Phonon Assisted Multimagnon Optical Absorption and Long Lived Two-Magnon States in Undoped Lamellar Copper Oxides. supr-con/9501001

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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 \((\pi, 0)\) and have a resonantly 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 to explain magnetically related IR absorption bands found many years ago by Newman and Chrenko in NiO. 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 in the presence of an electric field \(E\) and in which for simplicity Cu atoms are kept fixed and O ions are allowed to move with displacements \(u_{i+\delta/2}\). Here \(i\) labels Cu sites and \(\delta = \hat{x}, \hat{y}, \hat{z}\), so that \(i + \delta/2\) labels O sites.

Holes have an on-site interaction \(U_p\) 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 \(|u_i|\), the corresponding on-site energy of Cu changes to first order by \(-\beta|u_i|\) and the corresponding Cu-O hopping by \(\alpha|u_i|\). Opposite signs apply when the O moves in the opposite direction.

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 \(t \ll \Delta, \epsilon, U_p\) and when the phonon field and the electric field vary slowly with respect to typical gap frequencies, \(\hbar \omega\).

\[
H = \sum_{i,\delta} J(\epsilon_u, \delta) u_{i+\delta/2} + H_{ph} - EP_{ph}. \tag{1}
\]

Here \(B_{i+\delta/2} = S_i S_{i+\delta}\) with \(S_i\) the spin operators, \(H_{ph}\) is the phonon Hamiltonian containing spring constants and masses for the O ions \((M)\) and \(P_{ph}\) is the phonon dipole moment. The first term in Eq. \(\text{(1)}\) 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 we calculate the superexchange, \(J\), as the energy difference between the singlet and triplet states of the spins located at CuL and CuR in Fig. \(\text{(2)}\). We only need to consider the three configurations \((A, B, C)\) of the L-R bond and \(E\). Next we Taylor expand \(J\) to first order in \(E\) and \(\{u_{i+\delta/2}\}\)

\[
J = J_0 + \eta(u_L - u_R) - E[\eta u_0 + \lambda u_A (2u_0 - u_L - u_R)] \tag{2}
\]

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.
The direction of \( \vec{e} \) is the same as the arrows at the bottom of Fig. 2, \( u_L \) and \( u_R \) are only relevant in configuration A. \( u_L = u_{1,1} + u_{1,2} - u_{1,3}, \)
\( u_R = -u_{1,1} + u_{1,2} + u_{1,3}. \) The numbering and the direction of the displacements are shown in Fig. 2. The first term in Eq. (3) is the superexchange in the absence of the electric and phonon fields, \( J_0 = \frac{4t^4}{\Delta^2} \left[ \frac{1}{U_d} + \frac{2}{\epsilon} \right]. \) The remaining quantities are a magnon-phonon coupling constant, \( \eta = \frac{4t^4}{\Delta^2} \beta \left[ \frac{1}{U_d} + \frac{2}{\epsilon} \right] \) and effective charges associated with one phonon and multimagnon processes,

\[
q_1 = -e \frac{8t^4}{\Delta^2} \left[ \frac{1}{U_d} + \frac{2}{\epsilon} \right];
\]

\[
q_2 = -e \frac{4t^4}{\Delta^2} \beta a_{pd} \left[ \frac{2}{U_d} + \frac{1}{U_d} + \frac{1}{\Delta} \right].
\]

(3)

(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 \( P = -\frac{\partial H}{\partial \mathbf{B}} \) and using Eq. (2) in the relevant configurations. We get up to fourth order in \( t, \)

\[
P = P_{1ph} + P_{1ph + mag}
\]

(5)

The first term describes conventional phonon absorption. We define \( \delta B_{i+i/2} = B_{i+i/2} - \langle B_{i+i/2} \rangle \) and its Fourier transform, \( \delta \mathbf{B}_p \) and the Fourier transform of \( u_{i+i/2}, u_p. \)

After Fourier transforming, the dipole moment for one phonon and multimagnon processes for an in-plane field in the \( x \) direction has the form,

\[
P_{x,1ph + mag} = N \left[ q_1 \sum_{p,\delta} \delta \mathbf{B}_p u_{\delta x}^p + \lambda A q_A \sum_{p,\delta} \sin \left( \frac{B_p}{2} \right) \sin \left( \frac{B^{\delta}_{p}}{2} \right) \delta \mathbf{B}^{\delta}_p u_{\delta x}^p \right]
\]

(6)

and \( \lambda = 1. \) The case of an electric field perpendicular to the plane is obtained by putting \( \lambda = 0 \) and replacing \( u_{\delta x}^p \) by \( u_{\delta y}^p, N \) 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 \( \text{Cu}_L \) and \( \text{Cu}_R \) are parallel they cannot both transfer to \( O_0 \) whereas if they are antiparallel they can. Fig. 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 \( \text{Cu}_L - \text{Cu}_R \) bond (A in Fig. 2), and a phonon in which the O’s around \( \text{Cu}_L \) breathe in and the O’s around \( \text{Cu}_R \) breathe out. (We don’t 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 \( \text{Cu}_R \) decreases, and in \( \text{Cu}_L \) it increases, creating a displacement of charge from left to right that contributes to the dipole moment. Fig. 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 \( \text{Cu}_R. \)

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 \( u_{\delta x}^p \)’s with the same \( \delta \) and \( \delta' \) 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 \frac{q^2}{\omega \omega_p} \frac{\delta \mathbf{B}_p^{x} \delta \mathbf{B}_p^{x}}{\omega_i \omega_p} + 16\lambda a_q \sin^{2}(\frac{\omega}{2}) \sin^{2}(\frac{\omega}{2}) + (4\lambda a q^2 \sin^{2}(\frac{\omega}{2}) - q^2)^2 \]

(7)

Here \( \omega_{\parallel p} \) is the frequency of the \( u_{\delta x}^p \) and \( u_{\delta y}^p \) phonons and \( \omega_{\perp p} \) is the frequency of the \( u_{\delta x}^p \) and \( u_{\delta y}^p \) phonons. \( \omega_{\parallel p} \) can be associated with the frequency of \( \text{Cu}_O \)-stretching mode phonons and \( \omega_{\perp p} \) with that of \( \text{Cu}_O \) bending mode phonons. The supraindex in the Green functions indicates that the poles should be shifted by that amount. The absorption coefficient is obtained assuming weak absorption as \( \alpha = \frac{\pi}{\omega_{\parallel p}} \sigma \) with \( \epsilon_1 \) the real part of the dielectric constant [3] (b).

To compute the magnon-magnon Green functions we use interacting spin-wave theory [1] with a Holstein-Primakoff transformation. On the A (B) sublattice we put \( S_i^+ = (S_i^-)^2 = \sqrt{2}S(1 - b_i^0 b_i^0) \) 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 don’t need to distinguish between them. Accordingly we work in the non-magnetic Brillouin zone. The Heisenberg Hamiltonian in this representation is expanded to zero order in \( 1/S \) and normal ordered with respect to the non-interacting spin-wave ground state. The non-interacting part is diagonalized by the Bogoliubov transformation \( Q_k^i = u_k b_k^i - v_k b_{-k}, \) where \( b_k \) is the Fourier transform of \( b_i \) and \( u_k = \sqrt{(1 + \omega_k)/(2\omega_k)}, v_k = -\text{sgn}(\gamma_k) \sqrt{(1 - \omega_k)/(2\omega_k)}, \) with \( \gamma_k = 2/z \sum_A \delta(\mathbf{k}, \mathbf{\delta}), \omega_k = \sqrt{1 - \gamma_k} \) and \( z \) is the coordination number (\( z = 4 \) in our case). We define \( g_{pq,q_2} = \langle Q_i^p + q_1 Q_i^{p-q_1}; Q_i^p + q_2 Q_i^{p+q_2} \rangle. \) 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 \( \langle \delta \mathbf{B}_p^{x} \delta \mathbf{B}_p^{x} \rangle \) can be written as a sum of such quantities with proper weighting factors [3]. The dashed-dotted line in Fig. 3 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 shift appreciably the peak at \( p = (\pi, 0) \) and only decreases slightly the intensity \[12\]. The Green function takes the form \[\langle \delta B^+ \cdot \delta B^\ast \rangle = \frac{1}{N} G_{xx} \] where

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

When,

\[
G^{(0)}_{\delta q'} = \frac{1}{N} \sum_q \frac{u^2_{\delta p+q}u^2_{p-q} \cos(q_3) \cos(q_3')}{\omega - E_{\delta p+q} - E_{\delta p-q}},
\]

\( E_k = E_m \omega_k \), \( E_m = zSJ_0(1 + \zeta/2S) \) and \( \zeta \) is the Oguchi correction \[3\], \( \zeta \approx 0.158 \) in our case. Eq. \(8\) takes the familiar form at \( p = (\pi, 0) \), \( G_{xx} = \frac{G^{(0)}_{xx}}{1 + 2J_0G^{(0)}_{xy}} \). 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 life time or narrow peak. In the inset of Fig. 1 we show the imaginary part of the Green function calculation for the two-magnon peak \( G^{(0)}_{xy} \) for different values of \( p \). This shows how the bimagnon disperses around \( p = (\pi, 0) \) it goes upwards on going towards \((0, 0)\) and downwards on going towards \((\pi, \pi)\). This indicates that \( (\pi, 0) \) is a saddle point and hence it should give a Van Hove singularity when integrated over \( p \) \[Eq. \(8\)\]. The dashed curve in Fig. 1 is the theoretical line shape in the same approximation and assuming that the anisotropic processes dominate \( (q_3 = 0) \) and treating the phonons as Einstein like with \( \omega_\parallel = 0.08eV \) \[13\]. 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 change significantly 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 \( J_0 = 0.121eV \) which is in good agreement with other estimates \[2,14\].

The \( \omega_\parallel \) phonon is very anomalous in orthorhombic \( La_2CuO_4 \) since it splits due to anharmonicities \[13\] its partner being at \( \omega'_\parallel = 0.06eV \) at room temperature. Presumably this produces the shoulder observed at lower energies in the experiments \( \text{Fig. 1} \), 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 \[6\] made weakly allowed by the lower lattice symmetry according to the results of Ref. \[7\]. 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 \[10\] 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 \( qA = .1e \) and \( \epsilon_1 = 5 \) gives a value \( \sim 4 \) times smaller than observed which is quite reasonable given the uncertainties involved.

We interpret the side bands 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 side bands we have also computed the absorption using exact diagonalization of a small cluster \[3\]. The exact result confirms the Green function calculation for the two-magnon peak and shows also side bands corresponding to higher multimagnon processes which we associate with the higher energy side bands observed in the experiments. The relative weight of the side bands seem 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 \[3\]. 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 CuO 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 \( q_3 = 0 \).

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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