Magnetic ordering in the $S=\frac{1}{2}$ quasi-one-dimensional compound $La_6Ca_8Cu_{24}O_{41}$

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Magnetic-susceptibility, heat-capacity, and neutron-scattering measurements have been performed on the $S=\frac{1}{2}$ quasi-one-dimensional system $La_6Ca_8Cu_{24}O_{41}$, which has both simple chains and two-leg ladders of Cu^{2+} ions. The singlet state with dimerization observed in the chains of $Sr_{14}Cu_{24}O_{41}$ becomes magnetic in $La_6Ca_8Cu_{24}O_{41}$ and a magnetic ordering has been observed below 12.20 ± 0.05 K. The magnetic structure in the ordered phase is such that spins in the chains are parallel and these ferromagnetic chains have a modulated structure. [S0163-1829(96)50746-0]

One-dimensional (1D) spin-$\frac{1}{2}$ Heisenberg antiferromagnets (HAF's) have been studied for many years. When the exchange interaction is limited only to the nearest neighbors (NN), the ground state of the $S=\frac{1}{2}$ 1D HAF is a singlet[1] called the spin-liquid state and there is no energy gap between the ground and excited states.[2] On the other hand, when the next-nearest-neighbor (NNN) interaction becomes appreciable, the ground state of the $S=\frac{1}{2}$ 1D HAF is a singlet with dimerization[3,4] and there is an energy gap above this ground state. This dimerized state is distinguishable from the one found in a spin-Peierls system in that it is not associated with a lattice distortion. A different mechanism to produce a singlet state in Cu-O compounds has been proposed.[5] According to this theory, holes introduced in the Cu-O compounds couple with Cu^{2+} ions to form a local singlet.

In previous papers, Matsuda and Katsumata[6] and Matsuda *et al.*[7] have reported the observation of a dimerized singlet state in the $S=\frac{1}{2}$ quasi-1D HAF $Sr_{14}Cu_{24}O_{41}$. The structure of $Sr_{14}Cu_{24}O_{41}$ (Refs. 8 and 9) consists of two unique subcells. One is simple chains (space group *Amma*) of copper ions which are coupled by the nearly 90° Cu-O-Cu bonds. The other is two-leg ladder chains (space group *Fmmm*) of copper ions, which are coupled by the nearly 180° Cu-O-Cu bonds along the *a* and *c* axes. Each ladder is coupled by the nearly 90° Cu-O-Cu bonds. The interaction between the ladders is considered to be much weaker than that within the ladder. Each chain and Sr ions form layered structures in the *ac* plane and stack alternately along the *b* axis. Since the ladder in this compound is close to that in $SrCu_2O_3$,[10] it is natural to assume that the gap energy of the ladder in $Sr_{14}Cu_{24}O_{41}$ is close to that of $SrCu_2O_3$. The gap energy in $SrCu_2O_3$ is estimated to be 400–600 K.[11] Therefore, the magnetism in $Sr_{14}Cu_{24}O_{41}$ below room temperature originates mainly from the chains.[6] It is noted that the valence state of copper ions in the stoichiometric $Sr_{14}Cu_{24}O_{41}$ is +2.25. A bond-valence-sums calculation has shown that holes preferably exist in the chain.[12] One can estimate that the number of holes in the chain is 60% of the Cu ions in the chain in $Sr_{14}Cu_{24}O_{41}$. Since $Sr_{14}Cu_{24}O_{41}$ is highly insulating,[8,9] the holes are considered to be localized at oxygen sites. In order to clarify the nature of the dimerized state found in $Sr_{14}Cu_{24}O_{41}$, it is important to study the effects of holes on the magnetic properties. For this purpose we chose the compound $La_6Ca_8Cu_{24}O_{41}$ in which there is no hole and all the Cu ions are in 2+ valence state.

The crystal structure of $La_6Ca_8Cu_{24}O_{41}$ is almost the same as that of $Sr_{14}Cu_{24}O_{41}$.[8,9] The chains of $Sr_{14}Cu_{24}O_{41}$ are slightly shifted alternately along the *c* axis, while those of $La_6Ca_8Cu_{24}O_{41}$ are staggered.[9] The chain and the ladder of copper ions in $La_6Ca_8Cu_{24}O_{41}$ are shown in Fig. 1. It has been reported that the susceptibility of a $La_6Ca_8Cu_{24}O_{41}$ powder shows a broad peak at ~ 25 K which is ascribed to a magnetic ordering.[13] It is suggested that the interaction in the chain is ferromagnetic and that perpendicular to the chain is antiferromagnetic.[13]

In this paper, we report the results of magnetic-

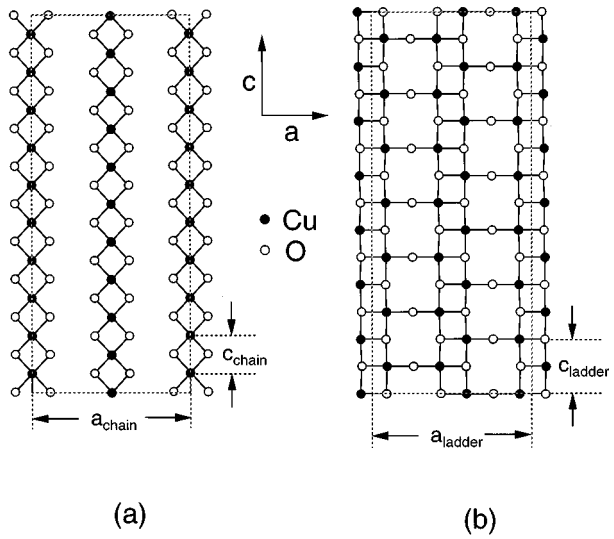

FIG. 1. The chain (a) and the ladder (b) of copper ions in $La_6Ca_8Cu_{24}O_{41}$. Filled circles represent copper atoms and open circles oxygen atoms. The dashed rectangles represent the universal unit cell in the (010) crystallographic plane. Here, c_{chain} and c_{ladder} represent the lattice constant *c* for the subcells which contain the chain and the ladder, respectively.

susceptibility, heat-capacity, and neutron-scattering measurements on a $La_6Ca_8Cu_{24}O_{41}$ single crystal. The dimerized singlet ground state observed in the chains of $Sr_{14}Cu_{24}O_{41}$ disappears in this compound. Instead, we observed that the chains in $La_6Ca_8Cu_{24}O_{41}$ show a magnetic ordering at 12.20 ± 0.05 K. The magnetic structure in the ordered state is such that spins in a chain couple ferromagnetically and these ferromagnetic chains have a modulated structure.

The single crystals of $La_6Ca_8Cu_{24}O_{41}$ were grown using a traveling solvent floating zone (TSFZ) method at 3 bar oxygen atmosphere. The magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (Quantum Design MPMS2). The heat capacity was measured using a MagLab^{HC} microcalorimeter of Oxford Instruments, U.K. The neutron-scattering experiments were carried out on the H4M polarized and unpolarized neutron triple-axis spectrometer at the High Flux Beam Reactor at the Brookhaven National Laboratory. For most of the experiments the horizontal collimator sequence was $40'$-$40'$-S-$40'$-$80'$. The final neutron energy was fixed at $E_f=14.7$ meV. Pyrolytic graphite single crystals were used as monochromator and analyzer for unpolarized neutron experiments. Heusler alloy (111) was used as monochromator and analyzer for polarized neutron experiments. Contamination from a higher-order beam was effectively eliminated using a pyrolytic graphite filter after the sample. The dimension of the cylindrically shaped crystal used in the experiments is about $5\times5\times20$ mm^3. The effective mosaic of the single crystal is less than 0.4° with the spectrometer condition as described above. The lattice constants are almost the same as those reported by Siegrist *et al.*[9] The single crystal was mounted in a closed-cycle refrigerator which allowed us to perform the measurements over a wide temperature range 4–300 K. The experiments for scattering in the $(h,0,l)$ zone were performed on the single crystal. Note that there are two different values for the lattice constant c as shown in Fig. 1. The lattice constants of the two subcells have the relation $10\times c_{\text{chain}}\simeq 7\times c_{\text{ladder}}$, where c_{chain} and c_{ladder} represent the lattice constant c for the subcell which contains the chain and the ladder, respectively.[8] Since we mainly studied magnetic properties in the chain, c_{chain} will be used to express Miller indices.

The temperature dependence of the magnetic susceptibility in the $La_6Ca_8Cu_{24}O_{41}$ single crystal is shown in Fig. 2(a). The susceptibility with the external field along the b axis shows a broad peak around 20 K. The susceptibilities with the external field along the a and c axes decrease with increasing temperature up to $\sim$10 K, above which they become almost constant, and decrease again with increasing temperature above 20 K. These indicate that an antiferromagnetic transition occurs below 20 K. The number of spins which contribute to the susceptibility is estimated from the Curie constant to be $\sim$50% of the total Cu^{2+} spins, which is consistent with the fact that only the chains contribute to the susceptibility below room temperature due to the large spin gap in the ladder.[6]

The heat-capacity data are shown in Fig. 2(b). A sharp peak is observed at $T_c\sim12$ K, indicating a magnetic transition. By subtracting the lattice contribution, we estimate the magnetic entropy below 12 K as $\sim$50 mJ/(mol K). This amount corresponds to less than $\sim$2% of the total magnetic

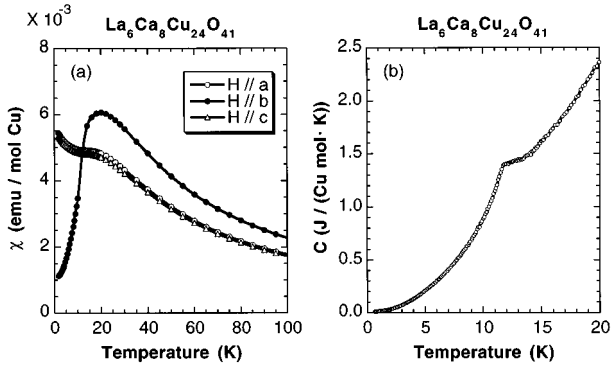

FIG. 2. (a) Temperature dependence of magnetic susceptibility in a single crystal of $La_6Ca_8Cu_{24}O_{41}$. (b) Temperature dependence of heat capacity in a single crystal of $La_6Ca_8Cu_{24}O_{41}$.

entropy $N_Ak_B\ln(2)$ expected for $S=\frac{1}{2}$, where N_A is the Avogadro number. This is natural because in a one-dimensional magnet, a large amount of magnetic entropy is lost in the short-range ordered state above the magnetic ordering temperature.

From the susceptibility and the heat-capacity measurements, we confirmed that a static magnetic ordering takes place in $La_6Ca_8Cu_{24}O_{41}$. Neutron elastic measurements were performed to determine the magnetic structure. Magnetic Bragg reflections were observed at incommensurate positions of $(2n\pm\delta,0,2l+1)$ (n,l: integer) and a commensurate position of (0,0,1) below $\sim$12 K. Figure 3 shows an elastic scan at $(h,0,1)$ along the h direction at 4 K measured with polarized neutrons in the horizontal field spin-flip mode which give only magnetic scattering. A modulation of the intensity is observed as indicated by the dotted line in Fig. 3. From the positions of the magnetic Bragg peaks alone, several spin structures can be deduced. The susceptibility data as shown above indicate that the easy axis is the b axis. This fact eliminates the possibility of some spin structures. The spin structure is basically as follows. The moments lie in the bc plane and are aligned ferromagnetically along the chain (c axis) and the b axis. From the incommensurability δ it is estimated that there is a rotation of spins by $2\pi/5$ along the a axis. The modulation of the intensity in Fig. 3 is probably

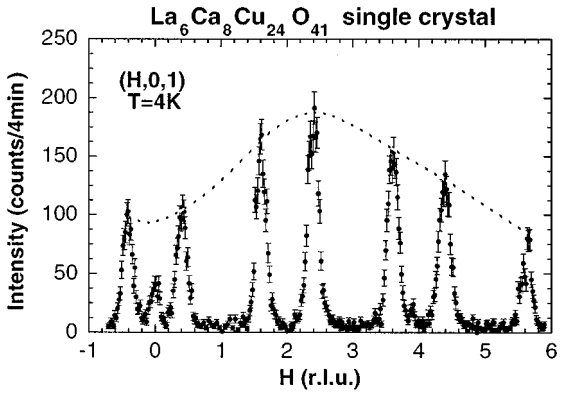

FIG. 3. An elastic neutron scan of $La_6Ca_8Cu_{24}O_{41}$ along $(H,0,1)$ at $T=4$ K measured with polarized neutrons in the horizontal field spin-flip mode. The dotted line is a guide to the eye.

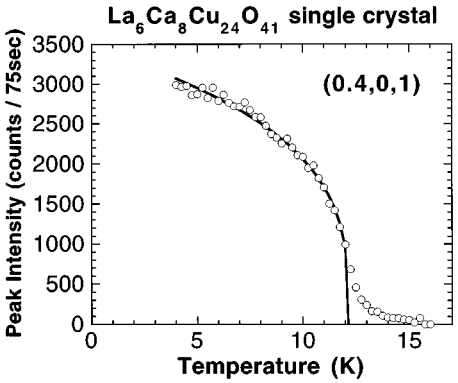

FIG. 4. Temperature dependence of peak intensity at (0.4,0,1) in $La_6Ca_8Cu_{24}O_{41}$ measured with unpolarized neutrons. The background (250 cts/75 s) was subtracted. The solid line is a power-low fit with $T_c = 12.20 \pm 0.05$ K and $2\beta = 0.31 \pm 0.02$.

caused by the c component. It is noted that the presence of a peak at (0,0,1) is not understood. Further study is needed to determine the exact mode of the modulation.

The temperature dependence of the peak intensity at (0.4,0,1) measured with unpolarized neutrons is shown in Fig. 4. The solid line shows the result of a power-low fit, which yields the transition temperature $T_c = 12.20 \pm 0.05$ K and a critical exponent $2\beta = 0.31 \pm 0.02$ over the range from 4 to 12 K. The fit unexpectedly describes the data down to a low temperature of $T_c/3$. The transition temperature is consistent with that obtained from the heat-capacity measurement.

The long-range magnetic ordering found in $La_6Ca_8Cu_{24}O_{41}$ gives a key to understand the dimerized singlet state in $Sr_{14}Cu_{24}O_{41}$. The singlet state means that the intradimer interaction is antiferromagnetic. The dimerized state in the chain of $Sr_{14}Cu_{24}O_{41}$ has a unique property in the sense that the dimers are formed between spins which are separated by two and four times the distance between the nearest-neighbor copper ions in the chain.[7] This is probably related with holes in the chain which couple with copper ions to form a singlet.[5] When the number of holes is reduced, the number of spins is increased. The ferromagnetic ordering in the chains of $La_6Ca_8Cu_{24}O_{41}$ indicates that the dimerized state in the chain becomes unstable due to the reduction of the holes which makes the ferromagnetic nearest-neighbor interactions more dominant and the antiferromagnetic further-neighbor interaction less dominant.

We now discuss the origin of the incommensurability observed in $La_6Ca_8Cu_{24}O_{41}$. A likely cause of incommensurability is a competition between nearest-neighbor (J_1) and second-neighbor (J_2) interactions along the a axis.[14] To realize the incommensurability of $2\pi/5$ in $La_6Ca_8Cu_{24}O_{41}$ $|J_2/J_1| \sim 0.8$ is required. It is puzzling that J_2 is so large in spite of the fact that this compound is an insulator and long-range coupling such as the RKKY interaction is not expected. Note that the spin structure of $La_6Ca_8Cu_{24}O_{41}$ is different from that observed in Li_2CuO_2 which has the similar CuO_2 chains as in $La_6Ca_8Cu_{24}O_{41}$. Li_2CuO_2 has a commensurate spin structure with ferromagnetic spin arrangement along the chain.[15]

In conclusion, we have found that the singlet state in the chains of $Sr_{14}Cu_{24}O_{41}$ becomes magnetic in $La_6Ca_8Cu_{24}O_{41}$ and that a magnetic ordering occurs at 12.20 ± 0.05 K. We have now established a modulated magnetic structure for the chains of $La_6Ca_8Cu_{24}O_{41}$. Further polarized neutron experiments and further unpolarized neutron experiments in the $(0,k,l)$ zone are now in progress. We also plan to make detailed model calculations to determine the exact spin structure.

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