Observation of a dimerized state in the $S=1/2$ quasi-one-dimensional antiferromagnet $Sr_{14}Cu_{24}O_{41}$

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(Received 8 December 1995)

We have performed magnetic susceptibility and electron spin resonance measurements on the quasi-one-dimensional magnet $Sr_{14}Cu_{24}O_{41}$, which has simple chains and two-leg ladder chains of copper ions. The magnetic signals which we observed below room temperature mainly come from the simple chains. The experimental results show that the simple chain unexpectedly has a spin gap in the excitation spectrum, which originates from a dimerized state. [S0163-1829(96)03218-3]

I. INTRODUCTION

One-dimensional (1D) antiferromagnets have attracted many researchers since they exhibit interesting phenomena originating from quantum fluctuations. The most striking effect in a 1D Heisenberg antiferromagnet (HAF) is that integer and half-integer spins show qualitatively different properties, as suggested by Haldane.[1] The recent discovery[2] of a spin-Peierls transition in $CuGeO_3$ has stimulated the study of 1D antiferromagnetism. Another interesting quantum phenomenon in a spin quantum number (S) $\frac{1}{2}$ 1D antiferromagnet has been predicted theoretically by Majumdar and Gosh[3] and later by Haldane.[4] The former authors showed rigorously that the ground state of the $S=\frac{1}{2}$ 1D AF with competing nearest-neighbor (NN) (J_1) and next-nearest-neighbor (NNN) interactions (J_2) is in a dimerized state for $J_2/J_1=\frac{1}{2}$. Haldane argued that a spontaneously dimerized ground state exists in a wider range of J_2/J_1. This dimerized state is distinguished from the one found in spin-Peierls systems in that the former is not associated with a lattice distortion. The spontaneously dimerized state is a superposition of two states in one of which a spin forms a dimer with the spin on its right and in the other of which with the spin on its left. Thus the dimerized state appears as the result of quantum phenomena.

The structure of $Sr_{14}Cu_{24}O_{41}$[5,6] consists of two unique subcells as is shown in Fig. 1. One is simple chains (space group *Amma*) of copper ions which are coupled by the nearly 90° Cu-O-Cu bond. The other is two-leg ladder chains (space group *Fmmm*) of copper ions which are coupled by the nearly 180° Cu-O-Cu bond along the a and c axes. Each ladder is coupled by the nearly 90° Cu-O-Cu bond. The interaction between the ladders is considered to be much weaker than that within the ladders.[7] Each chain and the Sr ions form a layered structure in the ac plane and stack alternately along the b axis. It is noted that the valence state of the copper ions in the stoichiometric $Sr_{14}Cu_{24}O_{41}$ is $+2.25$. It has been reported that there exists excess strontium in $Sr_xCu_{24}O_{41}$ ($x=14.74$),[5] and oxygen deficiency in $(Sr_{0.4}Ca_{0.6})_{14}Cu_{24}O_y$ ($y=40.07$).[8] If these values are taken into account, the valence state of the copper ions becomes $+2.11$. The hole carriers are considered to be localized because the compound is highly insulating.[5,9]

Susceptibility measurements on a single crystal of $Sr_{14}Cu_{24}O_{41}$ have been performed by McElfresh *et al.*[9] They found a broad peak around 60 K and claimed that it originated from antiferromagnetic long-range ordering. Susceptibility measurements on a powder sample of $Sr_{14}Cu_{24}O_{41}$ have been performed by Kato *et al.*[10] and Uehara, Ogawa, and Akimitsu.[8] The latter authors claimed that there exists a spin gap of 87 K which originates from the ladder chain. In this paper, we report the results of susceptibility and electron spin resonance (ESR) measurements on single crystals of the $S=\frac{1}{2}$ quasi-1D AF compound $Sr_{14}Cu_{24}O_{41}$. These results can be interpreted with a model based on dimerized $S=\frac{1}{2}$ spins. These dimers are probably formed in the simple chain.

II. EXPERIMENTAL METHOD

Single crystals of $Sr_{14}Cu_{24}O_{41}$ were grown by a traveling-solvent floating-zone (TSFZ) method in air. They were confirmed to be single crystals by neutron diffraction and the x-ray back-reflection Laue method. The dimensions of the crystal used in both the magnetic susceptibility and ESR experiments were about 3, 0.5, and 2 mm parallel to the a, b, and c axes, respectively. The magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS2). The ESR measurement was done with an X-band spectrometer (JEOL-JES-RE2X).

III. EXPERIMENTAL RESULTS

We show in Fig. 2 the temperature dependence of the magnetic susceptibility in a single crystal of $Sr_{14}Cu_{24}O_{41}$. The core diamagnetic susceptibility of this sample is estimated to be -4.02×10^{-5} emu/mol Cu and the value of the Van Vleck paramagnetism (4.47×10^{-5} emu/mol Cu) is assumed to be the same as in the similar compound $SrCu_2O_3$.[11] The sum of the two terms, 4.5×10^{-6} emu/mol Cu, is almost negligible compared with the observed value. The susceptibility decreases with increasing temperature and shows a minimum around 20 K and a broad peak around 80 K. There is an anisotropy in the susceptibility ($\chi_b>\chi_a\simeq\chi_c$). Most of the anisotropy comes from the an-

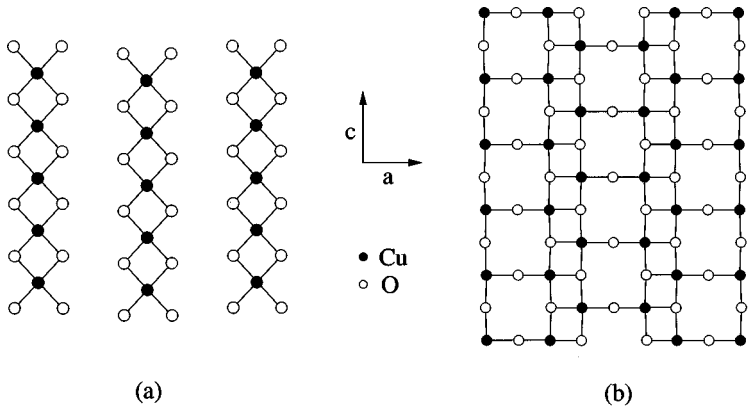

FIG. 1. The simple chain (a) and the ladder chain (b) of copper ions in $Sr_{14}Cu_{24}O_{41}$. Filled circles represent copper atoms and open circles represent oxygen atoms.

isotropy in the g value as described below. The data below 10 K were fitted with a Curie-Weiss law of $C/(T+1.72)$ emu/mol Cu, where C and T represent the Curie constant and temperature, respectively. We obtained the anisotropic Curie constant along the a, b, and c axes as $C_a=5.95\times10^{-3}$, $C_b=6.89\times10^{-3}$, and $C_c=5.77\times10^{-3}$, respectively. The magnetic impurity density, assuming Cu^{2+} as impurities, is estimated to be $\sim1.4\%$. The Curie-type susceptibility ($\chi^{\rm imp}$) shows the same anisotropy ($\chi_b^{\rm imp}>\chi_a^{\rm imp}\simeq\chi_c^{\rm imp}$) as in the bulk. This suggests that the Curie-type susceptibility originates not from the free moments in another phase but from those in the main phase. The magnetic-field dependence of the magnetization of this sample at low temperatures follows a Brillouin function for $S=\frac{1}{2}$, which means that the Curie-Weiss tail in the low-temperature susceptibility comes from free moments.[12] The magnetic impurity density is consistent with that estimated from the Curie constant. In order to get conclusive evidence that the increase of the susceptibility at low temperatures comes from paramagnetic impurities, we performed specific heat measurements in magnetic fields. A Schottky anomaly is observed. The magnetic impurity density is also consistent with that estimated from the Curie constant. The data in the inset of Fig. 2 show the susceptibility after the Curie-Weiss term was subtracted. The susceptibility becomes almost zero below 20 K.

Figure 3 shows typical ESR spectra of $Sr_{14}Cu_{24}O_{41}$. We obtained the g values along the a, b, and c axes as $g_a=2.05$, $g_b=2.26$, and $g_c=2.04$, respectively. The g values are almost temperature independent. The integrated intensity of the absorption spectra along the a, b, and c axes in $Sr_{14}Cu_{24}O_{41}$ is plotted in Fig. 4. The intensity (A) has a broad peak around 80 K. This shows clearly that the ESR signal comes from a transition within excited states. The linewidth of the absorption spectrum is almost temperature independent below about 150 K and begins to increase when the temperature is increased further.

IV. DISCUSSION

The nearly 180° Cu-O bond lengths (1.90 Å perpendicular to the ladder chain and 1.97 Å along the ladder chain) of the two-leg ladder chains in $Sr_{14}Cu_{24}O_{41}$ are close to the corresponding values in $SrCu_2O_3$ (1.93 Å perpendicular to the ladder chain and 1.97 Å along the ladder chain).[13] Then it is natural to assume that the gap energy of the ladder chain in $Sr_{14}Cu_{24}O_{41}$ is close to that of $SrCu_2O_3$ (420 K from susceptibility measurements and 680 K from NMR measurements[11]). This means that the ladder chain in $Sr_{14}Cu_{24}O_{41}$ has a singlet ground state with a fairly large gap and that the magnetic susceptibility and the ESR signal intensity from the ladder chain are very small below room temperature. Therefore the magnetic susceptibility and the ESR signal which we observed essentially come from the simple chain. In order to clarify this, susceptibility measurements at higher temperatures (600–800 K) are desirable. The susceptibility is expected to show a broad peak at a much higher temperature.

From the magnetic susceptibility and ESR measurements on $Sr_{14}Cu_{24}O_{41}$, we are convinced that there is a spin gap in the excitation spectrum of the simple chains. We first analyze the results of the ESR measurements with the following simple model: the ground state is a singlet and there is an energy gap (Δ) between the singlet and the first excited state. In an $S=\frac{1}{2}$ 1D HAF elementary excitations are spin-wave-like and are not localized. Also, a spin-wave excitation with a large gap energy is not expected in Cu^{2+} compounds.

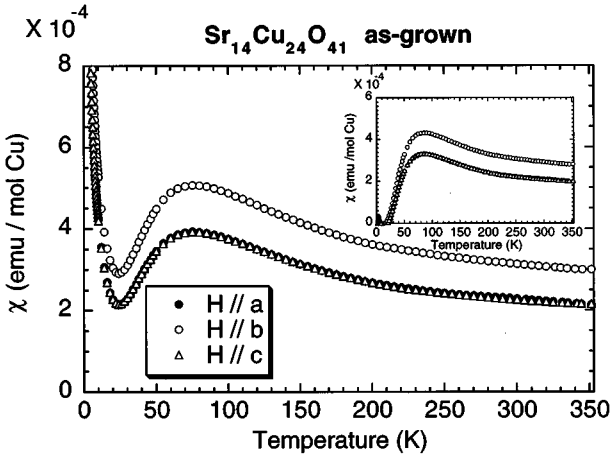

FIG. 2. Temperature dependence of magnetic susceptibility in a single crystal of $Sr_{14}Cu_{24}O_{41}$.

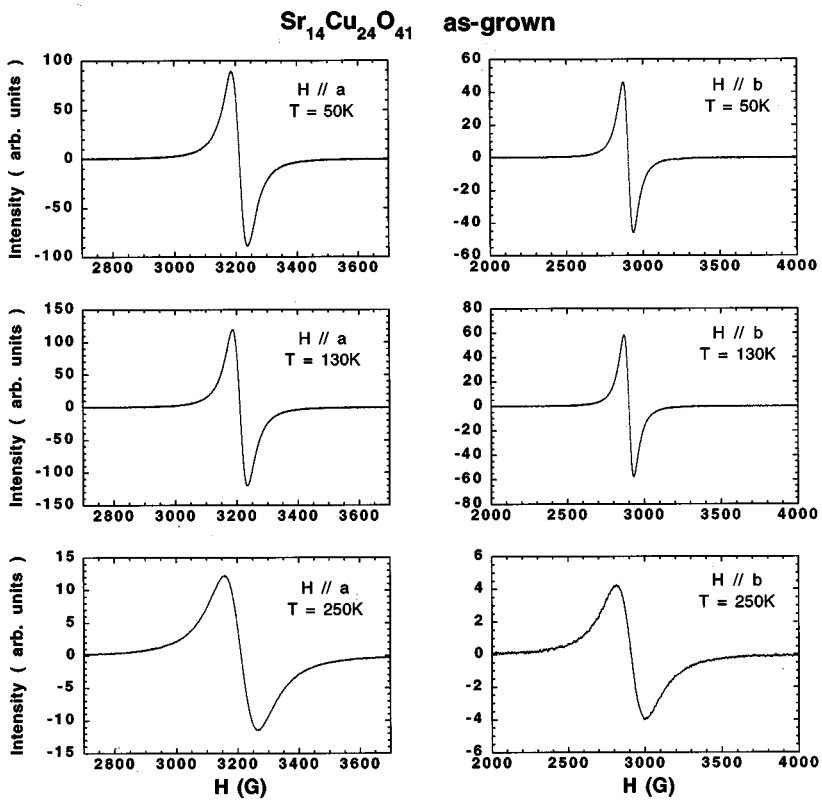

FIG. 3. Typical ESR spectra of $Sr_{14}Cu_{24}O_{41}$ at various temperatures.

Then we take a triplet for the first excited state. In this case the ESR intensity (A) should follow the equation

$$A \propto 2Z^{-1}\exp(-\Delta/k_BT)\sinh(g\mu_BH/k_BT),$$

$$Z \equiv 1+\exp(-\Delta/k_BT)\{1+2\ \cosh(g\mu_BH/k_BT)\}, \quad (1)$$

where k_B and H represent Boltzmann's constant and the applied magnetic field, respectively. The solid lines in Fig. 4 are fits to Eq. (1) with $\Delta=120$ K. The model reproduces the experimental data fairly well. It should be noted, however, that the model explains the temperature dependence of the relative intensity. We have not studied the absolute intensity.

Stimulated by this finding, we have analyzed the magnetic susceptibility data. The magnetic susceptibility (χ_{total}) in Fig. 2 consists of the following four terms:

$$\chi_{\text{total}}=\chi_{\text{const}}+\chi_{\text{Curie-Weiss}}+\chi_{\text{chain}}+\chi_{\text{ladder}}, \quad (2)$$

where χ_{const} represents the sum of the core diamagnetic and Van Vleck terms, which is negligible as discussed above. For χ_{ladder} we take the susceptiblility of the similar compound $SrCu_2O_3$.[11] The spin gap behavior in $S=\frac{1}{2}$ 1D HAF's is expected to be observed in the spin-Peierls, the alternating interactions, and the competing NN and NNN interactions systems. In an ideal spin-Peierls system, the susceptibility follows the Bonner-Fisher[14] curve (χ_{BF}) above the transition temperature T_{SP} and shows a rapid drop below T_{SP}. In the alternating interactions system, the susceptibility should have a value between χ_{BF} and the susceptibility of the noninteracting dimers. Using the same energy level scheme used to derive Eq. (1), we obtain for the susceptibility of the noninteracting dimers

$$\chi_D=\frac{Ng^2\mu_B^2}{k_BT}\frac{1}{3+\exp(2J/k_BT)}, \quad (3)$$

where N, μ_B, and J ($=\Delta/2$) represent the number of Cu atoms, the Bohr magneton, and the exchange interaction between nearest-neighbor Cu moments, respectively. In the competing NN and NNN interactions system with $J_2=J_1/2$, the susceptibility (χ_{SS}) was calculated by Shastry and Sutherland[15] as

$$\chi_{\text{SS}}=\frac{Ng^2\mu_B^2}{4k_BT}\exp\left(-\frac{1.25J}{k_BT}\right)I_0\left(\frac{J}{k_BT}\right), \quad (4)$$

where I_0 is a Bessel function. The susceptibility χ_{SS} becomes smaller than χ_D due to many-body effects Also, the decrease of the susceptibility at high temperatures is slower than that in the noninteracting dimer state. This originates from the contribution of the excited states in which pairs of $S^z=\pm\frac{1}{2}$ solitons propagate.[4,15]

Figure 5 shows the averaged susceptibility $(\chi_a+\chi_b+\chi_c)/3$ after subtraction of the Curie-Weiss term. The solid line represents χ_{ladder}, which is the susceptibility of $SrCu_2O_3$ multiplied by 0.58. Here, 0.58 is the ratio of the copper ions at the ladder chain site to the total copper ions in the crystal. As is seen from this figure χ_{ladder} is negligibly small compared to the observed data. The dotted line represents χ_D [Eq. (3)] with $g=2.21$, $2J/k_B=133$ K, and

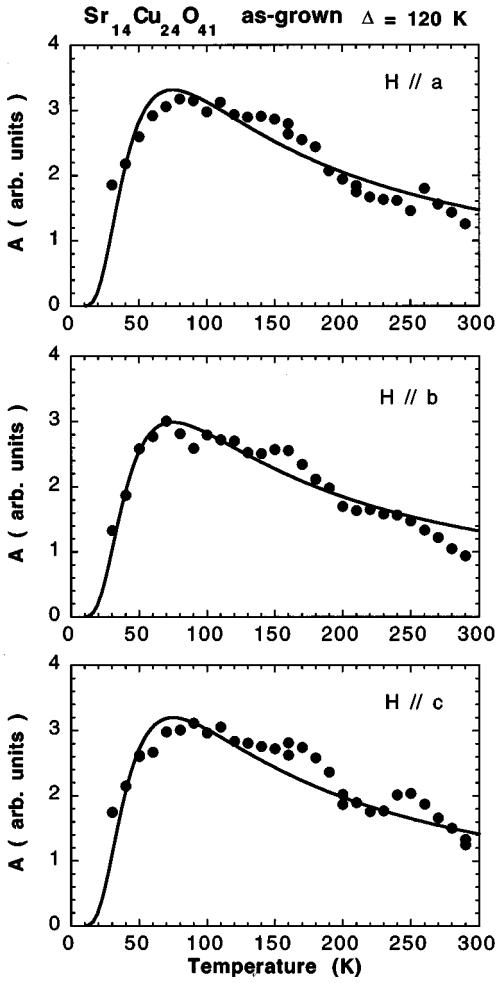

FIG. 4. Temperature dependence of the integrated intensity (A) of the ESR spectra in $Sr_{14}Cu_{24}O_{41}$.

$N=0.42N_A$, where N_A represents Avogadro's number. Here, 0.42 is the ratio of the copper ions at the simple chain site to the total copper ions in the crystal. The dash-dotted line represents $\chi_{\rm BF}$ with $2J/k_B=133$ K. The broken line represents $\chi_{\rm SS}$ [Eq. (4)] with $2J/k_B=300$ K. In these fittings, we adjusted the value J so that the theoretical and experimental temperatures at which the susceptibility is maximum coincide.

We now discuss the origin of the dimerized state observed in $Sr_{14}Cu_{24}O_{41}$. In the alternating interactions and the spin-Peierls systems, there exists structural distortion, which causes an alternating interaction to the Cu^{2+} moments in the chain. Since the distance between NN Cu atoms is uniform in the simple chain,[5] there should be no alternating interactions in the chains at least at room temperature. The structural distortion, if present, should be reflected in the temperature dependence of susceptibility as observed in the spin-Peierls material $CuGeO_3$.[2] However, we have observed no anomaly in our susceptibility measurements below 300 K. Furthermore, no specific heat anomaly has been observed in the range of $5.3\leqslant T\leqslant 350$ K.[16] From these facts, we exclude the possibility of structural distortion. This is consistent with the fact that the susceptibility data in Fig. 5 do not fit at all with the models which are based on structural distortion.

In the competing NN and NNN interactions system, a spontaneously dimerized ground state is expected to be observed as predicted by Majumdar and Gosh[3] and by Haldane.[4] As is seen from Fig. 1(a), the following two exchange interaction paths between Cu^{2+} spins are possible. One is the nearly 90° Cu-O-Cu superexchange interaction which is probably antiferromagnetic as in $CuGeO_3$ ($J=88$ K).[2] The other is the superexchange interaction between next-nearest-neighbor Cu spins. If the latter interaction is antiferromagnetic and has a value in the range of $J_2/J_1\geqslant 0.25$,[17] the ground state becomes spontaneously dimerized. Very recently, Castilla, Chakravarty, and Emery[18] have reported that the competing NN and NNN interactions play an important role in $CuGeO_3$. They have shown that the magnetic susceptibility and the magnetic excitation spectrum are well described by the Heisenberg model with a competing interaction with the ratio of $J_2/J_1\simeq 0.24$, which is slightly smaller than the critical value required to produce a spontaneously dimerized state. The observed susceptibility in Fig. 5 is close to the theoretical curve with $J_2/J_1=\frac{1}{2}$.[15] A more elaborate calculation is expected to give a better agreement between theory and experiment.

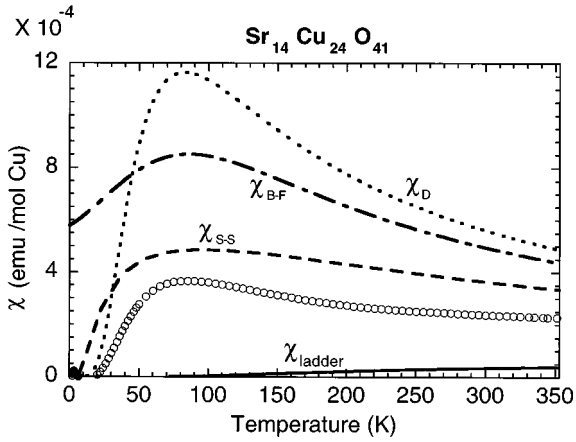

FIG. 5. Temperature dependence of the averaged magnetic susceptibility $(\chi_a+\chi_b+\chi_c)/3$ in $Sr_{14}Cu_{24}O_{41}$. The solid line represents $\chi_{\rm ladder}$. The dotted line represents χ_D calculated by using Eq. (3) with $2J/k_B=133$ K. The dash-dotted line represents $\chi_{\rm BF}$ calculated with $2J/k_B=133$ K. The broken line represents $\chi_{\rm SS}$ calculated by using Eq. (4) with $2J/k_B=300$ K.

In conclusion, we have performed magnetic susceptibility and ESR measurements on the quasi-one-dimensional magnet $Sr_{14}Cu_{24}O_{41}$, which has simple chains and two-leg ladder chains of copper ions. The magnetic signals which we observed below room temperature mainly come from the simple chains. The experimental results show that the simple chain unexpectedly has a spin gap in the excitation spectrum, which originates from a dimerized state.

ACKNOWLEDGMENTS

We would like to thank M. Hase and T. Tonegawa for many helpful discussions. This work was partially supported by the MR Science Research Program from RIKEN, by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, Sports and Culture, and by a Grant from the Yazaki Memorial Foundation for Science and Technology.

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