Disappearance of the Spin Gap in a Zn doped 2-Leg Ladder Compound Sr(Cu_{1-x}Zn_x)_{2}O_3

M. Azuma and M. Takano

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

R. S. Eccleston
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX10 OQX, United Kingdom
(September 4, 2018)

Abstract

An inelastic neutron scattering study was performed on a Zn-substituted spin-1/2 Heisenberg 2-leg ladder compound Sr(Cu_{1-x}Zn_x)_{2}O_3 (x \leq 0.04) to investigate nonmagnetic impurity effects on the quantum spin system with a large spin gap of about \sim 400 K. The magnitude of the spin gap was found to be independent of Zn concentration, 33 meV, while the integrated magnetic scattering which corresponds to the singlet-triplet excitation decreased monotonically with increasing x. On account of the total-sum rule, this result supports the existence of a finite in-gap density of states at E = 0 which was suggested from the T-linear magnetic specific heat.

75.10.Jm, 75.25.+z, 75.50.Ee

Typeset using REVTeX
Recently, one dimensional antiferromagnets which with gapped singlet spin states have attracted much attention. Such singlet ground states are realized in three classes of Heisenberg 1D antiferromagnetic (AF) systems, a $S = 1/2$ alternate chain found in a spin-Peierls system below the transition temperature, a uniform integer-spin chain (Haldane material), and a $S = 1/2$ two leg spin ladder compound [1]. SrCu$_2$O$_3$ [2] is the most typical compound comprising such 2-leg ladder lattice. In this compound, the ladders made of AF Cu-O-Cu linear bonds are connected with each other spatially so that they form 2D Cu$_2$O$_3$ sheets, but the ladders are separated from each other magnetically because of the inter-ladder 90$^\circ$ Cu-O-Cu bond causing spin frustration at the interface. The existence of a wide spin gap was found through the measurements of magnetic susceptibility [3] and nuclear spin relaxation time, $T_1$ [4]. However the former measurement gave the magnitude of a gap magnitude of 420 K, whereas that estimated from the temperature dependence of $T_1$ was 680 K. This apparent discrepancy was explained theoretically by Kishine and Fukuyama based on a Majonara fermion representation [5], and they showed that both experimental data could be explained assuming a gap of 440 K. Nevertheless, a neutron scattering study has been required to determine the magnitude of the spin gap directly.

Nonmagnetic impurities introduced into quantum antiferromagnets have been expected to affect the magnetic properties in various ways. Of particular interest is the coexistence of lattice dimerization and long-range AF ordering in an impurity-substituted spin-Peierls material, Cu$_{1-x}$Zn$_x$GeO$_3$ [6,7]. The coexistence of the two seemingly exclusive phenomena was observed also in CuGe$_{0.993}$Si$_{0.007}$O$_3$ [8,9] in which the Cu-sublattice was kept clean. We have studied the nonmagnetic impurity effects on a 2-leg ladder compound through the measurements of magnetic susceptibility and specific heat of Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ [10]. The influence of the Zn substitution was found to be much more extended than naively expected : Instead of the creation of free localized spin-1/2’s studding the matrix in its singlet state [11], an antiferromagnetic transition at an $x$-dependent temperature below 10 K was seen in the above measurements. An NQR study confirmed the AF ordering and revealed that essentially all the Cu ions are involved in the ordering even for the $x = 0.01$ sample [12]. Moreover, suppression of the spin gap was suggested from the linear temperature dependence of magnetic specific heat above $T_N$ for $x \geq 0.02$. It should be noted here that such a linear behavior has been considered to be characteristic of a gapless 1D AF system [13]. Our data thus implied that there is a finite impurity-induced density of state at $E = 0$ for $x \geq 0.02$ at least, most probably for $x = 0.01$ also. However, it has not been clear how the gap size and the density of states change.

In this letter, we report the result of an inelastic neutron scattering study on Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ ($x = 0, 0.003, 0.006, 0.01, 0.02$ and $0.04$). For the pure ($x = 0$) sample the opening of a gap of 33 meV (380 K) was clearly observed. The gap size remained the same independent of $x$, whereas the integrated intensity of the magnetic scattering, which is proportional to the probability of the singlet-triplet excitation over the gap, decreased monotonically until it became almost negligible at $x = 0.04$.

In the case of a polycrystalline sample the scattering law for a one-dimensional system is the powder average of the dynamic spin-spin correlation function [14].

$$S(Q,\omega) = \frac{1}{4\pi Q^2} T(\omega)|F(Q)|^2 \int_{q=q_o+q_\perp} |q|=Q S(q||,q_\perp,\omega) dq.$$ (1)
where $F(Q)$ is the ionic form factor, $q_\parallel$ and $q_\perp$ are the parallel and perpendicular projections of the total momentum transfer $q$ relative to the chain axis, and $T(\omega)$ is the temperature factor

$$T(\omega) = \left[1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)\right]^{-1}.$$  \hspace{1cm} (2)

Clearly for any given $Q$, all values of $4 \leq Q$ will contribute to the scattered spectrum. For dispersive excitations $S(Q, \omega)$ is proportional to the density of states of the dispersion, consequently, where there is a singularity in the density of states, such as at a band minima, one expects a peak in the scattered intensity. For a mode with minima at $q_\parallel = q_1$ and energy transfer $\omega = E_g$ for example, one would expect no contribution to the scattering for $\omega = E_g$, $Q < q_1$, but a peak in the scattering at $\omega = E_g$, $Q = q_1$ which would persist to higher $Q$ with the intensity modulated by $Q$ and the form factor following Eq. (1).

Powder samples were prepared as described before \cite{10}. The neutron-scattering data were collected on the HET direct geometry chopper spectrometer at the ISIS pulsed neutron facility at the Rutherford Appleton Laboratory \cite{15}. The white pulsed neutron beam was monochromated by a Fermi chopper which rotates at frequencies of up to 600 Hz and was phased to the neutron pulse. The energy transferred to the sample was then calculated from the time of flight of the scattered neutron. HET is optimized for scattering at low momentum transfers over a wide energy range, with banks of detectors at 4 an 2.5m covering the angular ranges 2.6° to 7° and 9° to 29° degrees respectively. Two further detector banks at mean scattering angles of 115° and 133° are used to collect high $Q$ data which are used for the estimation of the neutron background signal. About 5 g of a powder sample of each composition was wrapped in a flat Al foil sachet and attached to the cold finger of a closed cycle refrigerator (CCR).

From the susceptibility data, we anticipated a gap of 36 meV at a momentum transfer $Q = 0.8$ Å$^{-1}$ because the Cu-O-Cu distance along the ladder is 3.93 Å. An incident energy of 250 meV was chosen because we were able to reduce the $Q$ at the energy transfer of 35 meV to 0.93 Å. Figure 1(a) shows the data collected on SrCu$_2$O$_3$ ($x = 0.00$) at 10 K. The open circles show the experimental points collected at the mean scattering angle of 4.7°. The dashed line is an estimation of the scattering from nuclear and the single and multiphonon background. The latter was estimated from data collected in the high-angle detector banks, where the inelastic scattering is solely single and multiphonon in origin. Two scaling factors for the background were used as free parameters in the fit. The solid line is the result of fitting to the data after the subtraction of this background using the dispersion relation for a spin ladder with $J_\parallel = J_\perp$ predicted by Barnes and Riera \cite{16}. This fit yields a magnitude of the spin gap of 33 meV in good agreement with the value obtained from the susceptibility measurement. Figure 2 is the data collected for the same sample at 10, 100 and 200 K. Here, the solid lines represent the fit to the data. The peak was found to broaden with increasing temperature, providing a strong evidence that this is magnetic in origin. Such broadening of the peak had also been reported for a Haldane material Y$_2$BaNiO$_5$ \cite{17}. However, such a shift of the peak position as observed for that compound was not observed in the present case.

Figure 3 shows the data collected for Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ ($x = 0, 0.01, 0.04$). Surprisingly, the position of the peak does not shift even at $x = 0.04$. Instead, the broadening took place
in the data for the doped samples. The data was analyzed in the same way as described above and the results are summarized in Fig. 4. Figure 4 (a) shows the magnitude of the spin gap thus estimated, which is almost independent of Zn concentration. This might seem to be against the assertion that the Zn-substitution makes the ladder gapless. On the other hand, the integrated intensity of the magnetic scattering between 25 and 50 meV which corresponds to the possibility of the singlet-triplet excitation over the spin gap exhibits a different behavior. As shown in Fig. 4 (b), it decreases monotonically and the peak is not statistically significant any more at $x = 0.04$. The change in the low energy excitation could not be observed in this study because of the strong quasielastic scattering near $E = 0$. However, on account of the total-sum rule, our result implies that the in-gap density of state at $E = 0$ is finite and grows with increasing $x$. The survival of weight at energies of the order of the original spin gap had been predicted theoretically \[18\] at a small Zn concentration, however, our data revealed that it survives up to a Zn concentration where the $T_N$ reaches the maximum.

Present data seem to indicate that impurities introduced in the the singlet matrix makes the spins around it alive to a limited extent because of the short spin correlation length. Remaining singlet pairs are not affected, so the magnitude of the spin gap does not change. At $x = 0.04$, almost all singlet pairs are destroyed, therefore the spin gap closes. However, this interpretation cannot explain the $T$-linear magnetic specific heat and the fact that all the Cu ions are involved in the AF ordering. Instead, we propose the following picture. An impurity does not induce a localized magnetic moment only at its neighboring site, but small staggered spin moments appear in the whole region. This is the origin of the finite in-gap density of state and the $T$-linear magnetic specific heat as well. The enhancement of the correlation length and the possession of local staggered moments for the sites far from the impurities are suggested theoretically \[19–21\] and experimentally also by an NMR study \[22\]. Existence of a finite state only at $E = 0$ and $q = (\pi, \pi)$ seems to be enough for the possession of the staggered moments. An inelastic neutron scattering study on a single crystal sample is required to investigate the $q$ dependence of the excitation. It is the future work. Above the ground state, there still exist a pseudo gap and a triplet excitation band. Namely, every site has the two exclusive aspects, singlet ground state and staggered local moment. The in-gap state grows with increasing $x$ until the gap closes finally around $x=0.04$.

The induced moments get magnetically ordered at low temperatures because of the small three dimensionality. However, the ordered moment is quite small because of the spin frustration at the interface between the ladders. This is consistent with the result of the NQR study which revealed that the ordered moment is as small as 0.01 $\mu_B$ \[12\]. The $T_N$ first increases with increasing $x$, while it next descends because the impurity ions work to cut the correlation.

In summary, we have performed an inelastic neutron scattering study on Sr(Cu$_{1-x}$Zn$^x$)$_2$O$_3$ ($x \leq 0.04$) to investigate nonmagnetic impurity effects on the 2-leg spin ladder system. The existence of the spin gap of 33 meV (380 K) was confirmed in the pure sample. Its magnitude was found to be independent of Zn concentration, while the integrated intensity of the magnetic scattering which corresponds to the singlet-triplet excitation decreases monotonically. These data suggest the finite in-gap density of state at $E=0$ which leads to the $T$-linear term of the specific heat.
This work was partly supported by a Grant-in Aid for Scientific Research on Priority Areas, “Anomalous metallic state near the Mott transition”, of Ministry of Education, Science and Culture, Japan and CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).
REFERENCES

[1] for review, see E. Dagotto and T. M. Rice, Science 271, 618 (1996).
[2] Z. Hiroi, M. Azuma, M. Takano and Y. Bando, J. Solid State Chem. 95, 230 (1991).
[3] M. Azuma, Z. Hiroi, M. Takano, K. Ishida and Y. Kitaoka, Phys. Rev. Lett. 73, 3463 (1994).
[4] K. Ishida, Y. Kitaoka, K. Asayama, M. Azuma, Z. Hiroi and M. Takano, J. Phys. Soc. Jpn. 63, 3222 (1994); K. Ishida, Y. Kitaoka, Y. Tokushige, S. Matsumoto, K. Asayama, M. Azuma, Z. Hiroi and M. Takano, Phys. Rev. B 53, 2827 (1996).
[5] J. Kishine and H. Fukuyama, J. Phys. Soc. Jpn 66, 26 (1997).
[6] S. B. Oseroff, S-W. Cheong, B. Aktas, M. F. Hundley, Z. Fisk and L. W. Rupp, Jr., Phys. Rev. Lett 74, 1450 (1995).
[7] M. Hase, N. Koide, K. Manabe, Y. Sasago and K. Uchinokura, Physica B 215, 164 (1995); M. Hase, K. Uchinokura, R. J. Birgeneau, K. Hirota and G. Shirane, J. Phys. Soc. Jpn. 65, 1392 (1996).
[8] L. P. Regnault, J. P. Renard, G. Dhalenne and A. Revcolevschi, Europhys. Lett. 32, 579 (1995); J. P. Renard, K. Le Dang, P. Veillet, G. Dhalenne, A. Revcolevschi and L. P. Regnault, Europhys. Lett. 30, 475 (1995); M. Poirier, R. Beaudry, M. Gastonguay, M. L. Plumer, G. Quirion, F. S. Razavi, A. Revcolevschi and G. Dhalenne, Phys. Rev. B 52, R6971 (1995).
[9] H. Fukuyama, T. Tanimoto and M. Saito, J. Phys. Soc. Jpn. 65, 1182 (1996).
[10] M. Azuma, Y. Fujishiro, M. Takano, M. Nohara and H. Takagi, Phys. Rev. B 55, R8658 (1997).
[11] S. R. White, R. M. Noack and D. J. Scalapino, Phys. Rev. Lett 73, 886 (1994).
[12] S. Ohsugi, unpublished
[13] T. Wei, A. J. Heeger, M. B. Salamon and G.E. Delker, Solid State Commun., 21, 595 (1977).
[14] H. Mukta, C. Payen, P. Molinie, J. L. Soubeyroux, P. Colombert, and A. D. Taylor, Phys. Rev. Lett. 67 497 (1991).
[15] R. S. Eccleston, M. Azuma and M. Takano, Phys. Rev. B 53 R14721 (1996).
[16] T. Barnes and J. Riera, Phys. Rev. B 50, 6817 (1994);
[17] J. Darriet and L. P. Renault, Solid State Commun. 86, 409 (1993).
[18] G. B. Martins, E. Dagotto and J. Riera, Phys. Rev. B 54, 16032 (1996).
[19] H. Fukuyama, N. Nagaosa, M. Saito and T. Tanimoto, J. Phys. Soc. Jpn. 65, 2377 (1996).
[20] N. Nagaosa, A. Furusaki, M. Sigrist and H. Fukuyama, J. Phys. Soc. Jpn. 65, 2377 (1996).
[21] G. B. Martins, M. Laukamp J. Riera, and E. Dagotto, Phys. Rev. Lett. 78, 3563 (1997).
[22] N. Fujiwara, H. Yasuoka, Y. Fujishiro, M. Azuma and M. Takano, proceedings of ICM 97 (to be published in J. Magn. Magn. Mater.).
FIGURES

FIG. 1. Scattering from SrCu$_2$O$_3$ with an incident energy of 250 meV at a mean scattering angle of 4.7° collected at 10 K. The solid line is the magnetic component and the dashed line is the nuclear and single and multiphonon scattering.

FIG. 2. Scattering from SrCu$_2$O$_3$ at 10, 100 and 200 K. The solid lines represent the fit to the data.

FIG. 3. Scattering from Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ ($x = 0, 0.01$ and $0.04$) collected at 10K

FIG. 4. (a) Magnitude of the spin gap of Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ ($x = 0, 0.003, 0.006, 0.01, 0.02$ and $0.04$) estimated from the scattering data. (b) Integrated intensity of magnetic scattering observed between 25 and 50 meV.
Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ 10 K

$x = 0.00$

$x = 0.01$

$x = 0.04$
