Electron correlation effect on the semiconducting $La_{2-x}Sr_xCu_{1-z}M_zO_4$ (M = Zn and Ni): Zn- and Ni-induced Néel ordering

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Electron correlation effect on the semiconducting $La_{2-x}Sr_xCu_{1-z}M_zO_4$ (M = Zn and Ni): Zn- and Ni-induced Néel ordering

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Abstract
The non-magnetic impurity Zn ($S = 0$) and the magnetic impurity Ni ($S = 1$) induce Néel ordering of semiconducting $La_{2-x}Sr_xCuO_4$. A mechanism for the Ni-induced Néel ordering and the difference from the Zn-induced T_N in $La_{2-x}Sr_xCuO_4$ are explained by a frustration model with quenched holes. The interplay between the doped carriers and the impurities is a manifestation of an electron correlation effect on the semiconducting $La_{2-x}Sr_xCuO_4$.

1. Introduction

The Mott insulator La_2CuO_4 is a quasi-two-dimensional $S = 1/2$ square lattice Heisenberg antiferromagnet with a Néel temperature $T_N = 312$ K. The hole doping through Sr substitution for the La site suppresses the Néel ordering of $La_{2-x}Sr_xCuO_4$ with $x > 0.02$. The compounds of $La_{2-x}Sr_xCuO_4$ with $0.02 < x < 0.06$ and $x > 0.06$ are semiconductors and high-T_c superconductors, respectively.

Although the impurity substitution effects in the superconducting regime have been intensively studied, there are only a few reports on the Ni- and Zn-substitution effects in the semiconducting regime. The recent discovery of non-magnetic impurity Zn-induced Néel ordering in the semiconducting regime of $La_{2-x}Sr_xCuO_4$ has attracted much attention [1]. In contrast to the Zn-substitution effect on pure La_2CuO_4 [2], the non-magnetic impurity Zn substitution recovers the Néel ordering of $La_{2-x}Sr_xCuO_4$. Magnetic impurity Ni ($S = 1$)

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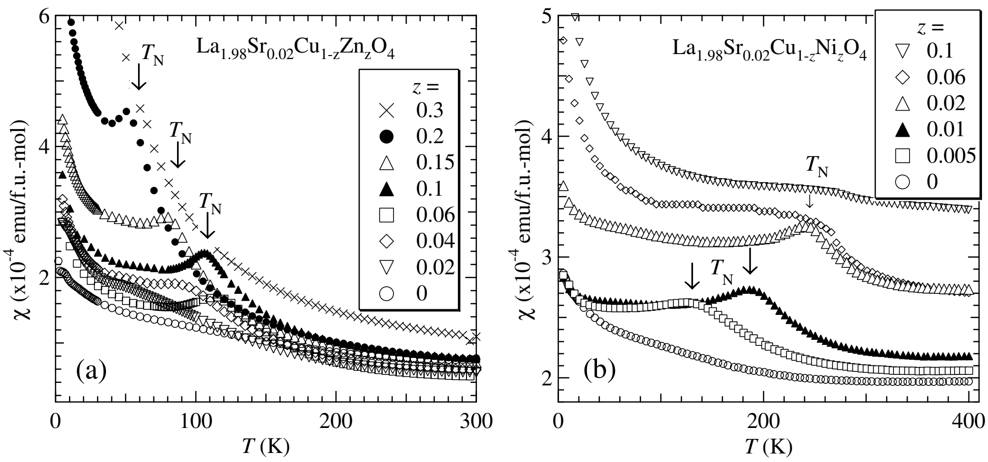

Figure 1. Impurity-induced antiferromagnetic ordering observed in the uniform magnetic susceptibility of $La_{1.98}Sr_{0.02}Cu_{1-z}M_zO_4$ with M = Zn (a) and Ni (b) at 1 T measured by a SQUID magnetometer. The arrows indicate T_N's.

substitution stabilizes the antiferromagnetic ordering more than the impurity Zn ($S = 0$) [3–5]. Ni-induced Néel ordering was also observed in the underdoped superconducting regime as well as in the semiconducting regime. The Ni-induced T_N was higher than the Zn-induced one. Such an impurity-induced antiferromagnetic ordering is widely known for quantum spin-gapped systems [6–8] but not for electron-correlated systems.

In this paper we present the Ni- and Zn-induced Néel ordering of semiconducting $La_{1.98}Sr_{0.02}Cu_{1-z}M_zO_4$ (M = Zn and Ni) from measurements of uniform magnetic susceptibility and show how their different effects on T_N can be explained by a frustration model with quenched holes [9].

2. Experiments

The $La_{1.98}Sr_{0.02}Cu_{1-z}M_zO_4$ powder samples with M = Zn and Ni were prepared by a conventional solid-state reaction method and by a post-annealing method in a reduced oxygen atmosphere [3]. The obtained samples were confirmed to be single phase by powder x-ray diffraction measurements. Each T_N was estimated from the temperature dependence of uniform magnetic susceptibility using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

3.1. Impurity Ni- and Zn-induced antiferromagnetic ordering

Figure 1 shows the impurity-substitution effects on magnetic susceptibility of $La_{1.98}Sr_{0.02}Cu_{1-z}M_zO_4$ with M = Zn (a) and Ni (b) at an external magnetic field of 1 T. No bulk Néel ordering is observed in $La_{1.98}Sr_{0.02}CuO_4$. The Ni- and Zn-impurity substitution immediately induce Néel ordering at T_N, where the magnetic susceptibility shows a peak. The antiferromagnetic long range ordering at the peak temperature was confirmed for the Ni-substituted $La_{2-x}Sr_xCuO_4$ by neutron scattering experiments [5].

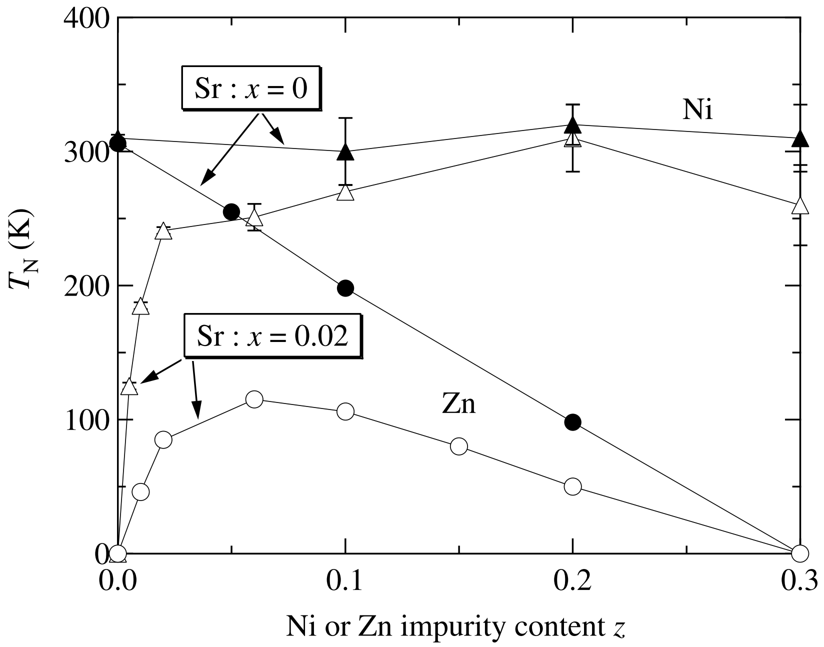

Figure 2. Experimental T_N against the impurity concentration z of Zn and Ni for pure $La_2Cu_{1-z}M_zO_4$ (reproduced from [3]) and the semiconducting $La_{1.98}Sr_{0.02}Cu_{1-z}M_zO_4$ (M = Ni and Zn).

Figure 2 shows the Ni- and Zn-substitution effects on T_N of $La_{2-x}Sr_xCu_{1-z}M_zO_4$ with $x = 0$ and 0.02 (M = Zn and Ni). For the pure La_2CuO_4, Zn ($S = 0$) suppresses the Néel ordering. The critical concentration z_c of the complete suppression was estimated to be about 0.3 [2]. On the other hand, Ni ($S = 1$) does not suppress the Néel ordering [3]. For the hole-doped $La_{1.98}Sr_{0.02}Cu_{1-z}M_zO_4$, both Zn and Ni substitution recover the Néel ordering. The recovered T_N levels off as Ni is heavily substituted, while the T_N decreases as Zn is heavily substituted.

3.2. A cancellation mechanism in a frustration model with quenched holes

Intuitive illustration. Figure 3 illustrates the Zn- and Ni-impurity effects on a square lattice Heisenberg antiferromagnet with quenched holes. The holes are doped into the oxygen sites. The doped holes are coupled with the surrounding Cu spins as Zhang–Rice singlets [10]. The bound Zhang–Rice singlets act as frustration bonds, destroy the Néel ordering and suppress T_N. Figure 3(a) illustrates a frustration bond and Zn-impurity effects. The Zn impurity acts as a spin vacancy $S = 0$ in the superexchange network. The Zhang–Rice singlet close to a spin vacancy is no longer the frustration bond. Zn and a doped hole cancel each other out. Figure 3(b) illustrates a frustration bond and Ni-impurity effects. In contrast to Zn, the Ni impurity carries a local moment $S = 1$ and does not act as a spin vacancy. The $S = 1$ of Ni cancels the frustration effect of the doped hole through a bound state of $3d^8\underline{L}$ ($S_{eff} = 1/2$), while keeping the superexchange pathways. The Ni impurity decreases the effective number of frustration bonds.

Model calculation. First, we briefly present the competing effect of frustration and dilution in the Zn-substituted hole-doped system in [9]. In a frustration model [9], a hole on a Cu–O–

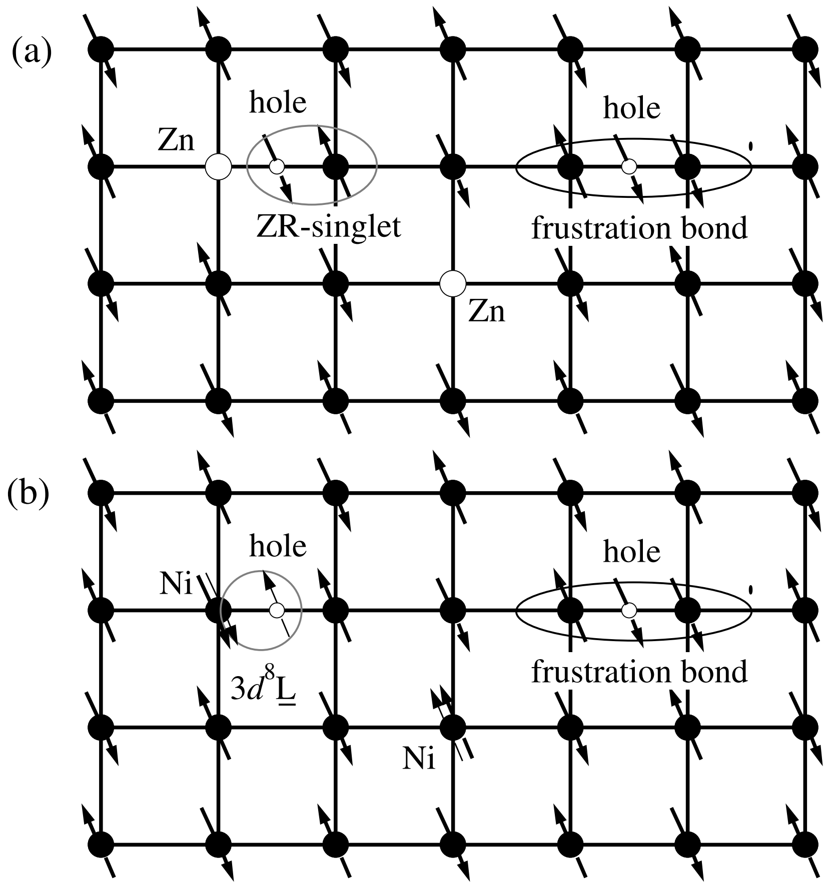

Figure 3. Illustrations of (a) Zn- and (b) Ni-impurity effects in a frustration model with quenched holes. The ZR (Zhang–Rice) singlets in the antiferromagnetic network act as frustration bonds. The ZR singlets close to Zn and Ni ions, however, do not act as the frustration bonds. Both Zn and Ni impurities cancel out the frustration effects of the doped holes. The ZR singlet bound state with a Ni $S = 1$ has an effective moment $S_{\mathrm{eff}} = 1/2$, similar to the underscreening Kondo effect.

Cu bond forms a frustrating spin bond, which acts as a magnetic dipole. In the Zn-substituted system, when a Cu ion is replaced from at least one end of the frustrating bond, this bond does not act as the magnetic dipole. The probability of finding a bond without spin vacancies on both ends is $(1 - z)^2$, and then the effective concentration of the magnetic dipole bonds is

$$y = x(1 - z)^2. \quad (1)$$

Spin vacancies destroy the antiferromagnetic network. When the doped holes are located away from the Zn, the probability of finding the spin vacancies is z. When one Cu ion at an end of a hole-doped frustrating bond is replaced by Zn, then a 'singlet' coupling between the second Cu spin and the doped hole spin on the oxygen site will recover. This is a cancellation mechanism on the antiferromagnetic superexchange network. Then, the effective concentration of the spin vacancies is

$$v = z[1 + 2x(1 - z)]. \quad (2)$$

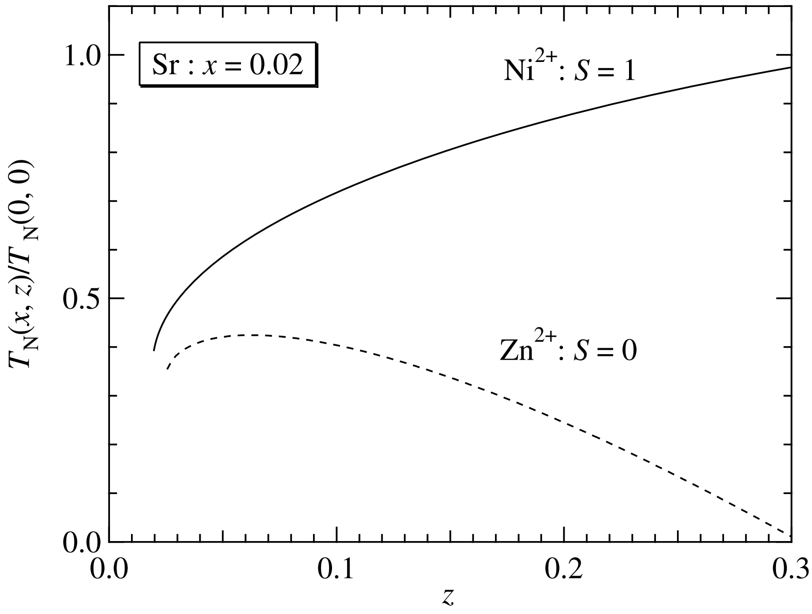

Figure 4. Theoretical T_N against the impurity concentration z of Ni ($S = 1$) and Zn ($S = 0$). The solid and dashed curves are the theoretical curves of equation (3) using equations (1), (2), (4) and (5).

Using the effective numbers of spin vacancies v and the effective concentration of magnetic dipole bonds y, the Néel temperature T_N is expressed by

$$\frac{T_N(x,z)}{T_N(0,0)} = (1-3.20v)\frac{ABy}{1-(1-3ABy)^{1/3}}, \tag{3}$$

where A and B are given in [9]. For the Zn substitution, we assume equations (1) and (2). Figure 4 shows the calculated $T_N(x = 0.02, z)/T_N(x = 0, z = 0)$ against the Zn ($S = 0$) impurity concentration z. The theoretical curve (dashed curve) well reproduces the experimental result for Zn impurities in figure 2. The Zn-induced effects were theoretically explained in [9].

Next we apply this model to the Ni-substituted holed-doped system. When one Cu ion at the end of a hole-doped frustrating bond is replaced by Ni, then a 'singlet' coupling between a Ni spin ($S = 1$) and a doped hole (spin $S = 1/2$) on the oxygen site will recover in the state of $3d^8\underline{L}$. The effective concentration of the magnetic dipole bonds is

$$y = x(1-z)(1-3z). \tag{4}$$

The impurity Ni does not destroy the antiferromagnetic network of the pure La_2CuO_4. This is because the Ni carries a local spin $S = 1$, and then it does not act as the spin vacancy. Then, the effective number of spin vacancies is

$$v = 0. \tag{5}$$

Using equation (3) with equations (4) and (5), we calculated $T_N(x = 0.02, z)/T_N(x = 0, z = 0)$ against the Ni ($S = 1$) impurity concentration z. The theoretical curve (solid curve) in figure 4 well reproduces the experimental result on Ni impurity in figure 2.

We neglect the itinerancy of the doped holes, so that the present model could not be applied to the superconducting regime of $La_{2-x}Sr_xCuO_4$ with $x > 0.06$ [3]. The t–J model is a low energy effective Hamiltonian for describing the interplay between the itinerant holes and the Cu spins. The theoretical development is desired to include the impurity-induced antiferromagnetic ordering in the superconducting regime.

4. Conclusion

A frustration model with quenched holes and impurities was shown to be applicable to Ni-induced Néel ordering in the semiconducting regime of $La_{2-x}Sr_xCuO_4$ and the difference between Ni- and Zn-impurity effects. The Ni impurity carries a local moment $S = 1$ and cancels the destructive effect of a doped hole through a bound state of $3d^8\underline{L}$, whereas the spin vacancy Zn competes with a doped hole. The impurity-induced Néel ordering in the semiconducting regime is a manifestation of an electron correlation effect.

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