Switching of the gapped singlet spin-liquid state to an antiferromagnetically ordered state in $Sr(Cu_{1-x}Zn_x)_2O_3$

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(Received 12 August 1996; revised manuscript received 14 January 1997)

Magnetic susceptibility and specific heat were measured for a Zn-substituted spin-1/2 Heisenberg two-leg ladder compound $Sr(Cu_{1-x}Zn_x)_2O_3$ ($x \leqslant 0.08$) to investigate nonmagnetic impurity effects on the quantum spin system with a large spin gap of about ~400 K. A clear anomaly attributed to the onset of an antiferromagnetic ordering was observed both in the magnetic susceptibility and the specific heat at low temperature even at only 1% of Zn. The Néel temperature showed a systematic Zn concentration dependence with a broad maximum at around 4% substitution ($T_{\mathrm{Nmax}} \sim 8$ K). A finite amount of a T-linear term with a coefficient of $\gamma \sim 3.5$ mJ/K^2 was observed in the specific heat above T_{N} for $x=0.02$ and 0.04, suggesting that the spin excitation in the substituted compound becomes gapless. [S0163-1829(97)50414-0]

It is well known that the spin excitation spectrum of a one-dimensional (1D) quantum antiferromagnet reflects its structural feature and the spin degree of freedom. A uniform Heisenberg half-integer spin chain has a gapless spin excitation spectrum, while alternation in the intrachain interaction leads to the opening of a spin gap[1] as typically seen in a spin-Peierls material $CuGeO_3$.[2] On the other hand, a uniform integer-spin chain has a ''Haldane gap''[3] as experimentally confirmed for $Ni(C_2H_8N_2)_2NO_2(ClO_4)$ (NENP)[4] typically. Recent theoretical[5] and experimental works have added another type of gapped quasi-1D antiferromagnets, that is spin-1/2 Heisenberg two-leg ladders found in $SrCu_2O_3$ (Refs. 6–9) and $(VO)_2P_2O_7$.[10] In $SrCu_2O_3$, the ladders made of antiferromagnetic (AF) Cu-O-Cu linear bonds are connected with each other spatially so that they form 2D Cu_2O_3 sheets,[6] but the ladders are separated from each other magnetically because of the interladder 90° Cu-O-Cu bond causing spin frustration at the interface. The existence of a wide spin gap of 420 K was found through measurements of magnetic susceptibility,[7] $1/T_1$ of Cu NMR,[8] and inelastic neutron scattering.[9] Contrarily, $Sr_2Cu_3O_5$ comprising three-leg ladders was found to be gapless[7] and a magnetic long-range ordering was found to set in at 52 K by a muon spin resonance (μSR) study.[11] These experimental results are consistent with theoretical results of the presence of a $J/2$-wide gap in a two-leg ladder (J:intraladder exchange interaction)[5,12] and the absence of spin gap in a three-leg ladder.[12] To be noted here is that some high-T_c cuprates in their underdoped region like $YBa_2Cu_3O_{7-\delta}$ with a T_c of 60 K have also been reported to have a ''spin gap,''[13] and this has further promoted investigations of spin and charge dynamics of low dimensional quantum antiferromagnets with spin gaps.

Nonmagnetic impurities introduced into quantum antiferromagnets have been expected to affect the magnetic properties in various fashions. For example, Cd ions cut the 1D spin-5/2 chains in $(CH_3)_4NMnCl_3$ (TMMC) into segments, every segment with an odd number of Mn ions having a localized spin 5/2.[14] Of particular interest is the coexistence of lattice dimerization and long-range AF ordering in $Cu_{1-x}Zn_xGeO_3$.[15,16] The coexistence of the two seemingly exclusive phenomena was observed also in $CuGe_{0.993}Si_{0.007}O_3$,[17,18] in which the Cu sublattice was kept clean.

However, there have been no reports on Cu-site impurity effects for ladder systems with spin gaps. An even-leg ladder is believed to have a short-range resonating valence bond (RVB) ground state[19] with a spin correlation length of only a few lattice spacings.[12] If so, an impurity ion would create a free spin 1/2 localized nearby, without affecting the gapped nature of the host, while an impurity-doped odd-leg ladder would provide the free spin with a counterspin to form a new singlet pair because of its longer spin correlation length. We have studied how $SrCu_2O_3$ and $Sr_2Cu_3O_5$ are influenced by different kinds of impurity ions. We report here a surprising result: the singlet spin liquid state with a large spin gap in $SrCu_2O_3$ is switched to an antiferromagnetically ordered state even by 1% of Zn ($x=0.01$).

Samples were prepared from mixtures of $SrCuO_2$ (the ambient-pressure form), CuO, and ZnO using a conventional cubic anvil-type high-pressure apparatus. The mixtures were treated for 30 min at 4.5 GPa and 1373 K. Samples characterized by powder x-ray diffraction showed no trace of impurities except for a small amount of CuO. This could be eliminated by slightly decreasing CuO content of the starting mixtures (~5%). Most likely, a small amount of CuO tended to remain intact as a result of the insufficiency of the one-shot reaction under pressure. Zn content was also decreased accordingly. Systematic variation of lattice parameters as a function of Zn content was observed at least up to $x=0.085$ for $Sr(Cu_{1-x}Zn_x)_2O_3$, indicating the substitution of Zn^{2+} for Cu^{2+}. dc magnetization was measured with a superconducting quantum interference device magnetometer in an external magnetic field (H) of 100 Oe in two ways, one on heating after zero-field cooling (ZFC) and the other on

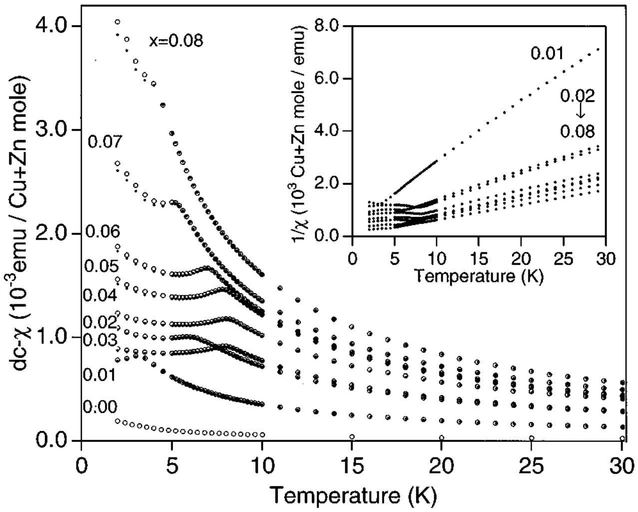

FIG. 1. Temperature dependence of the dc magnetic susceptibility of $Sr(Cu_{1-x}Zn_x)_2O_3$ measured in an external field of 100 Oe on heating (closed circles) and cooling (open circles). Inset shows temperature dependence of the inverse susceptibility for $x=0.01$ to 0.08 from the top to the bottom.

field cooling (FC). Specific heat measurements were performed using a small-sample relaxation calorimeter[20] on heating between 1.3 and 20 K.

Plotted in Fig. 1 are the magnetic susceptibility for $x = 0$ to 0.08 scaled by 1 mole of Cu+Zn. The increase of susceptibility at low temperatures is indicative of the existence of localized moments, the amount increasing with Zn content. As suggested from the linearity of the inverse-χ vs T plot shown in the inset of Fig. 1, the data between 15 and 30 K were reasonably fitted to the Curie-Weiss law with a temperature-independent component: $\chi(T)=C/(T-\theta)+\chi_0$. In all the samples examined, χ_0 was found to be as small as $\sim 10^{-5}$ emu/Cu+Zn mole. The Curie constant, C, thus estimated is plotted against x in Fig. 2. As mentioned

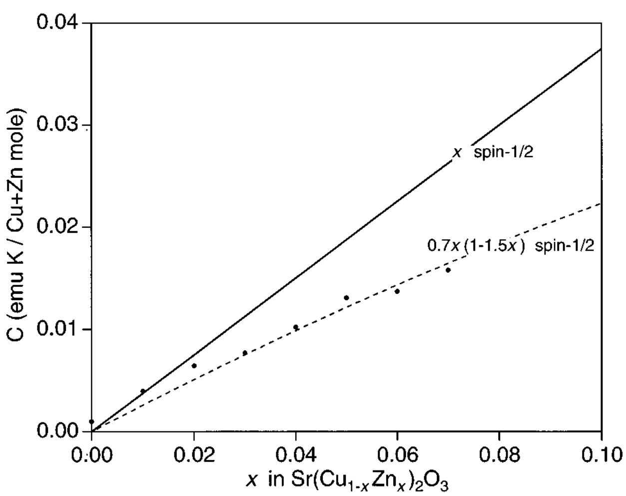

FIG. 2. Estimated Curie constant (●) of $Sr(Cu_{1-x}Zn_x)_2O_3$ plotted against Zn content. The solid line stands for the Curie constant expected from an assumption that every Zn ion produces a spin 1/2. See the text about the dotted line.

above, one Zn ion was naively expected to give rise to a spin 1/2 in a two-leg ladder. In the lightly doped region $x<0.03$, the experimentally obtained Curie constants are roughly consistent with the naive picture which is shown by a line in Fig. 2, while those for $x\geqslant 0.03$ are considerably smaller than expected. Consideration of the formation of Zn pairs occupying two adjacent sites which do not break singlet pairs makes the agreement slightly better, but the experimental value is still about 0.7 times as small as the expected value which is shown with the dotted line in Fig. 2. Here, each site has three intraladder nearest neighbors, and therefore the probability of the Zn-pair formation is approximately equal to $1.5x$. The Weiss temperature, θ, showed a small negative value (~ -2 K) for all the samples suggesting that the induced spins interact with each other very weakly.

At lower temperatures below 10 K, however, we found an unexpected behavior in the magnetic susceptibility, a cusp-like anomaly suggesting the onset of an antiferromagnetic ordering. The anomaly can be seen very clearly even at $x=0.01$. The cusp temperature increases with Zn content up to $x=0.04$ and then decreases, which is summarized in Fig. 3. Another point to note is that a tiny but finite difference was observed between the ZFC and FC data below the temperature of anomaly. Specific heat C_p was therefore measured to further clarify the origin of the anomaly. The C_p/T vs temperature and T^2 data (inset) for $x=0$, 0.02, and 0.04 are shown in Fig. 4. A λ-type anomaly is seen for the Zn-substituted sample around the temperature of magnetic anomaly, indicating that it is an AF transition, not a spin-glass freezing. Transition temperatures estimated from the specific heat data are also plotted in Fig. 3, which are in good agreement with the temperatures of the magnetic anomaly. The intrinsic nature of the magnetic ordering has been further confirmed very recently by a microscopic measurement, nuclear quadrupole resonance (NQR).[21]

For $x=0$, since the temperature range studied was much lower than the gap width, it is reasonable to assume that we measured only the lattice contribution (C_l) in the specific heat. Indeed, as shown in the inset of the figure, C_p/T decreased almost linearly toward zero with decreasing T^2 as expected from its gapped magnetic excitation spectrum. A small upturn at the lowest temperatures was assigned to a small amount of an unidentified impurity. The lattice term was fitted as $C_l=\beta_1 T^3+\beta_2 T^5$ with $\beta_1=1.3\times 10^{-1}$ mJ/K^4 Cu+Zn mole and $\beta_2=2.1\times 10^{-5}$ mJ/K^6 Cu+Zn mole. The value of β_1 corresponds to a Debye temperature $\Theta_D\sim 400$ K. Another interesting point seen in the specific heat data is that, in the Zn doped samples, an almost parallel shift by 3.5 mJ/K^2 Cu+Zn mole is observed at temperatures above the λ-like anomaly. This implies the appearance of a finite amount of the T-linear term, indicating a finite density of state at $E=0$ in the spin excitation spectrum. The coefficient γ is almost constant at 3.5 mJ/K^2 Cu+Zn mole for $x=0.02$ and 0.04. This doping insensitive γ appears to suggest that the T-linear term originates from the spin ladder as a whole rather than from the spin degree of freedom localized near the Zn ions. It may be interesting to note that the presence of such a T-linear term is characteristic of an isolated 1D Heisenberg AF system, where $\gamma=2Nk_B^2/3J$ for a homogeneous isolated spin-1/2 chain.[22] Applying this equation to the

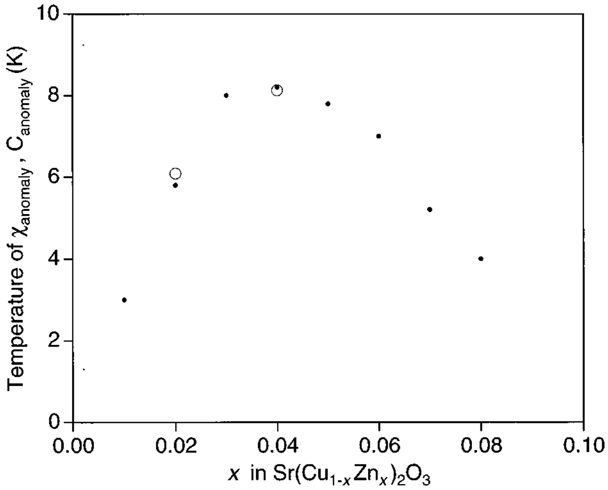

FIG. 3. Temperatures where susceptibility (closed circles) and specific heat (open circles) reach maxima are plotted against Zn content.

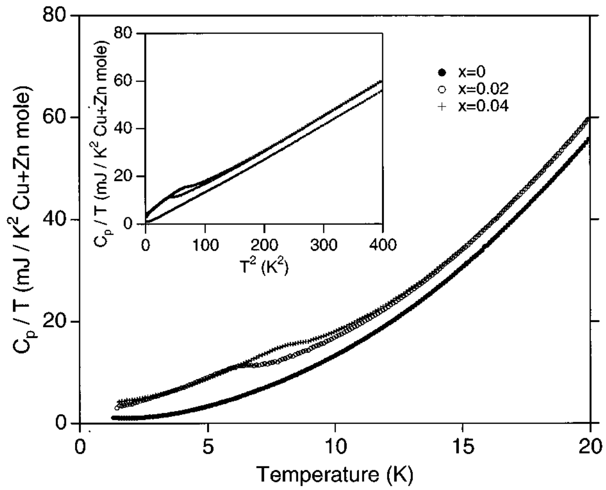

FIG. 4. Total specific heat divided by temperature C_p/T vs T and T^2 (inset) of $Sr(Cu_{1-x}Zn_x)_2O_3$ ($x=0$, 0.02, and 0.04).

present case assuming N is equal to the number of Cu ions, rather than to that of Zn ions, a J/k_B value of about 1600 K is obtained. Though the validity of this equation is not certified for the present ladder, the value of J appears reasonable in order of magnitude by comparing it with those in other 1D Cu-O chain compounds,[23] supporting the picture that the γT term arises from the whole ladder.

Based upon these results, we propose the following picture of impurity effects. Spins localized nearby the impurity ions might remain isolated in the gapped matrix at the low concentration limit, while within the composition region of $x<0.02$, the excitation spectrum becomes gapless for the whole ladder so that interactions between the localized moments can be mediated. The T_N first increases with increasing x, while it next descends because the impurity ions work to cut the correlation.

For information, it may be helpful to compare the magnetic transition temperature with those of gapless 1D chain compounds Sr_2CuO_3 and $Sr_2Cu_3O_5$. μSR studies have revealed that the former oxide experiences a magnetic ordering at 5 K (Ref. 24) and the latter at 52 K.[11] The maximum Néel temperature of $Sr(Cu_{1-x}Zn_x)_2O_3$, 8 K, seems to be close to that of the 1D chain system, but it could be even higher if the dilution effect was absent.

In summary, our magnetic susceptibility and specific heat study on $Sr(Cu_{1-x}Zn_x)_2O_3$ established the presence of long-range antiferromagnetic ordering induced by a very small amount of nonmagnetic impurity. Magnetic specific heats of Zn-substituted samples were linear to temperatures above T_N, indicating the existence of a finite density of state at $E=0$ in the spin excitation spectrum.

The authors express their thanks to Professor N. Nagaosa for useful discussions. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas, ''Anomalous metallic state near the Mott transition,'' from the Ministry of Education, Science and Culture, Japan, and CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Corporation (JST).

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