Interchain interactions and magnetic properties of Li_2CuO_2

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An effective Hamiltonian is constructed for an insulating cuprate with edge-sharing chains Li_2CuO_2. The Hamiltonian contains the nearest and next-nearest neighboring intrachain and zigzag-type interchain interactions. The values of the interactions are obtained from the analysis of the magnetic susceptibility, and this system is found to be described as coupled frustrated chains. We calculate the dynamical spin correlation function $S(\mathbf{q},\omega)$ by using the exact diagonalization method, and show that the spectra of $S(\mathbf{q},\omega)$ are characterized by the zigzag-type interchain interactions. The results of the recent inelastic neutron-scattering experiment are discussed in the light of the calculated spectra. [S0163-1829(99)11133-0]

One-dimensional cuprates have received much attention as reference systems of high-T_c superconductors with two-dimensional CuO_2 planes. Recently, a variety of the compounds with edge-sharing chains, where CuO_4 tetragons are coupled by their edges, were synthesized and found to show unique physical properties. Li_2CuO_2 is one of the typical compounds having such chains. As shown in Fig. 1(a), the chains run parallel to the *b* axis and are stacked along *a* and *c* axes.[1]

An important feature of the edge-sharing chains is that a nearest-neighboring (NN) magnetic interaction J_1 between Cu spins strongly depends on Cu-O-Cu bond angle θ. In the case that $\theta=90°$, the superexchange process via O ions, which contributes to antiferromagnetic (AFM) interaction, is suppressed due to the orthogonality of Cu $3d$ and O $2p$ orbitals, and ferromagnetic (FM) contribution caused by, for example, direct exchange mechanism between Cu $3d$ and O $2p$ orbitals, becomes dominant.[2,3] With increasing θ, the AFM superexchange interaction increases, and consequently J_1 changes from FM to AFM interaction at a critical angle θ_c. In an earlier study,[3] θ_c was estimated to be about 95° from the cluster calculation. For Li_2CuO_2 with $\theta=94°$, J_1 was evaluated to be FM (<0) with magnitude of 100 K. In addition to J_1, a next-nearest-neighboring (NNN) magnetic interaction J_2, which comes from Cu-O-O-Cu path, also plays an important role in the magnetic properties. The interaction J_2 is AFM (>0), and its magnitude is known to be comparable to $|J_1|$. Therefore, an appropriate model describing the edge-sharing chain is a spin-1/2 Heisenberg model with NN and NNN interactions (a J_1-J_2 model). The ground state of the J_1-J_2 model has been extensively studied:[4] For $J_2/|J_1|<1/4$, it is a FM state, while for $J_2/|J_1|>1/4$, it is a frustrated state with incommensurate spin correlation.

In Li_2CuO_2, AFM long-range order occurs at $T_N=9$ K, and the magnetic structure below T_N is FM along *a* and *b* axes and AFM along the *c* axis.[1] The recent inelastic neutron-scattering experiment showed the existance of interchain (IC) interactions that bring about the ordering.[5] The analysis of the dispersions along *a* and *c* axes in the linear spin-wave theory revealed that the IC interaction between NN Cu spins is of the order of 10 K. The band calculation also showed the existence of large effective hoppings between neighboring chains, and thus the superexchange interactions.[6] Following these facts, IC interaction plays an important role in the magnetic properties of Li_2CuO_2. The importance of IC interactions has also been pointed out in

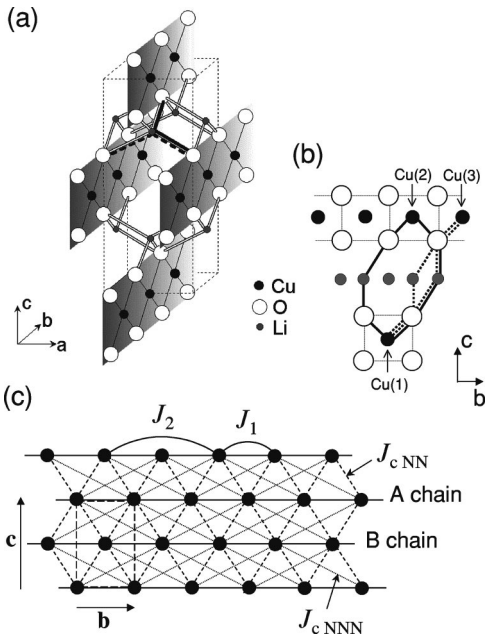

FIG. 1. (a) The crystal structure of Li_2CuO_2. The solid, open, and hatched circles denote Cu, O, and Li ions, respectively. The edge-sharing chains run along the *b* axis, and are stacked along *a* and *c* axes. The thin solid and open lines connect intrachain and interchain neighboring ions, respectively. The thick solid and dotted lines represent paths that give the IC interactions along *c* and *a* axes via Li ions, respectively. (b) The schematic picture of Cu-O-Li-O-Cu paths. NN Cu ions [Cu(1) and Cu(2)] and NNN Cu ions [Cu(1) and Cu(3)] in *c* direction are connected by the paths depicted by two solid and two dotted lines, respectively. (c) The J_1-J_2-J_c model. The Cu sites with $S=1/2$ spin are depicted by the solid circles. J_1 and J_2 are interactions between NN and NNN Cu spins in chains. Two chains are coupled by IC interactions $J_{c\mathrm{NN}}$ and $J_{c\mathrm{NNN}}$, which work between NN and NNN Cu spins in different chains, respectively. We take $J_{c\mathrm{NN}}=J_{c\mathrm{NNN}}\equiv J_c$. $\mathbf{b}=b\mathbf{e}_b$ and $\mathbf{c}=c\mathbf{e}_c$ are the primitive vectors. The rectangle represented by the broken lines denotes a unit cell.

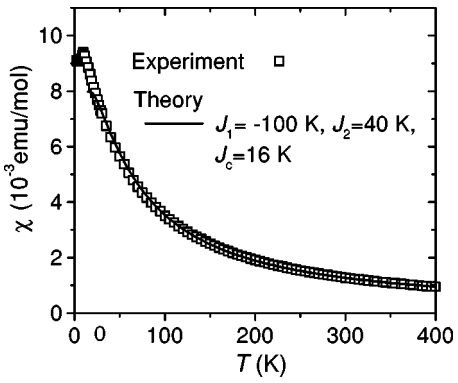

FIG. 2. The magnetic susceptibility $\chi(T)$ of Li_2CuO_2. The square symbols denote the experimental results in the magnetic field applied along the chains from Ref. 3. The solid curve is the theoretical result in the J_1-J_2-J_c model with $J_1=-100$ K, $J_2=40$ K, and $J_c=16$ K, obtained numerically on the system with 8×2 sites. g factor is taken to be 2 from Ref. 10.

other edge-sharing cuprates, $CuGeO_3$ (Ref. 7) and $Sr_{14}Cu_{24}O_{41}$ (Refs. 8,9).

In this paper, paying attention to the IC interaction, we examine the magnetic properties of Li_2CuO_2, such as magnetic susceptibility and magnetic excitation, by applying the exact diagonalization method on finite-size clusters. We construct a minimal model, taking into account the IC interaction to the J_1-J_2 model. A set of parameter values is obtained from the analysis of the temperature dependence of the magnetic susceptibility $\chi(T)$. We find that the compound is described as a system with frustrated chains coupled by zigzag-type IC interactions. In order to examine the magnetic excitation, we calculate the dynamical spin correlation function $S(\mathbf{q},\omega)$ in the chain direction. The calculated spectra show a flat dispersion caused by the frustration due to J_2 in the low-energy region. On the other hand, in the high-energy region, there is a dispersion, the energy position of which corresponds to that obtained from the linear spin-wave theory. The spectra of the dispersion are, however, broad. We show that this dispersion is brought about by the IC interaction with zigzag-type structure. The experimental results are discussed in the light of our theoretical results.

We first construct a minimal model for Li_2CuO_2 including IC interaction. As shown in Fig. 1(a), Li ions are located between the chains. The IC interaction works in a and c directions via Li ions. Since the hatched chains in Fig. 1(a) are situated in the b-c plane, the orbitals relevant to the electronic states in each chain are Cu $3d_{y^2-z^2}$ and O $2p_{y,z}$ ones. The possible paths that give IC interactions along c axis J_c and along a axis J_a are shown in Fig. 1(a) by thick solid and dotted lines, respectively. For J_c (solid line), the orbitals of Li ions (Li $1s$, $2s$) couple to O $2p_x$ in *one* chain, but to O $2p_{y,z}$ orbitals in *another* one. On the other hand, for J_a, they couple to only O $2p_x$ orbitals in *both* chains. As a result, the magnitude of J_a is expected to be much smaller than that of J_c due to orthogonality of Cu $3d_{y^2-z^2}$ and O $2p_x$ orbitals. In fact, the neutron scattering experiment[5] indicates that the width of magnon dispersion along a axis is narrower than that along c axis, and J_a is ~4 K, which is less than half of J_c. In the present study, we neglect J_a for simplicity.

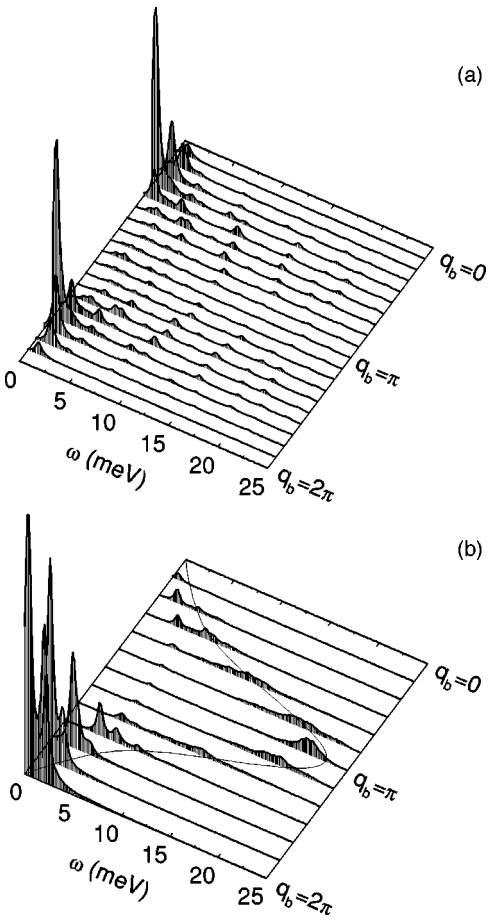

FIG. 3. (a) $S(\mathbf{q},\omega)$ along the chain direction q_b with $J_1=-100$ K, $J_2=40$ K, and $J_c=0$ K. The chain has 20 sites. (b) The same as (a) but $J_c=16$ K. The system has 12×2 sites, simulating the coupled edge-sharing chains in Li_2CuO_2. The δ functions are convoluted with a Lorentzian broadening of 0.3 meV. The thin solid curve denotes a magnon dispersion [Eq. (3)] obtained by the linear-spin-wave theory.

For J_c, there are two paths connecting between NN Cu ions [Cu(1) and Cu(2)] and between NNN Cu ions [Cu(1) and Cu(3)] as shown by two solid and two dotted lines in Fig. 1(b), respectively. They give rise to zigzag-type IC interactions between NN Cu spins and between NNN ones, $J_{c\mathrm{NN}}$ and $J_{c\mathrm{NNN}}$, respectively. From the consideration of the crystal structure and the orbital configuration, the magnitudes of $J_{c\mathrm{NN}}$ and $J_{c\mathrm{NNN}}$ are found to be the same because each path makes an equal contribution to the two interactions. Therefore, we take $J_{c\mathrm{NN}}=J_{c\mathrm{NNN}}\equiv J_c$.

Based on the above consideration, we adopt a J_1-J_2-J_c model shown in Fig. 1(c). In the previous study,[3] J_1 was evaluated to be -100 K. We determine J_2 and J_c based on the analysis of the experimental data of $\chi(T)$. By diagonalizing the Hamiltonian of the J_1-J_2-J_c model for finite-size clusters with $M\times N$ sites (M is the number of sites in a chain and N is the number of chains), the theoretical $\chi(T)$ is obtained. We preliminarily calculated it in 4×2 and 4×4 clusters in order to check the size effect along the IC direction (N dependence), and found that the difference of $\chi(T)$ between $N=2$ and 4 is so small that clusters with $N=2$ are enough to investigate the effect of the IC interaction on $\chi(T)$. In Fig. 2, we show the result for an 8×2 cluster by

solid line together with the experimental data denoted by square symbols. A good agreement between theory and experiment is obtained for $J_2=40$ K and $J_c=16$ K. This value of J_c is not far from the value determined by the neutron-scattering experiment.[5] The theoretical results of $\chi(T)$ reproduce well the divergent behavior of the experimental ones at low temperatures. We examined $\chi(T)$ of the single chain (the J_1-J_2 model) in the previous study,[3] and obtained a peak in $\chi(T)$ at $T=40$ K. Therefore, we conclude that $\chi(T)$ is not explained unless J_c is not taken into account.

Next, we calculate the dynamical spin-correlation function $S(\mathbf{q},\omega)$ in order to investigate the magnetic excitation. This is defined as follows:

$$S(\mathbf{q},\omega)=\sum_m |\langle m|S^z_{\mathbf{q}}|0\rangle|^2 \delta(\omega-E_m+E_0), \tag{1}$$

where $|0\rangle$ and $|m\rangle$ are the ground and excited states with energies E_0 and E_m, respectively. $S^z_{\mathbf{q}}$ is the Fourier transform of spatial spin density.

It is instructive to consider $S(\mathbf{q},\omega)$ for the single chain ($J_c=0$ case) in order to understand the effect of IC interaction on the magnetic excitation. The calculation is performed by applying the exact diagonalization technique on a 20-site single chain with $J_1=-100$ K and $J_2=40$ K. Because the ratio of $J_2/|J_1|(=0.4)$ is more than 1/4, the system is described as a frustrated chain. The calculated results of $S(\mathbf{q},\omega)$ are shown in Fig. 3(a), in which q_b denotes a momentum of the chain direction. The spectra have a period of 2π, and are symmetric with respect to $q_b=\pi$. Since the ground state has incommensurate spin correlation, the spectral intensity is much larger at $q_b\sim 1/2\pi$ and $3/2\pi$ than that at other momenta. Much of the spectral weight is concentrated in the very low-energy region ($\omega\lesssim 2$ meV), and small weight spreads over the high-energy region.

We turn our attention to the system with finite J_c. Since we are interested in the effect of the IC interaction on the spectra of frustrated chain, $S(\mathbf{q},\omega)$ along the chain direction is examined. $S(\mathbf{q},\omega)$'s for 12×2 and 6×4 clusters, where $\mathbf{q}$ is the two-dimensional vector with $\mathbf{q}=(q_b,q_c)$, are calculated to understand the effect of the IC interaction. By comparing results between the two clusters, we found that there is no essential difference along the chain direction. Therefore, we consider $S(\mathbf{q},\omega)$ for the 12×2 cluster.

The operator $S^z_{\mathbf{q}}$ for the 12×2 cluster is written as

$$S^z_{\mathbf{q}}=\frac{1}{\sqrt{N_s}}\sum_i e^{iq_by_i}(S^z_{A,i}+S^z_{B,i}e^{i(q_b/2+q_c/2)}), \tag{2}$$

where $S^z_{A,i}$ and $S^z_{B,i}$ are the z component of spin operators at ith sites on A and B chains in Fig. 1(c), respectively. y_i is the y component of the position vector at ith sites, and N_s is the number of Cu sites. Since in the case of finite J_c, the system has two Cu sites in unit cell as shown in Fig. 1(c), the lattice period in the chain direction is changed from $|\mathbf{b}|$ to $|\mathbf{b}|/2$. Correspondingly, the period of $S(\mathbf{q},\omega)$ is changed from 2π to 4π.

The result of $S(\mathbf{q},\omega)$ for the 12×2 cluster is shown in Fig. 3(b), where the momentum of q_c is taken to be 0.[11] The spectrum is completely different from that for the single chain shown in Fig. 3(a). The strong intensity is seen at $q_b\sim 2\pi$, and thus the spectrum becomes asymmetric with respect to $q_b=\pi$. The asymmetry is understood as follows. For example, consider the spectra at $\mathbf{q}=(0,0)$ and $(2\pi,0)$. $S^z_{\mathbf{q}}$ at these momenta is given by $(1/\sqrt{N_s})\Sigma_i(S^z_{A,i}+S^z_{B,i})$ and $(1/\sqrt{N_s})\Sigma_i(S^z_{A,i}-S^z_{B,i})$, respectively. From these expressions, it is clear that the weight at $\mathbf{q}=(2\pi,0)$ is larger than that at $\mathbf{q}=(0,0)$, when the A and B chains are coupled antiferromagnetically. A flat dispersion with small intensity is seen around $q_b\sim\pi$ at $\omega\lesssim 5$ meV. This is a remnant of the continuum seen in Fig. 3(a). In addition, a dispersive spectrum with energy maximum at $q_b=\pi$ is seen in Fig. 3(b). This dispersion is consistent with that obtained by the linear spin-wave theory in which the intrachain FM and interchain AFM ordering is assumed;

$$\omega(q_b)=\left([J_1(\cos q_b-1)+J_2(\cos 2q_b-1)+8J_c]^2-64J_c^2\cos^2 q_b\cos^2\frac{q_b}{2}\right)^{1/2}. \tag{3}$$

Here, we note that J_c of zigzag type is responsible for this dispersion. J_c connects *four* spins in a chain with *one* spin in the neighboring chain as shown in Fig. 1(c). Therefore, these *four* spins tend to align parallel so as to reduce the magnetic energy. This is why the IC interactions have a large contribution to the dispersion. The spectra of the dispersion are rather broad. This is clearly different from the single-peak structure in a simple FM chain. This is because FM alignment in the chain is disturbed by the quantum fluctuation caused by J_c and frustration by J_2.

Finally, we discuss the recent inelastic neutron-scattering data along b axis for Li_2CuO_2 in the light of our theoretical results. The experiment has shown that (i) when the momentum is far from magnetic zone center $q_b=2\pi$, the spectral intensity is very small, and (ii) the lowest excitation appears at the magnetic zone center, and the dispersion has a minimum at $q_b=\pi$.[5] The feature (i) is in good agreement with the momentum dependence of the spectral intensity shown in Fig. 3(b).[12] For the feature (ii), the structure at π in the experiment may correspond to that at $\omega\lesssim 5$ meV which is a remnant of the frustrated state.[13] On the other hand, the dispersion at $\omega\lesssim 20$ meV has not been observed experimentally. In order to find the dispersion, it will be necessary to do more detailed experiments, especially in the higher-energy region.

We have studied the magnetic excitation spectra of Li_2CuO_2, and found that the zigzag-type IC interaction brings about the dramatic difference seen in the spectra between Figs. 3(a) and 3(b). Therefore, it is meaningful to examine the spectra of other edge-sharing compounds such as

$La_6Ca_8Cu_{24}O_{41}$ and $Ca_2Y_2Cu_5O_{10}$ because they have different IC interactions, reflecting the difference of the crystal structures. For example, in $La_6Ca_8Cu_{24}O_{41}$, which has the structure similar to $Sr_{14}Cu_{24}O_{41}$, IC interactions are expected to be smaller than that in Li_2CuO_2.[8,9] We thus suppose that the weight of the dispersion at the high-energy region ($\lesssim 20$ meV) is very small and much of the weight is concentrated in the low-energy region ($\lesssim 5$ meV) in $La_6Ca_8Cu_{24}O_{41}$ in contrast to Li_2CuO_2. A comparison among these materials will yield a clearer understanding of the effect of IC interactions on the magnetic excitation.

In summary, we have investigated the magnetic properties of Li_2CuO_2 with edge-sharing chains, taking into account the interchain interaction. We determined the magnetic interactions in a chain and between chains by the analysis of the magnetic susceptibility. We also calculated the dynamical spin correlation function. The results show a dispersion with broad spectra induced by the interchain interaction. The zigzag-type interchain interaction causes the dramatic effects on the magnetic properties of Li_2CuO_2. It is highly desirable that the inelastic neutron-scattering experiment be performed in the wide energy region to understand the characteristics of the dispersion along the chain.

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[11] In the 12×2 cluster, $q_c=0$ and 2π are defined. Since $S(\mathbf{q},\omega)$ at $\mathbf{q}=(q_b,0)$ is equivalent to that at $\mathbf{q}=(2\pi-q_b,\pi)$, we show only the results with $q_c=0$.

[12] The experiment shows a gap due to anisotropy of magnetic interactions (Ref. 5). We have checked the effect of the anisotropy on $S(\mathbf{q},\omega)$, and confirmed that the feature of the spectral structure is unchanged except the opening of a small gap.

[13] Because the minimum exists at $q_b=\pi$, it has been concluded that J_1 is AFM and J_2 is FM (Ref. 5). We also calculated $S(\mathbf{q},\omega)$ for the case that J_1 is AFM and J_2 is FM. In this case, the intensity at $q_b=\pi$ becomes much larger than those at other momenta, which suggests that the spectrum at π should be observed distinctly. However, the experimental data show rather large error bars for the dispersion along the chain (Ref. 5).