Phonon Assisted Multimagnon Optical Absorption and Long Lived Two-Magnon States in Undoped Lamellar Copper Oxides

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We calculate the effective charge for multimagnon infrared (IR) absorption assisted by phonons in the parent insulating compounds of cuprate superconductors and the spectra for two-magnon absorption using interacting spin-wave theory. Recent measured bands in the mid-IR [Perkins *et al.*, Phys. Rev. Lett. **71**, 1621 (1993)] are interpreted as involving one phonon plus a two-magnon virtual bound state, and one phonon plus higher multimagnon absorption processes. The virtual bound state consists of a narrow resonance occurring when the magnon pair has total momentum close to $(\pi, 0)$.

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The discovery of high-T_c superconductivity in doped cuprate materials [1] has triggered a lot of attention in the parent quasi-two-dimensional spin-$\frac{1}{2}$ quantum antiferromagnets. So far complementary information on the antiferromagnetism has come from different probes like neutron scattering and Raman light scattering [2]. In this Letter we reinterpret recent infrared absorption measurements [3] (Fig. 1) in terms of phonon assisted multimagnon absorption. The narrow primary peak in Fig. 1 is explained in terms of a long lived virtual bound state of two magnons here referred to as a bimagnon. These new states are narrow resonances occurring when the magnon pair has total momentum close to $(\pi, 0)$ and have a reasonably well defined energy and momentum in a substantial portion of the Brillouin zone.

In principle IR absorption of magnons is not allowed in the tetragonal structure of cuprate materials. This is because in a typical two-magnon excitation the presence of a center of inversion inhibits any asymmetric displacement of charge, and hence the associated dipole moment vanishes. However, the situation changes if phonons are taken into account. In a process in which one phonon and two magnons are absorbed, the symmetry of the lattice is effectively lower, and the process is allowed. A similar theory was put forward by Mizuno and Koide [4] to explain magnetically related IR absorption bands found many years ago by Newman and Chrenko in NiO [5]. To the best of our knowledge, we present the first explicit calculation of coupling constant for phonon assisted absorption of light by multimagnon excitations and the line shape for two-magnon absorption. We consider a Cu-O layer, but generalization of our results to other magnetically ordered insulators is trivial.

Consider a three-band Peierls-Hubbard model [6] in the presence of an electric field ($\boldsymbol{E}$) and in which for simplicity Cu atoms are kept fixed and O ions are allowed to move with displacements $\boldsymbol{u}_{i+\delta/2}$. Here $\boldsymbol{i}$ labels Cu sites and $\boldsymbol{\delta} = \hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}$, so that $\boldsymbol{x} + \boldsymbol{\delta}/2$ labels O sites.

Holes have an on-site interaction U_d on Cu and U_p on O, a Cu-O repulsion U_{pd}, on-site energies on Cu E_d, and on O E_p, and Cu-O hopping t (O-O hopping is neglected here). We define $\Delta = E_p - E_d + U_{pd}$, $\epsilon = 2(E_p - E_d) + U_p$. When an O ion moves in the direction of a Cu with displacement $|u|$, the corresponding on-site energy of Cu changes to first order by $-\beta|u|$ and the corresponding Cu-O hopping by $\alpha|u|$. Opposite signs apply when the O moves in the opposite direction [6].

To calculate the coupling constants of light with one-phonon–multimagnon processes we first obtain a low energy Hamiltonian as a perturbation expansion valid when $t \ll \Delta, \epsilon, U_d$ and when the phonon field and the electric field vary slowly with respect to typical gap frequencies,

$$H = \sum_{i,\delta} J(\boldsymbol{E}, \{\boldsymbol{u}_{i+\delta/2}\}) B_{i+\delta/2} + H_{\rm ph} - \boldsymbol{E}\boldsymbol{P}_{\rm ph}. \quad (1)$$

Here $B_{i+\delta/2} = \boldsymbol{S}_i \boldsymbol{S}_{i+\delta}$ with $\boldsymbol{S}_i$ the spin operators, $H_{\rm ph}$ is the phonon Hamiltonian containing spring constants

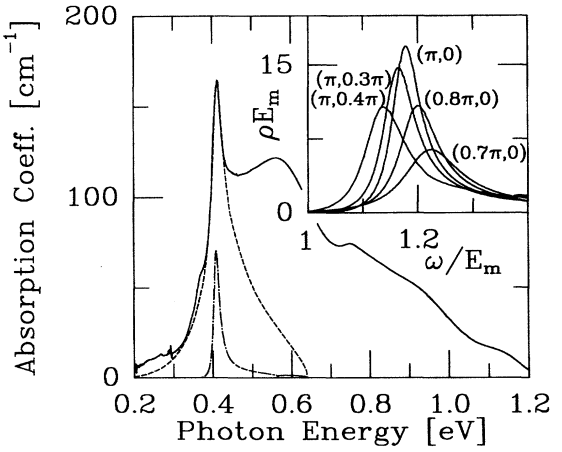

FIG. 1. Experimental data from Ref. [3] (solid line) and theoretical line shape for two-magnon absorption (dashed line) in La_2CuO_4. The dash-dotted line is the contribution to the line shape from the bimagnon at $\boldsymbol{p} = (\pi, 0)$. The inset shows a blowup of $\rho = -\mathrm{Im}(G_{xx})$ at the energy of the bimagnon for different values of the total momentum.

and masses for the O ions (M), and $\boldsymbol{P}_{\rm ph}$ is the phonon dipole moment. The first term in Eq. (1) contains spin-dependent fourth order corrections in t, whereas fourth, second, and zero order spin-independent processes are collected in the last two terms. As usual [7] we calculate the superexchange, J, as the energy difference between the singlet and triplet states of the spins located at Cu_L and Cu_R in Fig. 2. We only need to consider the three configurations (A,B,C) of the L-R bond and $\boldsymbol{E}$. Next we Taylor expand J to first order in $\boldsymbol{E}$ and $\{\boldsymbol{u}_{i+\delta/2}\}$ [8],

$$J = J_0 + \eta(u_L - u_R) - E[q_I u_0 + \lambda q_A(2u_0 - u_L - u_R)]. \quad (2)$$

Here $\lambda = 1$ for configuration A and $\lambda = 0$ for configurations B and C. In each configuration the displacement of the central O and the electric field are parallel, i.e., $\boldsymbol{E} = E\hat{\boldsymbol{e}}, \boldsymbol{u}_0 = u_0\hat{\boldsymbol{e}}$. The direction of $\hat{\boldsymbol{e}}$ is the same as the arrows at the bottom of Fig. 2. u_L and u_R are only relevant in configuration A. $u_L = u_{L1} + u_{L2} - u_{L3}$, and $u_R = -u_{R1} + u_{R2} + u_{R3}$. The numbering and the direction of the displacements are shown in Fig. 2. The first term in Eq. (2) is the superexchange in the absence of the electric and phonon fields, $J_0 = (4t^4/\Delta^2)[1/U_d + 2/\epsilon]$. The remaining quantities are a magnon-phonon coupling constant, $\eta = (-4t^4/\Delta^2)\beta[\Delta^{-1}(1/U_d + 2/\epsilon) + 2/\epsilon^2]$ and effective charges associated with one-phonon and multimagnon processes,

$$q_I = -e\frac{8t^4}{\Delta^2}\left[\frac{1}{\Delta}\left(\frac{1}{U_d} + \frac{2}{\epsilon}\right) + \frac{2}{\epsilon^2}\right], \quad (3)$$

$$q_A = -e\frac{4t^4}{\Delta^2}\beta a_{pd}\left[\frac{2}{\Delta^2}\left(\frac{1}{U_d} + \frac{2}{\epsilon}\right) + \frac{1}{U_d}\left(\frac{1}{\Delta} + \frac{2}{U_d}\right)^2\right]. \quad (4)$$

a_{pd} is the Cu-O distance. Within a point charge estimation the parameter $\beta a_{pd} \approx 2U_{pd}$. The dipole moment is obtained as $\boldsymbol{P} = -\partial H/\partial \boldsymbol{E}$ and uses Eq. (2) in the relevant configurations. We get up to fourth order in t,

$$\boldsymbol{P} = \boldsymbol{P}_{\rm 1ph} + \boldsymbol{P}_{\rm 1ph+mag}. \quad (5)$$

The first term describes conventional phonon absorption. We define $\delta B_{i+\delta/2} = B_{i+\delta/2} - \langle B_{i+\delta/2}\rangle$ and its Fourier transform δB_p^δ and the Fourier transform of $\boldsymbol{u}_{i+\delta/2}$, $\boldsymbol{u}_p^\delta$. After Fourier transforming, the dipole moment for one-phonon and multimagnon processes for an in-plane field in the x direction has the form

$$P_{x,\rm 1ph+mag} = N\left[q_I \sum_{p,\delta} \delta B_p^\delta u_{xp}^\delta + \lambda 4 q_A \sum_{p,\delta} \sin\left(\frac{p_x}{2}\right)\sin\left(\frac{p_\delta}{2}\right)\delta B_p^x u_{\delta p}^\delta\right] \quad (6)$$

and $\lambda = 1$. The case of an electric field perpendicular to the plane is obtained by putting $\lambda = 0$ and replacing u_x^δ by u_z^δ. N is the number of unit cells. The first term is isotropic, being present in any configuration. Looking at the cluster in Fig. 2 it can be understood as a spin-dependent correction to the charge in O_0. Its physical origin is that fourth order corrections to the charges involve spin-dependent processes. For example, if the spins in Cu_L and Cu_R are parallel, they cannot both transfer to O_0, whereas if they are antiparallel they can. Figure 3(a) illustrates a typical process efficient in configuration B. The second term is anisotropic being present for an in-plane field only. It originates from a "charged-phonon-like" effect [10]. Consider the configuration in which the electric field and the displacement of O_0 are both parallel to the Cu_L-Cu_R bond (A in Fig. 2), and a phonon in which the O's around Cu_L breathe in and the O's around Cu_R breathe out. (We do not need to consider zero momentum phonons to couple to light since it is the total momentum, magnons plus phonons, which has to add to zero.) The Madelung potential in Cu_R decreases, and in Cu_L it increases, creating a displacement of charge from left to right that contributes to the dipole moment.

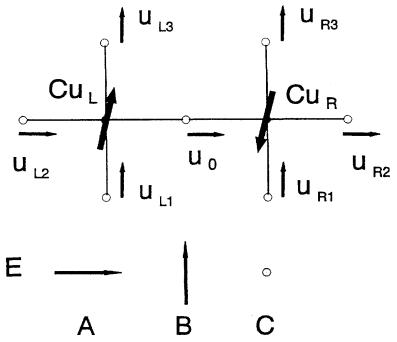

FIG. 2. Schematic representation of the cluster used in the calculations. Full dots represent Cu's and open dots O's. Thick arrows represent the spin, thin short arrows represent lattice displacements, and thin long arrows represent the direction of the electric field. We have represented $\mathbf{u}_0$ in A configuration. In general its direction is equal to the direction of the electric field.

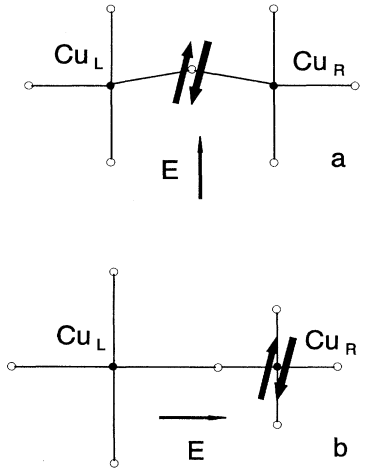

FIG. 3. Typical processes contributing to the isotropic (a) and anisotropic (b) effective charges. The meaning of the symbols is the same as in Fig. 2.

Figure 3(b) illustrates a typical process. But again this effect is spin dependent, since if the two spins are parallel they cannot both transfer to Cu_R.

The real part of the optical conductivity due to these processes is given by the dipole-moment–dipole-moment correlation function. Assuming, for simplicity, that only the $u^{\delta}_{\delta' p}$'s with the same δ and δ' mix, and decoupling the phonon system from the magnetic system which is valid in lowest order in the magnon-phonon coupling we get ($\hbar = 1$)

$$\sigma = -\frac{\pi\omega}{M}\sum_{p}\mathrm{Im}\left[\frac{q_I^2}{\omega_{\perp p}}\langle\langle \delta B^{y}_{-p};\delta B^{y}_{p}\rangle\rangle^{\omega_{\perp p}} + \frac{16\lambda^2 q_A^2\sin^2(p_x/2)\sin^2(p_y/2) + [4\lambda q_A\sin^2(p_x/2) - q_I]^2}{\omega_{\parallel p}}\langle\langle \delta B^{x}_{-p};\delta B^{x}_{p}\rangle\rangle^{\omega_{\parallel p}}\right]. \tag{7}$$

Here $\omega_{\parallel p}$ is the frequency of the u^{x}_{xp} and u^{y}_{yp} phonons, and $\omega_{\perp p}$ is the frequency of the u^{y}_{xp} and u^{x}_{yp} phonons. $\omega_{\parallel p}$ can be associated with the frequency of Cu-O stretching mode phonons and $\omega_{\perp p}$ with that of Cu-O bending mode phonons. The superscript in the Green functions indicates that the poles should be shifted by that amount. The volume associated with a Cu ion has been set to 1. The absorption coefficient is obtained assuming weak absorption as $\alpha = 4\pi\sigma/c\sqrt{\epsilon_1}$ with ϵ_1 the real part of the dielectric constant [3(b)].

To compute the magnon-magnon Green functions we use interacting spin-wave theory [11] with a Holstein-Primakoff transformation. On the A (B) sublattice we put $S_{+i}(S_{-i}) = \sqrt{2S(1 - b_i^{\dagger}b_i)}b_i$ and the corresponding Hermitian conjugates. $S = 1/2$ in our case, and b_i is a boson operator. With this definition the Hamiltonian is invariant under the exchange of the sublattices, and we do not need to distinguish between them. Accordingly we work in the nonmagnetic Brillouin zone. The Heisenberg Hamiltonian in this representation is expanded to zero order in $1/S$ and normal ordered with respect to the noninteracting spin-wave ground state. The noninteracting part is diagonalized by the Bogoliubov transformation $Q_k^{\dagger} = u_k b_k^{\dagger} - v b_{-k}$, where b_k is the Fourier transform of b_i and $u_k = \sqrt{(1 + \omega_k)/2\omega_k}$, $v_k = -\mathrm{sgn}\,(\gamma_k)\sqrt{(1 - \omega_k)/2\omega_k}$, with $\gamma_k = 2/z\sum_{\delta}\cos(k\delta)$, $\omega_k = \sqrt{1 - \gamma_k^2}$, and z is the coordination number ($z = 4$ in our case). We define $g_{pq_1q_2} = \langle\langle Q_{\frac{1}{2}p+q_1}Q_{\frac{1}{2}p-q_1};Q^{\dagger}_{\frac{1}{2}p+q_2}Q^{\dagger}_{\frac{1}{2}p-q_2}\rangle\rangle$. Next we apply a standard RPA-like decoupling for the equation of motion of g which can be solved for integrals over the Brillouin zone of g weighted with products of u's and v's [11]. Finally $\langle\langle \delta B^{x}_{-p};\delta B^{x}_{p}\rangle\rangle$ can be written as a sum of such quantities with proper weighting factors [9]. The dash-dotted line in Fig. 1 gives the contribution to the line shape from magnon pairs with $p = (\pi, 0)$ *without* the approximations that follow. A very sharp resonance occurs there indicating that a virtual bound state (bimagnon) is formed.

Analytic expressions for the Green functions can be obtained neglecting the contributions involving v's. The resulting error is small because at short wave length v is small to start with, and at long wave length (low energies) the spectral weight is small [12]. This approximation does not appreciably shift the peak at $p = (\pi, 0)$ and only decreases slightly the intensity [9]. The Green function takes the form $\langle\langle \delta B^{x}_{-p};\delta B^{x}_{p}\rangle\rangle = S^2 G_{xx}/N\pi$ with

$$G_{xx} = \frac{G^{(0)}_{xx} + 2J_0[G^{(0)}_{xx}G^{(0)}_{yy} - (G^{(0)}_{xy})^2]}{1 + 2J_0(G^{(0)}_{xx} + G^{(0)}_{yy}) + 4J_0^2[G^{(0)}_{xx}G^{(0)}_{yy} - (G^{(0)}_{xy})^2]}, \tag{8}$$

where

$$G^{(0)}_{\delta\delta'} = \frac{1}{N}\sum_{q}\frac{u^2_{\frac{1}{2}p+q}u^2_{\frac{1}{2}p-q}\cos(q_\delta)\cos(q_{\delta'})}{\omega - E_{\frac{1}{2}p+q} - E_{\frac{1}{2}p-q}}, \tag{9}$$

$E_k = E_m\omega_k$, $E_m = zSJ_0(1 + \zeta/2S)$, and ζ is the Oguchi correction [2], $\zeta \approx 0.158$ in our case. Equation (8) takes the familiar form at $p = (\pi, 0)$, $G_{xx} = G^{(0)}_{xx}/(1 + 2J_0G^{(0)}_{xx})$. In this case the imaginary part of $G^{(0)}_{xx}$ starts to be different from zero at $\omega = E_m$ ($\sim 2J_0$) and rises very slowly as the frequency is increased so that it is very small at the bimagnon energy resulting in a long lifetime or narrow peak. In the inset of Fig. 1 we show the imaginary part of the Green function from Eq. (8) for different values of p. This shows how the bimagnon disperses around $p = (\pi, 0)$, it goes upward on going toward $(0, 0)$ and downward on going toward (π, π). This indicates that $(\pi, 0)$ is a saddle point, and hence it should give a Van Hove singularity when integrated over p [Eq. (7)]. The dashed curve in Fig. 1 is the theoretical line shape in the same approximation, assuming that the anisotropic processes dominate ($q_I = 0$) and treating the phonons as Einstein-like with $\omega_{\parallel} = 0.08$ eV [13]. It gives a surprisingly good fit for the primary peak. Such a good fit, especially for the width, was not possible within RPA in the Raman case [14]. This can be partially reconciled by the fact that a structure that is artificially broadened at $p = (\pi, 0)$ (but still much narrower than the integrated line shape) does not significantly change the final result.

Because of the Van Hove singularity the position of the $p = (\pi, 0)$ bimagnon peak coincides with the peak in the line shape and is given by $1.179E_m + \omega_{\parallel} = 2.731J_0 + \omega_{\parallel}$. This provides an alternative way to estimate J_0. We found $J_0 = 0.121$ eV which is in good agreement with other estimates [2,14].

The $\omega_{\|}$ phonon is very anomalous in orthorhombic La_2CuO_4 since it splits due to anharmonicities [13], its partner being at $\omega'_{\|} = 0.06$ eV at room temperature. Presumably this produces the shoulder observed at lower energies in the experiments (Fig. 1), although the distance to the primary is larger than expected which may be due to other phonons involved. This feature was assigned to direct two-magnon absorption [3] made weakly allowed by the lower lattice symmetry according to the results of Ref. [15]. However, we found that the dipole moment for this process is directed in the direction bisecting an angle made by the Cu-O-Cu bond [16] and hence can only contribute for a field perpendicular to the plane.

The oscillator strength in Fig. 1 was adjusted to fit the experiments. A rough estimate of the strength using $q_A = 0.1e$ and $\epsilon_1 = 5$ gives a value ~ 4 times smaller than observed which is quite reasonable given the uncertainties involved.

We interpret the sidebands at higher energy to be due to higher multimagnon processes, neglected in the above approximations. In order to check both the validity of our approximations and the origin of the sidebands we have also computed the absorption using exact diagonalization of a small cluster [9]. The exact result confirms the Green function calculation for the two-magnon peak and shows also sidebands corresponding to higher multimagnon processes which we associate with the higher energy sidebands observed in the experiments. The relative weight of the sidebands seems to be smaller than in the experiments presumably because of finite site effects or the presence of other processes in the magnetic Hamiltonian as was suggested in the Raman case [17].

For an electric field polarized perpendicular to the plane only phonons perpendicular to the Cu-O bond contribute. We estimate the absorption to be roughly a factor of 8 smaller than the in-plane contribution. From the experimental side the anisotropy seems to be larger. One should be aware that the cuprates are in a regime where covalency is not small with respect to typical gap energies and hence a perturbation in t is helpful to identify the important processes and discuss trends, but quantitative estimations are to be taken with care [7]. As higher orders in t are included we expect that the anisotropic contributions grow with respect to the isotropic ones. For example, the charged phonon effects of Fig. 3(b) can become very efficient if the second hole forms a Zhang-Rice singlet with the hole already present in Cu_L since that process involves a much smaller gap. Note also that the larger the order in t the longer the range of the processes that contribute to the anisotropic charges, whereas only local processes contribute to the isotropic charge. Longer range processes have in general very large form factors. These effects should give a stronger anisotropy in accordance with the experiments. This also partially justifies our simplifying assumption of taking $q_l = 0$.

To conclude we have computed effective coupling constants of light with multimagnon excitations assisted by phonons and determined the line shape of the primary peak. Our results explain recent measured absorption bands in the mid-IR of parent cuprate superconductors and demonstrate the existence of very sharp virtual bound states of magnons.

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