quite consistent with the prediction based on the spiral model. The Zn concentration dependence of ϵ indicates that $\gamma\sim 3$, which is roughly consistent with the prediction.[17,18] However, the stripe model also can explain this behavior if one assumes that the holes around the Zn sites are slightly localized (~0.15 hole/Zn) so that the effective hole density is reduced. This is consistent with the quantitative transport properties that the resistivity increases and the Hall coefficient decreases with Zn doping in $La_{1.85}Sr_{0.15}CuO_4$.[21] Therefore, it is difficult to distinguish between the two models from the results of the Zn doping effect alone.

As shown in Figs. 1(b) and 1(c), Ni doping affects the magnetic properties greatly. In the z=0.01 sample the values of ξ_a, ξ_b, and ϵ are similar to those in $La_{1.95}Sr_{0.05}Cu_{0.95}Zn_{0.05}O_4$, indicating that the impurity effect is larger in the Ni doped system by a factor of ~5. In the z=0.03 sample, resolution-limited sharp magnetic Bragg peaks develop gradually below ~120 K. It is found that the magnetic structure is the same as in pure La_2CuO_4. The ordered moment has been calculated to be $0.08(5)\mu_B$ at 20 K.[22] At ~30 K a broad peak develops around (1,0,0) and (0,1,0) and at the same time the sharp magnetic Bragg intensity decreases slightly.[23] The temperature dependence of the sharp magnetic Bragg peak intensity at (1,0,0) and the broad magnetic peak intensity at (0,1,0) is shown in Fig. 2(b).

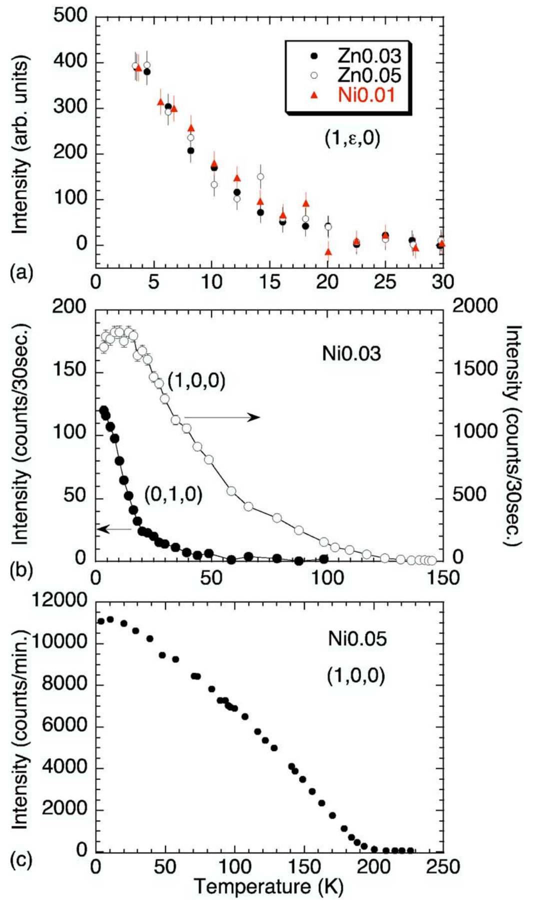

FIG. 2. (Color online) Temperature dependence of the magnetic signals. (a) The magnetic intensity at the diagonal incommensurate position $(1,\epsilon,0)$ in $La_{1.95}Sr_{0.05}Cu_{1-z}Zn_zO_4$ (z=0.03, and 0.05) and $La_{1.95}Sr_{0.05}Cu_{0.99}Ni_{0.01}O_4$. Background intensities measured at a high temperature have been subtracted. The intensities are normalized to that at the lowest temperature. (b) The (100) magnetic Bragg intensity and the magnetic diffuse scattering at (0,1,0) in $La_{1.95}Sr_{0.05}Cu_{0.97}Ni_{0.03}O_4$. Background intensities measured at a high temperature have been subtracted. The diffuse component at (1,0,0) is subtracted so that the (100) intensity originates entirely from a sharp magnetic Bragg peak. (c) The (100) magnetic Bragg intensity in $La_{1.95}Sr_{0.05}Cu_{0.95}Ni_{0.05}O_4$.

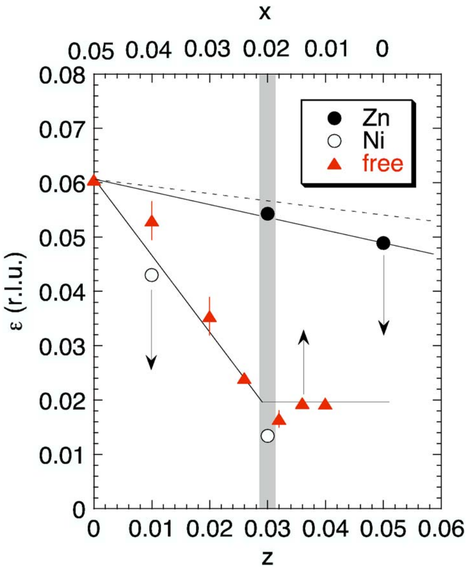

FIG. 3. (Color online) Impurity concentration (z) dependence of the incommensurability (ϵ) in $La_{1.95}Sr_{0.05}Cu_{1-z}Zn_zO_4$ (z=0.03 and 0.05) and $La_{1.95}Sr_{0.05}Cu_{1-z}Ni_zO_4$ (z=0.01 and 0.03). Hole concentration (x) dependence of ϵ in impurity-free $La_{2-x}Sr_xCuO_4$ (Ref. 5) is also shown. The solid lines are visual guides. The broken line corresponds to z dependence of ϵ expected in the spiral model (γ=2). The thick shaded bar represents the boundary between the long-range antiferromagnetic and spin-glass phases in $La_{2-x}Sr_xCuO_4$. As shown in Table I, it is possible that ϵ is almost zero in $La_{1.95}Sr_{0.05}Cu_{0.97}Ni_{0.03}O_4$.

These results remind us of the reentrant spin-glass behavior observed in lightly doped $La_{2-x}Sr_xCuO_4$ ($0<x<0.02$), in which an electronic phase separation is suggested below the glass temperature.[5] Therefore, it is expected that the hole concentration in the z=0.03 sample is below 0.02 although the transition is smeared and the peak width is very broad. Two methods of fitting were performed. One is fitting with a commensurate peak. The other is fitting with incommensurate peaks at $(0,1\pm\epsilon,0)$. The two fittings reproduce the observed data almost equally well. The parameters are shown in Table I. ϵ is fitted to be 0.0134, which is smaller than 0.02 observed in $La_{2-x}Sr_xCuO_4$ ($0<x<0.02$).[5] ξ_b is much smaller than ~200 Å observed in $La_{2-x}Sr_xCuO_4$ ($0<x<0.02$) but ξ_a is larger than 500 Å as in $La_{2-x}Sr_xCuO_4$ ($0<x<0.02$).[5] In the z=0.05 sample an antiferromagnetic three-dimensional order, which is the same as in pure La_2CuO_4, develops below ~200 K as shown in Fig. 2(c). The ordered moment has been calculated to be $0.56(5)\mu_B$ at 7 K,[22] which is almost the same as that in pure La_2CuO_4. There is no sign of diagonal incommensurate magnetic peaks. This suggests that the hole concentration is close to zero.

Figure 3 shows the impurity concentration dependence of ϵ in both Zn and Ni doped $La_{1.95}Sr_{0.05}CuO_4$. ϵ decreases with Ni doping much faster than with Zn doping. If each Ni localizes one hole, the effective hole concentration x has the relation $x=0.05-z$. As shown in Fig. 3, x dependence of ϵ in Ni doped $La_{1.95}Sr_{0.05}CuO_4$ is almost the same as in impurity-free $La_{2-x}Sr_xCuO_4$.[5] One possible reason for this behavior is that Ni is introduced as Ni^{3+}, which consumes one hole per Ni ion. It was previously reported that Ni^{3+} is stable in the superconducting $La_{2-x}Sr_xCuO_4$.[24,25] This probably applies also in a lightly doped region. Another possibility is that Ni ions are substituted as Ni^{2+} and localize the doped holes (~1 hole/Ni^{2+}) much more strongly than Zn^{2+} ions do. In this case, Ni^{2+} moment and surrounding hole spins couple antiferromagnetically, as in the Zhang-Rice singlet,[26] as has already been reported in hole-doped La_2NiO_4.[19,20] In either case, however, the effective spin value S_{eff} is $\frac{1}{2}$ and the effective valence is trivalent. The drastic change in magnetism such that the Néel order is quickly restored with Ni doping is consistent with the above mechanisms. Stabilization of Néel order is also reported in the Ni doped $La_{1.99}Sr_{0.01}CuO_4$.[27]

The Ni concentration dependence of ϵ indicates that γ ~20, which is larger than that in the Zn doped system by a factor of 7. Assuming the spiral model, Ni substitution is also expected to reduce the frustration since Ni strongly consumes holes. The stripe model also explains the Ni doping dependence of ϵ since this model predicts that the effective hole concentration will be quickly reduced with Ni doping. However, it is to be noted that the magnetic state is very disordered in the $z=0.03$ sample, since the diagonal incommensurate magnetic peaks along the a axis are much broader than those in $La_{2-x}Sr_xCuO_4$. It turned out that this gives useful information as to whether the stripe or the spiral models is more appropriate. We will first consider this problem in view of magnetic characteristics, which are relevant to the spiral model. As mentioned above, a Ni impurity carries $S_{\rm eff}=\frac{1}{2}$. Therefore, the Ni impurity in the magnetic background with Cu^{2+}, carrying $S=\frac{1}{2}$, should not disturb the magnetic correlations considerably, although the exchange interaction between Ni and Cu moments is expected to be smaller than that between Cu moments. In addition, as we learn from the results of the Zn doped sample, the randomness caused by 3% impurity does not impart much disorder to the system. These results suggest that the broadening in peak width is not caused by the magnetic disorder. On the other hand, from the point of view of the charge distribution, which is relevant to the stripe model, the random and static distribution of effectively trivalent impurities in the Cu^{2+} background should greatly disturb the system. This is considered to be the crucial difference between the Zn and Ni doping. This may suggest that the "charge relevant" stripe model better describes the diagonal incommensurate magnetic peaks in $La_{2-x}Sr_xCuO_4$ than the "charge irrelevant" spiral model. However, a theoretical study based on the spiral model, in which the localization of holes around Ni is taken into consideration, is strongly required in order to finalize the answer.

It is interesting to compare the results in Ni doped $La_{2-x}Sr_xCuO_4$ with those in Li doped La_2CuO_4, in which Li^+ is substituted for Cu^{2+} so that holes are doped in the CuO_2 plane. Bao *et al.* reported that $La_2Cu_{1-z}Li_zO_4$ ($z=0.06$ and 0.1) shows commensurate spin correlations.[28,29] By analogy with our results, this is probably because the random Li^+ distribution prevents the stripe from forming so that only short-ranged antiferromagnetic correlations are observed.

In conclusion, from the Ni impurity effect on the diagonal incommensurate spin correlations in lightly doped $La_{2-x}Sr_xCuO_4$, we found the interesting behavior that doped Ni strongly localizes the doped holes, which gives rise to a drastic change in magnetic properties with only a small amount of Ni impurity. The result also gives us valuable information indicating that the stripe model may be more appropriate than the spiral model.

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