PHYSICAL REVIEW B **68**, 060406(R) (2003)

Frustrating interactions and broadened magnetic excitations in the edge-sharing CuO_2 chains in $La_5Ca_9Cu_{24}O_{41}$

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(Received 19 May 2003; published 27 August 2003)

Inelastic neutron scattering measurements have been performed on $La_5Ca_9Cu_{24}O_{41}$, which consists of edge-sharing CuO_2 chains and shows an antiferromagnetic long-range order below $T_N = 10.5$ K with ferromagnetic arrangement within the chain. Although the intrachain coupling is expected to be ferromagnetic from the geometrical structure, it is found that the interactions are weakly antiferromagnetic both parallel and perpendicular to the chain and there exist frustrating interactions between them. It is also found that magnetic excitations are broadened significantly. The broadening is probably enhanced by the frustration and a disorder originating from a structural distortion and doped holes although the broadening at finite Q is expected even in the pure system without frustration and disorder.

DOI: 10.1103/PhysRevB.68.060406 PACS number(s): 75.40.Gb, 75.30.Ds, 75.10.Jm

One-dimensional (1D) cuprates have been studied extensively because they are good realization of spin (S) $\frac{1}{2}$ 1D Heisenberg magnets, which show novel phenomena originating from quantum fluctuations. Some copper oxides with 1D Cu^{2+} ions, which were discovered or rediscovered as high-T_c byproducts, are appropriate for studies in $S=\frac{1}{2}$ 1D Heisenberg magnets. Copper oxides with the edge-sharing CuO_2 chain, in which copper spins are coupled by the nearly 90° Cu-O-Cu interaction, are good candidates and exhibit various interesting phenomena. The sign and the absolute value of the exchange interaction between copper spins depend sensitively on the bond angle and the distance between copper and oxygen ions.[1] In particular, the $S=\frac{1}{2}$ 1D antiferromagnetic Heisenberg system is considered to be an interesting system since quantum effect is pronounced. On the other hand, ferromagnetic chains have been considered to be less interesting because quantum fluctuations are less significant. However, magnetic excitations from the ferromagnetic chains are considerably affected when a finite antiferromagnetic interchain coupling exists or frustration is introduced between the nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions in the chain.[2]

$La_{14-x}Ca_xCu_{24}O_{41}$ consists of both CuO_2 chains and Cu_2O_3 two-leg ladders.[3] The ground state of the Cu_2O_3 ladders is singlet with a large excitation gap of ~ 35 meV. An interesting feature in this system is that it can be hole doped. It is expected that, when the hole concentration is low, the holes are localized at oxygen sites in the chain and couple with the copper spins to form the Zhang-Rice singlet.

In this study we are interested in magnetism of the edge-sharing CuO_2 chains, which are shown in Fig. 1. The magnetic properties of the CuO_2 chains in $La_{14-x}Ca_xCu_{24}O_{41}$ were studied extensively.[4–6] The end material $La_6Ca_8Cu_{24}O_{41}$, which has no holes, shows a long-range magnetic order below 12.2 K. The Cu moments are aligned ferromagnetically along the chain (c axis) with antiferromagnetic correlations between NN chains along the b axis. The spins have a spiral structure along the a axis with a rotation angle of $\sim 2\pi/5$.[5] With hole doping, the transition temperature decreases gradually. $La_5Ca_9Cu_{24}O_{41}$, in which holes are slightly introduced ($\sim 10\%$), has an antiferromag-

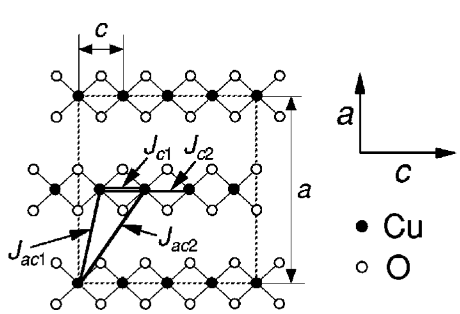

FIG. 1. Structure of the edge-sharing CuO_2 chains in the ac plane. Below $T_N = 10.5$ K the Cu^{2+} spins align ferromagnetically along the chain (c axis) with the propagation vector $\boldsymbol{k} = [110]$. The spins point along the b axis. J_{c1} and J_{ac1} are NN couplings along the c (chain) and (1/2, 0, 1/2) directions, respectively. J_{c2} is a NNN coupling along the c axis. J_{ac2} is a coupling along (1/2, 0, 3/2).

netic long-range order below $T_N=10.5$ K with a commensurate structure (ferromagnetic arrangement within the chain and antiferromagnetic correlations between chains).[6] The origin of the incommensurate magnetic structure in $La_6Ca_8Cu_{24}O_{41}$ is not known. One of the purposes of this study is to investigate the frustrated interactions from the viewpoint of magnetic excitations.

The most characteristic feature in this system is that the magnetic interactions are highly anisotropic. It was reported from the magnetization, heat capacity,[7] and electron spin resonance measurements[8] that the compound has an Ising-like anisotropy. This is unusual for Cu oxides, in which spin-orbit coupling is believed to be negligibly small. Therefore, it is important to measure spin-wave excitations and determine exchange interactions between Cu^{2+} moments. This study shows that the uniaxial anisotropic interaction is comparable with the isotropic interactions both parallel and perpendicular to the chain, which is unexpected from the geometrical structure. This gives rise to an enhancement of the Ising-like anisotropy. It is also found that the spin-wave excitations are broadened considerably. The broadening is probably enhanced by frustrating interactions between intra and interchain interactions and disorder caused by a structural distortion and doped holes. This behavior is also unexpected from the simple geometrical structure.

The single crystal of $La_5Ca_9Cu_{24}O_{41}$ was grown using a traveling solvent floating zone method at 3 bars oxygen atmosphere. The crystal used in this study was the one that was employed in the previous neutron-scattering study.[6] The lattice constants are $a=11.29$ Å, $b=12.58$ Å, and $c=2.761$ Å at 1.7 K.

The neutron scattering experiments were carried out on the IN8, IN12, and IN14 spectrometers installed at Institut Laue Langevin. The final neutron energy was fixed at $E_{\rm f}=8.0$ meV on IN8 and at $E{\rm f}=4.7$ meV on IN12 and IN14. Pyrolytic graphite (002) was used as monochromator and analyzer. Contamination from higher-order beam was effectively eliminated using a Be filter after the sample on IN12 and IN14. A pyrolytic graphite filter worked sufficiently well on IN8. The single crystals were mounted in a ^{4}He pumped cryostat, which allowed us to perform the measurements down to 1.5 K. The crystals were oriented in the $(h,0,l)$ scattering planes.

Figures 2 and 3 show typical inelastic neutron spectra observed at $(H,\ 0,\ L)$. Since we expected, by analogy with $Ca_2Y_2Cu_5O_{10}$, that the energy scale of the magnetic excitations is large, we first performed experiments with thermal neutrons on IN8. As shown in Fig. 2, the excitation energy is $\sim 2-3$ meV even around the zone boundary along the chain, indicating that the exchange interactions are not so large. It is also found that the peak width in energy is broader than the instrumental resolution. We then continued inelastic neutron scattering experiments using cold neutrons, with which high energy resolution experiments are possible in an energy range of $0.3\leqslant\omega\leqslant 5$ meV. Figure 3 shows excitation spectra measured on IN14. A relatively sharp peak can be seen around 1 meV at the zone center as shown in Fig. 3(a) although the peak width in energy is slightly larger than the instrumental resolution. The excitation peak becomes broader with increasing Q parallel and perpendicular to the chain as shown in Figs. 3(b) and 3(c), respectively.

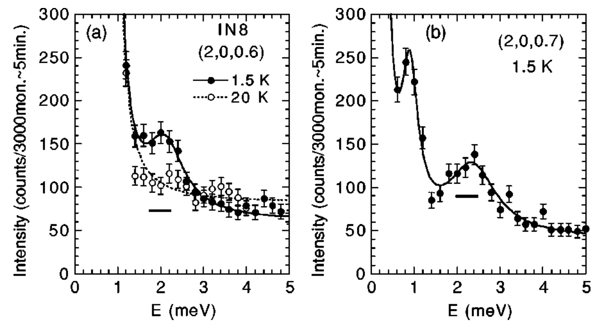

FIG. 2. Constant-Q scans at $(H,\ 0,\ L)$ measured on IN8 below and above T_N for the edge-sharing CuO_2 chain in $La_5Ca_9Cu_{24}O_{41}$. The solid lines are guides to the eyes. The horizontal bars represent the instrumental energy resolution. Note that the sharp peak at 0.9 meV in (b) is spurious.

Figure 4 shows the image plot of the inelastic neutron scattering intensity measured with cold neutrons. It is clear that the magnetic excitations are distinct only around the zone center. Although the excitation peak in energy is very broad so that the peak position is difficult to be determined except around the zone center [Figs. 3(b) and 3(c)], we could observe reasonably sharp peak in the medium Q region along a^* in constant-ω scans, as shown in Fig. 3(d). The peak positions are plotted in Fig. 4(b).

In order to analyze the observed dispersion relation, we used a model Hamiltonian that includes uniaxial anisotropy:

$$H=\sum_{i,j} J_{i,j}\boldsymbol{S}_i\cdot\boldsymbol{S}_j+\sum_{i,j} J''_{i,j}S^z_j\cdot S^z_j, \qquad (1)$$

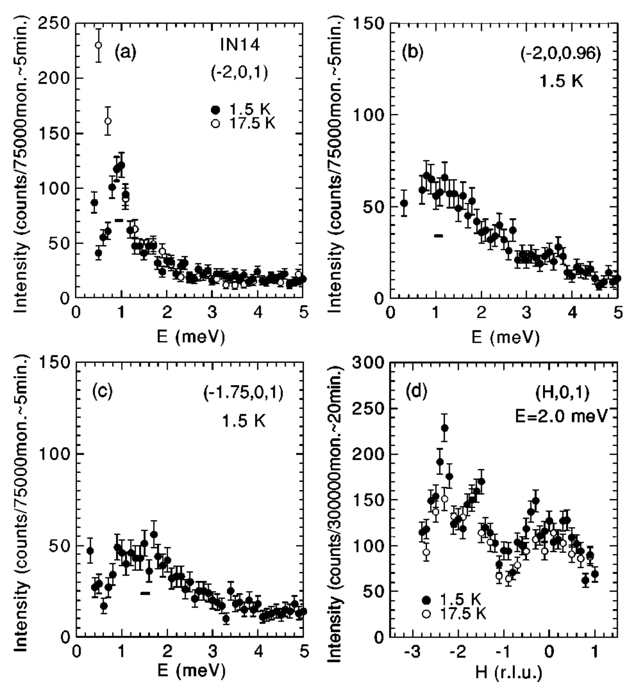

FIG. 3. Constant-Q and constant-ω scans at $(H,\ 0,\ L)$ measured on IN14 below and above T_N for the edge-sharing CuO_2 chain in $La_5Ca_9Cu_{24}O_{41}$. The horizontal bars represent the instrumental energy resolution.

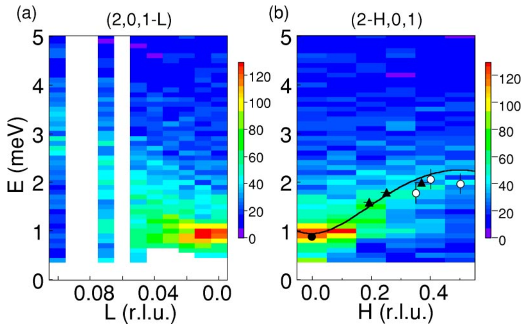

FIG. 4. (Color online) Image plot of the neutron scattering intensity in $\omega-Q_a$ and $\omega-Q_c$ (chain) space for the edge-sharing CuO_2 chain in $La_5Ca_9Cu_{24}O_{41}$. The filled and open circles represent data observed on IN14 and IN8, respectively. The circles and triangles represent data obtained in constant-Q and -ω scans, respectively. The solid curve represents the theoretical dispersion with $J_{ac1}=0.68$ meV and $D=-0.21$ meV.

where $J''=J^z-J^{x,y}$. In the calculation of the dispersion relation, we introduced NN couplings J_{c1} and J_{ac1} along the c (chain) and (1/2, 0, 1/2) directions, respectively. In addition to these interactions, a NNN coupling in the chain J_{c2}, a coupling along (1/2, 0, 3/2) J_{ac2}, and an effective uniaxial anisotropic interaction D (Ref. 9) are introduced. The interactions are shown in Fig. 1. Since the crystal structure in the ac plane in $La_5Ca_9Cu_{24}O_{41}$ is similar to that in $Ca_2Y_2Cu_5O_{10}$, the dispersion relation should be represented by the same equation.[10,11] The solid curve in Fig. 4(b) represents the result of a fit with $J_{ac1}=2J_{ac2}=0.681(1)$ meV and $D=-0.211(1)$ meV. The calculated values reproduce the experimental result reasonably well. The excitation gap at the zone center originates from the uniaxial anisotropy along the b axis probably originating from an anisotropic exchange interaction. The interchain coupling (0.68 meV) is consistent with another compounds such as $Sr_{14}Cu_{24}O_{41}$ [1.7 meV (Ref. 12) and 0.75 meV (Ref. 13)] and $Ca_2Y_2Cu_5O_{10}$ (1.494 meV),[10] which has an arrangement of the edge-sharing CuO_2 chains similar to that in $La_5Ca_9Cu_{24}O_{41}$.

Figure 5 shows the observed excitation energies along chain direction. The broken curve in Fig. 5 represents the result of a fit with using only $J_{c1}=0.01(7)$ meV along the chain. Other interactions are fixed at the values determined above. The dip around the zone boundary cannot be reproduced only with J_{c1}. The solid curve represents the result of a fit with $J_{c1}=0.20(7)$ meV and $J_{c2}=-0.18(5)$ meV. The calculated values reproduce the experimental result reasonably well.

The antiferromagnetic NN and ferromagnetic NNN interactions prefer an antiferromagnetic order in the chain even when the magnetic arrangement is ferromagnetic along the chain. On the other hand, the antiferromagnetic interchain couplings J_{ac1} and J_{ac2} are comparable to J_{c1} and have a number of bonds twice as much as that of J_{c1}. Although there exists competing interactions between the intrachain couplings (J_{c1} and J_{c2}) and interchain couplings (J_{ac1} and J_{ac2}), the latter is dominant and the magnetic arrangement in the chain becomes ferromagnetic. It is noted that the end material $La_6Ca_8Cu_{24}O_{41}$ shows an incommensurate magnetic structure perpendicular to the chain (a axis) with ferromagnetic arrangement along the chain.[5] It is possible that the incommensurate structure is realized because of a delicate balance of the frustrating interactions between the intra- and interchain interactions.

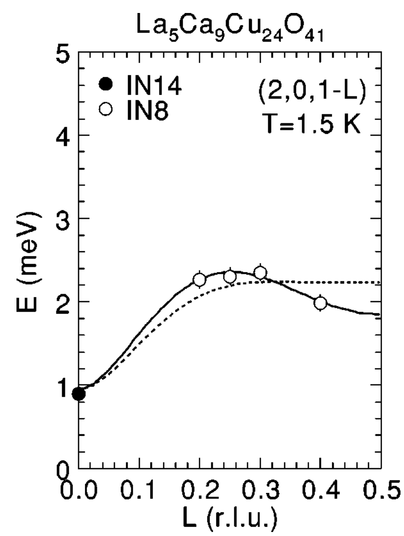

FIG. 5. $\omega-Q$ dispersion relation along the c (chain) axis for the edge-sharing CuO_2 chain in $La_5Ca_9Cu_{24}O_{41}$. The solid curve represents the theoretical ones with $J_{c1}=0.2$ meV, $J_{c2}=-0.18$ meV, $J_{ac1}=0.68$ meV, $J_{ac2}=0.34$ meV, and $D=-0.21$ meV. All the data were obtained in constant-Q scans. The broken curve represents the theoretical one with $J_{c1}=0.01$ meV, $J_{ac1}=0.68$ meV, $J_{ac2}=0.34$ meV, and $D=-0.21$ meV.

The magnetic interactions in $La_5Ca_9Cu_{24}O_{41}$ determined in this study are remarkable. The NN interaction is unexpectedly weak and antiferromagnetic. It is also found that frustration exists between the intra and interchain interactions. This is in contrast to the results of theoretical calculations[1] and also to the experimental results in the related compound $Ca_2Y_2Cu_5O_{10}$.[10] A theoretical calculation showed that the NN interaction in the chain is ferromagnetic and rather large (-18.5 meV) in $La_6Ca_8Cu_{24}O_{41}$.[1,14] In $Ca_2Y_2Cu_5O_{10}$, which has the same magnetic structure as in $La_5Ca_9Cu_{24}O_{41}$ in the ac plane, the ferromagnetic NN interaction is fairly large (~-8 meV).[10] Another puzzling feature is that the Néel temperature of 10.5 K is rather large for the weak and frustrating interactions. Therefore, there may be some uncertainties in our model for the magnetic interactions, in which just a minimum number of interactions is included. At present it is difficult to improve the model although further interactions may be needed. Detailed theoretical work is desired to fully understand the anomalous low-energy excitations in $La_5Ca_9Cu_{24}O_{41}$.

It is interesting to compare the result with that of magnetization and heat capacity measurements, which shows no spin-flop transition,[7] suggesting an Ising-like behavior in this compound. It was also shown that the uniaxial anisotropy perpendicular to the CuO_4 tetragon is not negligible in $Ca_2Y_2Cu_5O_{10}$ (Ref. 10) and Li_2CuO_2,[15] which has edge-sharing CuO_2 chains and shows an antiferromagnetic order below 9.3 K.[16] This originates from the large spin-orbit coupling.[17,18] The value of the anisotropic interaction -0.21 meV is similar to ~ -0.3 meV (Ref. 10) in $Ca_2Y_2Cu_5O_{10}$ and -0.31 meV (Ref. 15) in Li_2CuO_2. In $Ca_2Y_2Cu_5O_{10}$ the anisotropy is not effective since the isotropic exchange interaction in the chain is much larger and dominant. In $La_5Ca_9Cu_{24}O_{41}$ the anisotropic interaction is comparable to isotropic interactions so that the anisotropic behavior is much enhanced. Therefore, the anisotropic behavior occurs accidentally because of the anomalously small isotropic exchange interactions.

We now discuss the broadening of the spin-wave excitations. As described above, we observed very broad magnetic excitations even in the long-range magnetic ordered phase. The broadening is observed even at the zone center although the broadening becomes much larger at higher Q. This behavior is qualitatively similar to that in $Ca_2Y_2Cu_5O_{10}$.[10] Since there exist frustrating interactions in $La_5Ca_9Cu_{24}O_{41}$, the broadening should be much larger.[2] There are other possibilities to make the excitation broadened. One possibility is the small but non-negligible holes ($\sim 10\%$), which probably induce localized nonmagnetic sites in this system. A disorder caused by the nonmagnetic impurities probably enhances the broadening of the excitation. Another possibility is the small structural distortion caused by the connection between the Cu_2O_3 ladder planes and the CuO_2 chains.[3] This would also broaden the magnetic excitations.

Finally, we compare the result in $La_5Ca_9Cu_{24}O_{41}$ with that in Li_2CuO_2. The weak and antiferromagnetic NN interaction and the frustration between intra and interchain couplings were also reported in Li_2CuO_2.[15] If this is the case, the behavior is quite similar to that in $La_5Ca_9Cu_{24}O_{41}$. However, there is another interpretation for their data. Mizuno *et al.* first calculated the exchange interactions in Li_2CuO_2.[2] They estimated a ferromagnetic NN (-8.6 meV) and an antiferromagnetic NNN interaction (3.4 meV) along the chain. Using these interactions, they calculated $S(Q,\omega)$ along the chain, which also reproduces the observed data. Although the anisotropic interaction can be comparable to isotropic interactions also in Li_2CuO_2,[15] a spin-flop transition was observed,[19] suggesting a less pronounced Ising-like character. Therefore, the possibility of a relatively large ferromagnetic NN interaction cannot be excluded.

In summary, the magnetic excitations in the edge-sharing CuO_2 chains in $La_5Ca_9Cu_{24}O_{41}$ show anomalous properties although the geometrical structure is rather simple. It is revealed that the uniaxial anisotropy, which is characteristic in this system, is enhanced because the isotropic interactions both parallel and perpendicular to the chain are comparable to it. The broadened excitations are observed even when the magnetic order is static and long ranged. The broadening is probably enhanced by the frustrating interactions between intra and interchain interactions and the disorder originating from the structural distortion and doped holes although the broadening at finite Q is expected even in the pure system such as $Ca_2Y_2Cu_5O_{10}$, which is not frustrated and not disordered.

This work was partially supported by the U.S.-Japan Cooperative Program on Neutron Scattering operated by the U. S. Department of Energy and the Japanese Ministry of Education, Science, Sports, and Culture. Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-76CH00016, Division of Material Science, U. S. Department of Energy.

[1] Y. Mizuno, T. Tohyama, S. Maekawa, T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **57**, 5326 (1998).

[2] Y. Mizuno, T. Tohyama, and S. Maekawa, Phys. Rev. B **60**, 6230 (1999).

[3] T. Siegrist, L.F. Schneemeyer, S.A. Sunshine, J.V. Waszczak, and R.S. Roth, Mater. Res. Bull. **23**, 1429 (1988).

[4] S.A. Carter, B. Batlogg, R.J. Cava, J.J. Krajewski, W.F. Peck, Jr., and T.M. Rice, Phys. Rev. Lett. **77**, 1378 (1996).

[5] M. Matsuda, K. Katsumata, T. Yokoo, S.M. Shapiro, and G. Shirane, Phys. Rev. B **54**, R15626 (1996).

[6] M. Matsuda, K.M. Kojima, Y.J. Uemura, J.L. Zarestky, K. Nakajima, K. Kakurai, T. Yokoo, S.M. Shapiro, and G. Shirane, Phys. Rev. B **57**, 11467 (1998).

[7] U. Ammerahl, B. Büchner, C. Kerpen, R. Gross, and A. Revcolevschi, Phys. Rev. B **62**, R3592 (2000).

[8] V. Kataev, K.-Y. Choi, M. Grüninger, U. Ammerahl, B. Büchner, A. Freimuth, and A. Revcolevschi, Phys. Rev. Lett. **86**, 2882 (2001).

[9] $D = J''_{ac1} + J''_{ac2} - J''_{c1} - J''_{c2}$. The uniaxial anisotropy along the b axis is expected from the result of magnetic susceptibility measurements in Ref. 6.

[10] M. Matsuda, H. Yamaguchi, T. Ito, C.H. Lee, K. Oka, Y. Mizuno, T. Tohyama, S. Maekawa, and K. Kakurai, Phys. Rev. B **63**, 180403(R) (2001).

[11] It is noted that the crystal axes are different in two compounds. The a and c axes in $La_5Ca_9Cu_24O_{41}$ correspond to the c and a axes in $Ca_2Y_2Cu_5O_{10}$, respectively.

[12] L.P. Regnault, J.P. Boucher, H. Moudden, J.E. Lorenzo, A. Hiess, U. Ammerahl, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **59**, 1055 (1999).

[13] M. Matsuda, T. Yosihama, K. Kakurai, and G. Shirane, Phys. Rev. B **59**, 1060 (1999).

[14] One reason for the discrepancy would be that the calculation was based on homogeneous chains although the chains are slightly distorted and there are nine different bond distances between Cu and O in the edge-sharing CuO_2 chains (Ref. 3).

[15] M. Boehm, S. Coad, B. Roessli, A. Zheludev, M. Zolliker, P. Boeni, D.McK. Paul, H. Eisaki, N. Motoyama, and S. Uchida, Europhys. Lett. **43**, 77 (1998).

[16] A. Sapiña, J. Rodriguez-Carvajal, M.J. Sanchis, R. Ibanez, A. Beltran, and D. Beltran, Solid State Commun. **74**, 779 (1990).

[17] V.Y. Yushankhai and R. Hayn, Europhys. Lett. **47**, 116 (1999).

[18] S. Tornow, O. Entin-Wohlman, and A. Aharony, Phys. Rev. B **60**, 10206 (1999).

[19] H. Ohta, N. Yamauchi, T. Nanba, M. Motokawa, S. Kawamata, and K. Okuda, J. Phys. Soc. Jpn. **62**, 785 (1993).