Singularities in Optical Spectra of Quantum Spin Chains

H. Suzuura, H. Yasuhara, A. Furusaki, N. Nagaosa, and Y. Tokura
Department of Applied Physics, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan
(Received 5 January 1996)

The midinfrared optical absorption spectrum is reported of the one-dimensional Mott insulator Sr_2CuO_3. The spectrum has an asymmetric cusplike structure at 0.48 eV and is analyzed in terms of the phonon-assisted absorption in the one-dimensional quantum spin chain model. A good agreement is obtained between experiment and theory, and the exchange energy J is estimated to be $J \approx 0.26$ eV, which is consistent with the magnetic susceptibility measurement.

PACS numbers: 75.40.Gb, 75.50.Ee, 78.30.Hv

Infrared optical spectra of the undoped high-T_c cuprates have recently attracted great attention because they are expected to offer detailed information on the spin dynamics of these materials, which is believed to be essential to the understanding of the high-T_c superconductivity. The interpretation of the midinfrared optical properties, however, is still controversial. Since the ordinary optical transition due to a dipole interaction between an electron and a photon does not couple with electrons' spin degrees of freedom, other mechanisms are needed for explaining absorption spectra involving spin excitations. Perkins *et al.* [1] interpreted their midinfrared optical data in terms of the exciton at 0.4 eV from $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$ transition accompanied by the higher energy structures of the multimagnon sidebands [2].

On the other hand, Lorenzana and Sawatzky (LS) [3] proposed another mechanism, i.e., phonon-assisted multimagnon absorption, and ascribed the peak structure at 0.4 eV to the two-magnon virtual bound state. For a CuO layer, they considered a three-band Peierls-Hubbard model in the presence of an electric field, in which only O ions can move. They perturbatively derived an effective dipole moment for processes involving one phonon and spin excitations:

$$P_\alpha = \mu \sum_n u_{n+\alpha/2} \mathbf{S}_n \cdot \mathbf{S}_{n+\alpha} \qquad (\alpha = \hat{x}, \hat{y}), \qquad (1)$$

where μ is an effective charge associated with those processes and $u_{n+\alpha/2}$ displacement of the O ion between nth and $(n + \alpha)$th Cu sites.

In their recent experiment Perkins *et al.* measured optical spectra of La_2NiO_4 [4]. In this material the configuration of Ni ions is d^8, and the two spins in the two e_g orbitals are parallel due to the strong Hund coupling. The transition from $d_{x^2-y^2}$ to $d_{3z^2-r^2}$ is thus forbidden by the Pauli exclusion principle. They observed a peak at 0.25 eV, which is attributed to the LS's phonon-assisted creation of the two-magnon virtual bound state. Unlike La_2CuO_4, no higher energy structures are observed, suggesting that the structures from 0.4 to 1.0 eV observed in La_2CuO_4 are due to sidebands to the crystal field excitons, as originally proposed in Ref. [1].

There exist one-dimensional (1D) analogs of these materials, e.g., Sr_2CuO_3 and Ca_2CuO_3, which have 1D CuO chains. In these compounds the interchain exchange interaction is very weak compared with the intrachain exchange energy $J \sim 10^3$ K, and the three-dimensional antiferromagnetic long-range order is absent down to very low temperature ($T_N \approx 5$ K in Sr_2CuO_3). Therefore they are ideal systems for studying 1D quantum spin liquid, where the spin wave or magnon is no longer a useful concept. Thus it is particularly interesting to study by optical measurements the dynamics of spin liquids which have quantum coherency in contrast to the thermally disordered classical liquid. This coherency will manifest itself as a well-defined singular structure in the optical spectrum, which cannot be observed in incoherent classical liquids.

In this Letter we report the midinfrared optical absorption spectra of Sr_2CuO_3. We found for the first time a cusplike singularity in the line shape which is of magnetic origin and unique to the 1D system. The detailed analysis of the line shape in terms of the quantum spin chain model reproduces the observed spectrum very well and gives an accurate estimation of the exchange energy J. These results prove the usefulness of the optical means to study the coherent quantum dynamics of the one-dimensional spin liquid.

Single crystals of Sr_2CuO_3 and Ca_2CuO_3 with the 1D CuO chain structure were grown by the traveling-solvent floating-zone method, the details of which will be published elsewhere [5]. A thin plate of the specimen with the developed (100) face was cleaved out from the crystal ingot and then further polished to a prescribed thickness (about 50 μm) for measurements of optical transmittance by Fourier transformation spectroscopy (for <0.7 eV) and grating spectroscopy (for >0.4 eV). We show in Fig. 1 the optical absorption spectra of Sr_2CuO_3 in the midinfrared region below the onset of the strong charge-transfer $(2p\text{-}3d)$ gap excitation band peaking at ≈ 2 eV [6]. The frequency of the optical phonon mode due to the motion of an O atom between Cu ions is 0.07 eV, above which we observe the broad absorption band polarized along the chain axis ($\mathbf{E} \| \mathbf{b}$) and extending to 0.9 eV with a

0031-9007/96/76(14)/2579(4)$10.00

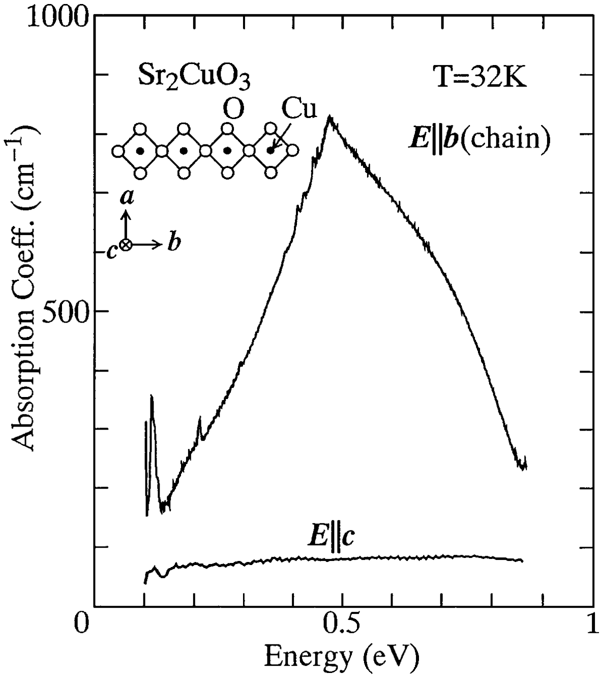

FIG. 1. Midinfrared absorption spectra of a Sr_2CuO_3 crystal for $\mathbf{E}\|\mathbf{b}$ (parallel to the CuO chain axis) and for $\mathbf{E}\|\mathbf{c}$ (perpendicular to the chain axis).

characteristic cusplike structure at 0.48 eV. Incidentally, spiky structures at 0.11 and 0.21 eV are due to multiphonon absorption. The weak, structureless spectrum for $\mathbf{E}\|\mathbf{c}$ (perpendicular to the chain axis) confirms the one dimensionality and that the electric polarization of the absorption band is along the chain. The isostructural compound, Ca_2CuO_3, was observed to show a nearly identical midinfrared spectrum accompanied by the cusp at 0.47 eV.

To interpret the experimental result, we apply LS's idea of phonon-assisted absorption, Eq. (1), to the one-dimensional Mott insulators, whose spin dynamics is known to be well described by the antiferromagnetic Heisenberg model,

$$H_{\text{spin}} = \sum_n J\mathbf{S}_n \cdot \mathbf{S}_{n+1} \,. \tag{2}$$

The absorption coefficient can be obtained with Fermi's golden rule as

$$I(\omega) = \frac{2\pi}{\hbar} \sum_f |\langle f|P|g\rangle|^2 \delta(\omega - E_{g\to f}) \,, \tag{3}$$

where $E_{g\to f}$ is the excitation energy from the ground state $|g\rangle$ to the final state $|f\rangle$. In the lowest order approximation, the final states are eigenstates of the total Hamiltonian

$$H_{\text{tot}} = H_{\text{spin}} + \sum_n \hbar\omega_0 a_{n+1/2}^\dagger a_{n+1/2} \,, \tag{4}$$

where the phonon and spin degrees of freedom are separated, and $a_{n+1/2}^\dagger$ ($a_{n+1/2}$) are the phonon creation (annihilation) operators. For simplicity, we use the Einstein model for phonons with frequency ω_0, neglecting the dispersion. This can be justified because the dispersion of the phonon is much smaller than the typical energy scale of the spin system, J. In terms of the phonon operators, the displacements $u_{n+1/2}$ of O ions can be given by $\sqrt{\hbar/2M\omega_0}\,(a_{n+1/2}^\dagger + a_{n+1/2})$ with M the reduced mass of the O ion. After taking the summation over the phonon states Eq. (3) becomes

$$I(\omega) = \frac{\pi|\mu|^2}{M\omega_0} \sum_{f,n} |\langle f|\mathbf{S}_n \cdot \mathbf{S}_{n+1}|g\rangle|^2 \delta(\omega - E_{g\to f}) \,, \tag{5}$$

where $|f\rangle$ and $|g\rangle$ now involve only the spin degree of freedom.

We first evaluate Eq. (5) for the XY spin chain, neglecting the S^zS^z terms in H_{spin} and P; the Heisenberg case will be discussed later. As is well known, the XY model can be mapped to the noninteracting spinless fermion model via Jordan-Wigner transformation. The spinless fermion, which we call spinon, has the dispersion $\varepsilon_k = -J\cos k$, and the ground state is the filled Fermi sea with the Fermi level at $\varepsilon = 0$ [Fig. 2(a)]. Since the operator $S_n^xS_{n+1}^x + S_n^yS_{n+1}^y$ becomes $\frac{1}{2}(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n)$ in the fermion representation, the final states excited by the polarization operator should have a particle-hole excitation, whose continuum spectrum is shown in Fig. 2(b). We note that the relative wave number q of the particle-hole excitation needs not be zero because of the phonon recoil. A straightforward calculation gives the absorption rate per spin

$$\begin{aligned} I_{XY}(\omega) = {} & \frac{\pi|\mu|^2}{M\omega_0}\langle g|S_n^xS_{n+1}^x + S_n^yS_{n+1}^y|g\rangle^2\delta(\omega - \omega_0) \\ & + \frac{2|\mu|^2}{\pi M\omega_0}\int_0^{\pi/2} dk_1 \int_{\pi/2}^{\pi} dk_2 (1 + \cos k_1 \cos k_2)\delta(\omega - \omega_0 + \varepsilon_{k_1} - \varepsilon_{k_2}) \,. \end{aligned} \tag{6}$$

The first term represents the one-phonon line without spin excitations, and the second term, plotted in Fig. 3 (solid line), is the contribution from the particle-hole excitations of spinons. Since the particle-hole excitations are possible for the shaded region of Fig. 2(b), the absorption band extends from ω_0 to $\omega_0 + 2J$. The absorption coefficient increases linearly in ω at $\omega \gtrsim \omega_0$ and has a cusp at $\omega = \omega_s \equiv \omega_0 + J$. Note that the overall feature is

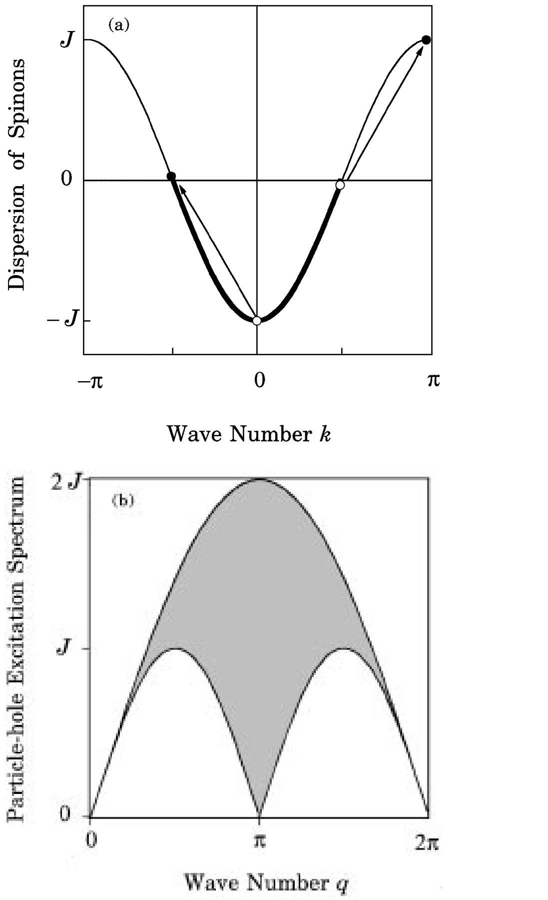

FIG. 2. (a) Dispersion of spinons in the *XY* model. (b) Particle-hole excitation spectrum of spinons in the *XY* model. The upper (lower) edge of the spectrum is $E_q = 2J\sin(q/2)$ ($E_q = J\sin q$), where q is the relative wave number of particle-hole excitations. The two-particle (two-kink) excitation spectrum in the Heisenberg model has the same shape, but with the lower (upper) edge given by $E_q = \frac{\pi}{2}J\sin q$ [$E_q = \pi J\sin(q/2)$].

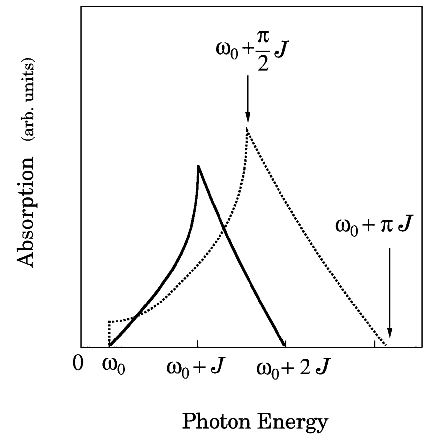

FIG. 3. Absorption coefficient of one-dimensional quantum spin chains due to the phonon-assisted absorption involving a particle-hole excitation of spinons. The solid line is the result for the *XY* model, and the dotted line is the one expected for the Heisenberg model.

very similar to the experimental result (Fig. 1). The position of the cusp coincides with the top of the lower edge of the particle-hole excitation, $E_q = J\sin q$, and the corresponding processes are the transition from the Fermi point to the top of the spinon band [Fig. 2(a)] and from the bottom of the band to the Fermi point. The singular behavior of $I_{XY}(\omega)$ around the cusp,

$$I_{XY}(\omega) - I_{XY}(\omega_s) = \begin{cases} -C_-\sqrt{\omega_s - \omega}, & \omega \lesssim \omega_s, \\ -C_+(\omega - \omega_s), & \omega \lesssim \omega_s, \end{cases} \tag{7}$$

where $C_\pm$ are positive constants, is the result of the square-root divergence in the single-particle density of states (DOS) at the top and bottom of the spinon band. Therefore this cusp structure arising from the Van Hove singularity of spinons is a characteristic feature of the one-dimensional Mott insulators.

Now we turn to the Heisenberg case of our main concern. The dotted line in Fig. 3 shows the absorption coefficient for the Heisenberg model. In the antiferromagnetic Heisenberg model, the Ising type coupling $S_n^z S_{n+1}^z$ introduces repulsive interaction between the spinless fermions, which makes the absorption spectrum slightly different from $I_{XY}(\omega)$. Although we cannot evaluate Eq. (5) for the Heisenberg model analytically, we can still deduce the exact position of the cusp singularity from the Bethe ansatz solution. In this model the one-particle excitation, corresponding to the free spinon in the *XY* model, is a doublet of spin-$\frac{1}{2}$ domain wall (kink) with the dispersion, $\varepsilon_k = \frac{\pi}{2}J\sin k$ $(0 \le k \le \pi)$ [7]. The two-particle excitations giving the main contribution to $I(\omega)$ form a continuum spectrum similar to the *XY* case [Fig. 2(b)]. In particular, the lower edge of the continuum, the des Cloizeaux–Pearson mode [8], is given by $E_q = \frac{\pi}{2}J\sin q$. It is clear from the argument given for the *XY* case that there appears a cusp in $I(\omega)$, due to the Van Hove singularity in the DOS, at the energy corresponding to the top of the des Cloizeaux–Pearson mode, i.e., at $\omega = \omega_0 + \frac{\pi}{2}J$ [9]. With this information we can estimate the exchange energy J from Fig. 1. Using the experimental values $\omega_0 = 0.07$ eV and $\omega_0 + \frac{\pi}{2}J = 0.48$ eV, we obtain $J = 0.26$ eV. This value is consistent with the estimation from the magnetic susceptibility [10]. For the Heisenberg case, we could not exclude the possible contributions from spin excitations involving more than two kinks. This means that there can be a nonzero contribution to $I(\omega)$ even above the upper edge ($\omega = \omega_0 + \pi J$) of the two-particle contribution drawn in Fig. 3 (dotted line). Experimentally, however, the upper edge ($\omega \approx 0.9$ eV) of the absorption band in Fig. 1 coincides well with that of the two-particle excitations $\omega = \omega_0 + \pi J = 0.89$ eV, implying that the dominant contribution to $I(\omega)$ indeed comes from the two-particle excitations.

In addition to the shift of the cusp, the repulsive interaction between the fermions changes the low-energy part of the absorption band. Using the bosonization method [11], we find that the long-time behavior of the correlation function of P is $\langle P(t)P(0)\rangle - \langle P\rangle^2 \sim t^{-1}$, since the scaling dimension of the operator $\mathbf{S}_n \cdot \mathbf{S}_{n+1}$ is $1/2$ [12]. This implies that the absorption coefficient is constant just above the absorption edge, in contrast to the *XY* case, $I_{XY}(\omega) \propto \omega - \omega_0$. Clearly the theoretical curve in Fig. 3 reproduces the essential feature of the experimental data, and we can conclude that the absorption spectra in Sr_2CuO_3 is explained by the phonon-assisted absorption process involving the spinon particle-hole excitations in the 1D Heisenberg model.

Now we briefly discuss the phonon-assisted absorption in a Heisenberg ladder system [13] which can be realized in two coupled CuO chains. To calculate $I(\omega)$ we use a π-flux mean-field approximation of the resonating valence bond which reproduces the essential feature of the ladder system, i.e., the presence of a spin gap. In this mean-field state the fermions (spinons) have two kinds of dispersions, $\varepsilon_k = \pm[(J_\parallel \cos k)^2 + J_\perp^2]^{1/2}$, where $J_\parallel$ and $J_\perp$ denote the effective intrachain and interchain exchange energy, respectively, and k the wave number in the direction parallel to the chain. In the ground state the lower band is completely filled. As in the single-chain case, the main contribution to the absorption coefficient comes from the particle-hole excitations of the spinons. The presence of the spin gap, however, leads to a qualitatively different behavior of $I(\omega)$. First, $I(\omega)$ is zero in the spin gap region, $\omega_0 < \omega < \omega_0 + J_\perp$. Second, just above the spin gap the spectrum has a nonzero oscillator strength like the single Heisenberg chain, i.e., $I(\omega) \propto \Theta(\omega - \omega_0 - J_\perp)$. Finally, the Van Hove singularity in the DOS of the spinon bands leads to a logarithmic divergence at $\omega = \omega_0 + J_\perp + \sqrt{J_\parallel^2 + J_\perp^2}$, instead of the cusp in the single-chain case. This is because, for the transition, say, from the top of the lower band to the top of the upper band, both the initial and the final state have the $\frac{1}{\sqrt{\varepsilon}}$-type DOS, leading to the logarithmic divergence upon integrating the product of the DOS over the energy. Thus the opening of the spin gap enhances the singular structure in the absorption spectra from the cusp to the logarithmic divergence.

In summary, we have measured the midinfrared optical absorption spectra of a one-dimensional Mott insulator Sr_2CuO_3. The spectra have been successfully analyzed in terms of the phonon-assisted absorption mechanism in the quantum spin chain model. The observed cusplike singularity is shown to be due to the Van Hove singularity in the spinon band.

The authors are grateful to Y. Okimoto and T. Arima for their help in experiments. This work was supported by Grant-in-Aid for Scientific Research on the Priority Area (No. 07237102, 06243103) from the Ministry of Education, Science, and Culture, Japan. H. S. was supported by the Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

[1] J. D. Perkins, J. M. Graybeal, M. A. Kastner, R. J. Birgeneau, J. P. Falck, and M. Greven, Phys. Rev. Lett. **71**, 1621 (1993).

[2] Y. Tanabe, T. Moriya, and S. Sugano, Phys. Rev. Lett. **15**, 1023 (1965).

[3] J. Lorenzana and G. A. Sawatzky, Phys. Rev. Lett. **74**, 1867 (1995); (unpublished).

[4] J. D. Perkins, D. S. Kleinberg, M. A. Kastner, and R. J. Birgeneau (unpublished).

[5] H. Yasuhara, Y. Okimoto, and Y. Tokura (unpublished).

[6] Y. Tokura, S. Koshihara, T. Arima, H. Takagi, S. Ishibashi, and S. Uchida, Phys. Rev. B **41**, 11 657 (1990).

[7] L. Faddeev and L. Takhtajan, Phys. Lett. **85A**, 375 (1981).

[8] J. des Cloizeaux and J. J. Pearson, Phys. Rev. **128**, 2131 (1962).

[9] The singular behavior of $I(\omega)$ around the cusp may also be changed from Eq. (7) due to the renormalization of the matrix elements. However, we expect that the profile of the cusp will remain qualitatively the same as the *XY* case.

[10] T. Ami, M. K. Crawford, R. L. Harlow, Z. R. Wang, D. C. Johnston, Q. Huang, and R. W. Erwin, Phys. Rev. B **51**, 5994 (1995).

[11] A. Luther and I. Peschel, Phys. Rev. B **12**, 3908 (1975).

[12] I. Affleck, in *Fields, Strings, and Critical Phenomena*, edited by E. Brézin and J. Zinn-Justin (North-Holland, Amsterdam, 1990), p. 563.

[13] E. Dagotto, J. Riera, and D. J. Scalapino, Phys. Rev. B **45**, 5744 (1992).