PHYSICAL REVIEW B VOLUME 62, NUMBER 18 1 NOVEMBER 2000-II

Midinfrared absorption in $YBa_2Cu_3O_6$: Evidence for a failure of spin-wave theory for spin $\frac{1}{2}$ in two dimensions

M. Grüninger,[1,*] D. van der Marel,[1] A. Damascelli,[1,†] A. Erb,[2,‡] T. Nunner,[3,4] and T. Kopp[3,4]
[1]*Laboratory of Solid State Physics, MSC, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[2]*Département de Physique de la Matière Condensée, Université de Genève, CH-1211 Genève, Switzerland*
[3]*Institut für Theorie der Kondensierten Materie, Universität Karlsruhe, D-76128 Karlsruhe, Germany*
[4]*Experimentalphysik VI, Universität Augsburg, D-86135 Augsburg, Germany*
(Received 1 August 2000)

The optical conductivity $\sigma(\omega)$ of undoped and very low doped $YBa_2Cu_3O_{6.0\delta}$ is studied in detail in the midinfrared range. We collect experimental evidence for a magnetic origin of the observed absorption. The main resonance peak is well described by a bimagnon-plus-phonon absorption spectrum calculated within spin-wave theory. But spin-wave theory fails to describe further resonances at higher frequencies with significant spectral weight, which grows with both temperature and doping. This underlines the importance of quantum fluctuations for the description of short-wavelength magnetic excitations in a two-dimensional spin-1/2 system.

The undoped parent compounds of the high-T_c cuprates are regarded as an almost ideal realization of a two-dimensional (2D) spin-1/2 Heisenberg antiferromagnet. Despite the low dimensionality and the low spin the excitations are thought to be spin waves with a well-defined dispersion,[1] as opposed to, e.g., 1D systems, where a spinon continuum is observed in neutron scattering.[2] In the cuprates, a spin-wave dispersion has been extracted throughout the whole Brillouin zone from neutron scattering data, but energies are rather high, large backgrounds are observed, and the magnitude of quantum corrections is unclear.[3] In principle, two-magnon (2M) Raman scattering should allow one to decide whether the magnetic excitations are well described by spin-wave theory. The data show several anomalies in the cuprates, in particular a very broad line shape, spectral weight at high energies, and a finite signal in A_{1g} geometry.[4] Interpretations in terms of an interaction with phonons[5] and extensions of the Heisenberg model[6] have been proposed. Their relevance is limited, since they neglect the dominant influence of the charge transfer resonance[7] on the data, which does not allow a decision on the nature of magnetic excitations at the present stage.

Optical spectroscopy probes the magnetic excitations more directly. The main midinfrared absorption (MIR) peak of La_2CuO_4 and other single-layer cuprates[8] has been interpreted by Lorenzana and Sawatzky[9] in terms of bimagnon-plus-phonon (BIMP) absorption. A similar feature was reported in the bilayer system $YBa_2Cu_3O_6$ ($YBCO_6$).[10] Above the main BIMP peak, the experimental spectra of both single-layer and bilayer cuprates show further resonances with considerable spectral weight, in disagreement with spin-wave theory. These high-energy excitations have not been seen in the $\mathbf{S}=1$ system La_2NiO_4 (Refs. 9 and 11) where excellent agreement is achieved between spin-wave theory and experiment[9] because fluctuations beyond spin-wave theory are small for $\mathbf{S}=1$. Neither does the *one-dimensional* $\mathbf{S}=1/2$ system Sr_2CuO_3 (Refs. 12 and 13) display additional high-energy resonances beyond the main BIMP resonance whose line shape and weight are in agreement with spinon theory. The large-weight high-energy resonances are only found in the $\mathbf{S}=1/2$ 2D systems. Interpretations in terms of multi-magnon-plus-phonon absorption,[9] d-d transitions,[11] and charge transfer excitons[14] have been proposed. We challenge these approaches and suggest that a full account of our MIR data in the undoped cuprates has to include quantum fluctuations *beyond* spin-wave theory. This might provide an important contribution to the basic picture of magnetic excitations in the undoped cuprates. Detailed knowledge about the character of magnetic excitations is particularly important for the physics at finite doping concentrations, since the charge dynamics in the doped cuprates are mainly determined by interactions with the magnetic background. The assumption that magnons are *not* well-defined particles at the Brillouin zone boundary was a key point in the successful description by Chubukov and Morr[15] of the photoemission data of insulating $Sr_2CuO_2Cl_2$. Laughlin interpreted the same photoemission data as evidence for the existence of spinons in 2D.[16]

Single crystals of $Y_{1-y}R_yBa_2Cu_3O_x$ ($y=0$ and 0.8; $R=$Pr, Gd) were grown in Y_2O_3-stabilized ZrO_2 crucibles.[17] In order to obtain an O content of $6.0\leqslant x\leqslant 6.05$ we annealed the samples in ultrahigh vacuum at 700 °C or for 2–5 days in a flow of high-purity argon (99.998%) at 750 °C. The full exchange of the O isotope in a sample grown in $BaZrO_3$ (Ref. 18) was described in Ref. 19. We calculated $\sigma(\omega)$ by inverting the Fresnel equations for the measured transmission and reflection data.

In Fig. 1 we display $\sigma(\omega)$ of $YBCO_6$ for $T=4$ and 300 K in the midinfrared range. The onset of charge transfer absorption is observed at about 10 000 cm^{-1}. Since phonons are limited in the cuprates to frequencies below 700 cm^{-1}, there are only three possibilities to explain the midinfrared absorption depicted in Fig. 1: magnetic excitations, crystal field transitions, or finite doping. The latter can be excluded since the same absorption occurs in $Sr_2CuO_2Cl_2$,[8,20] which cannot be doped. Both other processes are symmetry forbid-

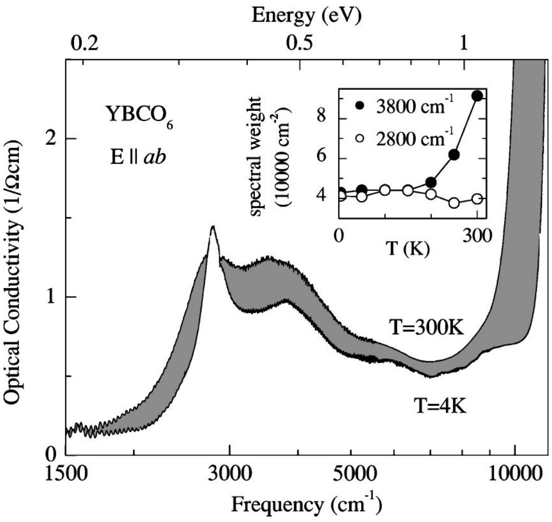

FIG. 1. Optical conductivity $\sigma(\omega)$ of $YBCO_6$ at 4 and 300 K. Inset: experimental temperature dependence of the spectral weight of the 2800 and 3800 cm^{-1} peaks.

den and can be weakly allowed due to a coupling to phonons.[21] In case of the crystal field d-d exciton suggested by Perkins *et al.*,[11] there is theoretical[22,23] and experimental[24] evidence that its energy is a factor of 2–3 too high to account for the data.[25] Moreover, quantum chemistry calculations show that also the dependence of the peak position on the different ligand configurations of La_2CuO_4, $Sr_2CuO_2Cl_2$, and $YBCO_6$ is not consistent with an exciton interpretation.[26] Wang *et al.* predict a charge transfer exciton at 0.8 eV (6500 cm^{-1}) from fits to electron energy-loss spectroscopy (EELS) data between 2.5 and 4 eV.[14] A charge transfer exciton should follow the strong redshift of the onset of charge transfer absorption with increasing temperature (10 500–9000 cm^{-1}; see Fig. 1), which is not observed.

Therefore we follow the interpretation of $\sigma(\omega)$ of the single-layer compounds[9] and ascribe the main peak at 2800 cm^{-1} to bimagnon-plus-phonon absorption. The lowest-order magnetic excitation contains *two* magnons in order to conserve spin. The single-magnon dispersion extends up to $\nu S Z_c J$, where $\nu=4$ is the number of nearest neighbors, $Z_c=1.158$ is a quantum correction, and J is the exchange constant. Therefore the two-magnon continuum has a cutoff at $4Z_cJ$. A rough estimate of the MIR and Raman peak frequency has to include the two-magnon binding energy. This is obtained by flipping two spins on neighboring sites in the Ising limit, which yields $3Z_cJ$. Spin-wave theory gives $3.38J$ for the 2M Raman peak and $2.73J$ plus the phonon frequency for the MIR absorption peak (inset of Fig. 4). The difference arises because Raman spectroscopy is only sensitive to two magnons with total momentum $k_{2M}=0$, whereas the MIR absorption is dominated by two-magnon bound states (bimagnons) with k_{BIM} from the Brillouin zone boundary and $k_{BIM}+k_{ph}=0$.[9] The experimental spectra of the substituted samples corroborate this assignment. Substitution of Y by Pr or Gd leads to a significant frequency shift of the main peak (left panel of Fig. 2). Similar shifts were observed in 2M Raman scattering[27,28] and were explained by the dependence of J on the lattice parameter a. A finite phonon contribution to the BIMP peak is evident from the frequency shift induced by oxygen isotope substitution in $YBCO_6$ (right panel of Fig. 2). The measured isotope shift of 28 ± 8 cm^{-1} is consistent with the BIMP interpretation, assuming that the longitudinal stretching phonon of approximately 550–600 cm^{-1} is excited. With increasing temperature the absorption increases (Fig. 1), in particular at high frequencies, where the spectral weight grows by a factor of more than 2 from 4 to 300 K (solid circles in inset of Fig. 1). A similar behavior can be detected in the temperature dependence of $\sigma(\omega)$ of $Sr_2CuO_2Cl_2$.[20] An increase of magnetic absorption is also observed upon very low doping ($x\leq6.05$), again in particular at high frequencies (Fig. 3). The finite background conductivity is discussed in Ref. 25.

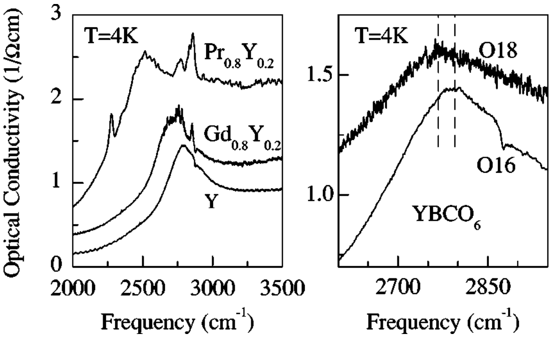

FIG. 2. Effect of rare earth and O isotope substitutions on the main bimagnon-plus-phonon peak.

For a more critical analysis of line shape and spectral weight we calculate the BIMP contribution to $\sigma(\omega)$ for the bilayer case. In order to obtain the coupling to light we start from a Heisenberg Hamiltonian which takes into account a dependence of the in-plane and interplane exchange constants J and J_{12} on the external electric field $\mathbf{E}$ and the phonon coordinates:[9]

$$H=\sum_{L=1,2}\sum_{\langle i,j\rangle} J(\mathbf{E},\mathbf{u})\mathbf{S}_{L,i}\mathbf{S}_{L,j}+\sum_{i} J_{12}(\mathbf{E},\mathbf{u})\mathbf{S}_{1,i}\mathbf{S}_{2,i},$$

where i and j label nearest-neighbor Cu sites in a 2D square lattice, L labels the two planes in a single bilayer, and $\mathbf{u}$

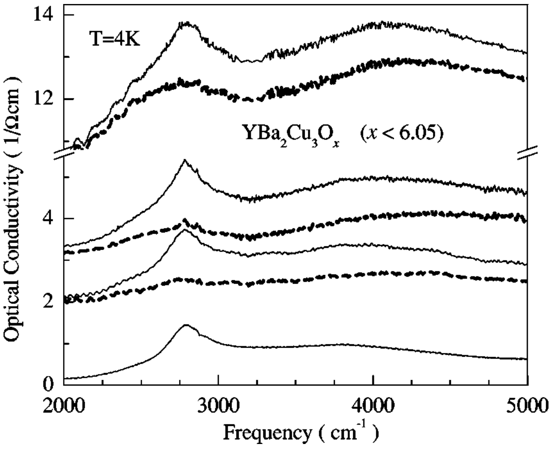

FIG. 3. Solid lines: very low doping $x\leq6.05$ causes a finite background in $\sigma(\omega)$ and an increase of magnetic absorption compared to the lowest curve (undoped, same as Fig. 1). Dashed lines: same data after subtraction of the undoped $\sigma(\omega)$.

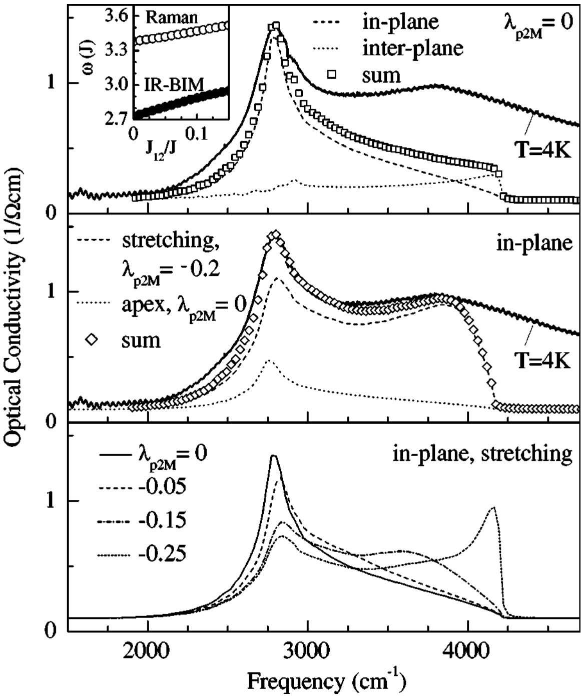

FIG. 4. Comparison of experimental and theoretical results for $J = 780$ cm^{-1}, $J_{12}/J = 0.1$, and $\hbar\omega_{ph} = 530$ cm^{-1} (stretching phonon mode). A small constant background of 0.1 $(\Omega\ \mathrm{cm})^{-1}$ has been added to all theoretical curves. Top panel, solid line: experimental data, same as Fig. 1. Dashed and dotted lines: in-plane and interplane contributions to BIMP absorption for $\lambda_{p2M} = 0$. Open squares: sum of the two. Midpanel: comparison with experiment (solid line) for finite λ_{p2M}. Diamonds depict the sum of the dashed and the dotted lines (Ref. 33) See text for details. Bottom panel: influence of a repulsive phonon-magnon coupling λ_{p2M} on the line shape for the in-plane contribution of the stretching phonon mode. Inset: 2M Raman and infrared bimagnon peak frequencies as a function of J_{12}/J. In the infrared case, the phonon frequency still has to be added for a comparison with experimental data.

TABLE I. Measured frequencies of the two main MIR absorption peaks, their ratio, and the 2M cutoff (all frequencies in cm^{-1}).

	Peak A	Peak B	A/B	2M cutoff
$YBa_2Cu_3O_6$	2800	3800	0.74	$3700 = 4.72J$
La_2CuO_4	3300 [a]	4500 [a]	0.73	$4500 = 4.63J$
$Sr_2CuO_2Cl_2$	2900 [a]	4000 [a]	0.73	$4000 = 4.63J$

[a] Taken from Ref. 8.

denotes the displacements of O ions. Only Einstein phonons are considered. The different phonons modulate the intersite hopping and the on-site energies on both Cu and O sites. We expand $J(\mathbf{E},\mathbf{u})$ to order $d^2J/d\mathbf{u}d\mathbf{E}$ which entails the coupling of a photon to a phonon and two neighboring spins. We calculate $\sigma(\omega)$ in spin-wave theory and treat interactions in the random phase approximation (RPA). This goes beyond Ref. 9 where a high-energy approximation had been used. Since it is not possible to determine both J and J_{12} from $\sigma(\omega)$, we have also calculated the 2M Raman spectrum within the nonresonant approach. From the calculated spectra both the Raman and infrared peak frequencies were derived as a function of J and J_{12} (inset of Fig. 4). At $T = 4$ K the experimental BIMP and 2M Raman[4] spectra peak at 2795 and 2720 ± 10 cm^{-1}, respectively. From these we obtain $J = 790 \pm 10$ cm^{-1} and $J_{12}/J = 0.08 \pm 0.04$ for $\hbar\omega_{ph} \approx 550 \pm 25$ cm^{-1}. Neutron data[30–32] suggest $J = 870 \pm 35$ cm^{-1}, $J_{12}/J = 0.09 \pm 0.02$, and $\hbar\omega_{ph} \approx 550$–$600$ cm^{-1} for the relevant longitudinal stretching phonon mode.

In the top panel of Fig. 4 the calculated BIMP absorption (open squares) for $J = 780$ cm^{-1}, $J_{12} = 0.1J$, and $\hbar\omega_{ph} = 530$ cm^{-1} is plotted together with the experimental curve (solid line). In a bilayer we have to distinguish an in-plane (dashed line) and an interplane contribution (dotted line). Due to the small value of $J_{12}/J = 0.1$, the interplane contribution has only a minor effect on the spectrum with an estimated relative spectral weight of only 0.06–0.3 of the in-plane contribution. Therefore we only consider the in-plane contribution below, and our analysis applies to both single-layer and bilayer materials. The total spectral weight is similar in the bilayer $YBCO_6$ and in single-layer La_2CuO_4 both experimentally and theoretically. The perturbatively estimated spectral weight is a factor of 4–7 too small compared to experiment, which in the case of the spectral weight should be considered as reasonable for a perturbative result.[34]

As in the single-layer cuprates, the real problem is obviously at higher frequencies: the large amount of spectral weight at high frequencies with a strong peak at 3800 cm^{-1} and its increase with both temperature and doping remain unexplained. The frequency ratio of the two dominant MIR peaks is about 0.73 in several cuprates and the second peak is located close to the 2M cutoff (Table I), strongly suggesting a common magnetic origin. It is likely that the high-energy anomaly has the same origin in both MIR and Raman spectra. Phonon-magnon scattering processes were considered for the explanation of the width of the 2M Raman resonance.[5,6] The adiabatic approach models static disorder which enhances the width but does not result in a second resonance. For this to appear we include multiple phonon-2M scattering processes which are generated by the modulations $\sim d^2J/d\mathbf{u}^2$ in the Hamiltonian. Details will be published elsewhere.[29] The coupling between phonons and two magnons,

$$\lambda_{p2M} = \left(\frac{1}{2J}\right)\left\langle\frac{d^2J}{du^2}\right\rangle\langle u^2\rangle,$$

is estimated perturbatively, $\lambda_{p2M} \approx -0.02 \ldots +0.01$, for the stretching phonon mode.[25,35,36] A negative value of λ_{p2M} translates into a repulsive phonon-2M interaction and shifts spectral weight to higher frequencies (bottom panel of Fig. 4). A way to test the reliability of our estimate of λ_{p2M} is to compare the *linear* coupling $dJ/d\mathbf{u}$ with the experimental pressure dependence of J.[37] There, our estimate is 1–2 times smaller. However, in order to reproduce the experimentally observed high-frequency spectral weight we need a very large coupling constant of $\lambda_{p2M} = -0.2$ (dashed line in the midpanel of Fig. 4).[33] In this scenario, a reasonable fit of the experimental line shape is obtained up to the 2M cutoff if we add the BIMP contribution of the apical stretching phonon (dotted line in the midpanel of Fig. 4), which is expected to have a 5 times smaller weight and a negligible phonon-2M coupling. The sum is depicted by the diamonds in the mid-panel of Fig. 4. The one order of magnitude too large value of $\lambda_{p2M}=-0.2$ for the stretching phonon makes such a scenario unlikely. This is substantiated by the absence of the anomaly in both MIR and Raman spectra in $\mathbf{S}=1$ La_2NiO_4 (Refs. 11 and 38) where one would not expect a phonon-magnon coupling one order of magnitude smaller.

We propose that these findings support the notion of a strong local deviation from the Néel state. Whereas the broken symmetry of the antiferromagnetic state will still support long-wavelength spin-wave excitations, the character of the *short-wavelength* magnetic excitations reflects the strong quantum fluctuations in the $\mathbf{S}=1/2$ system and consequently the excitations are insufficiently represented by spin waves. The MIR absorption is dominated by short-wavelength magnetic excitations which prohibits a full understanding within spin-wave theory. With increasing temperature the system loses the 3D correlations and becomes more two dimensional, which enhances quantum fluctuations and explains the observed temperature dependence. This scenario also elucidates the observed doping dependence (Fig. 3), since quantum fluctuations are enhanced by carrier doping. We emphasize that this interpretation does not contradict the good agreement of neutron scattering results with spin-wave theory for small momenta. Note that even in 1D the inapplicability of a spin-wave picture to neutron data was not realized for many years.[39]

Our treatment neglects four- or six-magnon processes, for which an interacting spin-wave calculation is beyond reach. Very recently, exact diagonalization studies of the Heisenberg model on clusters of up to 32 sites produced only a minor contribution to MIR absorption at high frequencies.[40] A slight increase of this high-energy weight was observed if four-spin terms and interactions between more distant sites were included in the Hamiltonian.[40] These additional terms are known to enhance quantum fluctuations.[41] However, finite-size scaling is not reliable for these cluster sizes of 16–26 sites as, e.g., the Raman spectrum varied strongly in exact diagonalization and quantum Monte Carlo studies even for much larger clusters.[42] Furthermore, it is questionable whether cyclic four-spin exchange terms can explain the increase of absorption with finite doping, as observed in our data, because doping reduces the number of plaquettes with four spins.

We conclude that present day understanding of magnetic excitations in undoped cuprates is not sufficient to explain both MIR and Raman data. Only a more appropriate treatment of the short-wavelength excitations of a 2D spin-1/2 system — one of the outstanding problems of quantum magnetism — will explain the observed anomalies. Any successful interpretation will not only have to describe the large amount of high-frequency spectral weight observed at 4 K, but also its strong increase with increasing temperature and doping concentration.

We want to thank G.A. Sawatzky, R. Eder, P. Wölfle, and J. Brinckmann for helpful discussions. This project was supported by the Netherlands Foundation for Fundamental Research on Matter (FOM) with financial aid from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and by the DFG, SFB 484, DFG-GK, and BMBF 13N6918/1.

---

*Present address: II. Physikalisches Institut, Universität zu Köln, Zülpicherstr. 77, 50937 Köln, Germany.

†Present address: Laboratory for Advanced Materials, Stanford University, Stanford, CA 94305.

‡Present address: Walther Meissner Institut, Bayerische Akademie der Wissenschaften, 85748 Garching, Germany.

[1] E. Manousakis, Rev. Mod. Phys. **63**, 1 (1991).

[2] D.A. Tennant, R.A. Cowley, S.E. Nagler, and A.M. Tsvelik, Phys. Rev. B **52**, 13 368 (1995).

[3] P. Bourges, H. Casalta, A.S. Ivanov, and D. Petitgrand, Phys. Rev. Lett. **79**, 4906 (1997).

[4] G. Blumberg, P. Abbamonte, M.V. Klein, W.C. Lee, D.M. Ginsberg, L.L. Miller, and A. Zibold, Phys. Rev. B **53**, 11 930 (1996).

[5] F. Nori, R. Merlin, S. Haas, A.W. Sandvik, and E. Dagotto, Phys. Rev. Lett. **75**, 553 (1995).

[6] J. Eroles, C.D. Batista, S.B. Bacci, and E.R. Gagliano, Phys. Rev. B **59**, 1468 (1999).

[7] A.V. Chubukov and D.M. Frenkel, Phys. Rev. Lett. **74**, 3057 (1995); D.K. Morr, A.V. Chubukov, A.P. Kampf, and G. Blumberg, Phys. Rev. B **54**, 3468 (1996).

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

[9] J. Lorenzana and G.A. Sawatzky, Phys. Rev. Lett. **74**, 1867 (1995); Phys. Rev. B **52**, 9576 (1995).

[10] M. Grüninger, J. Münzel, A. Gaymann, A. Zibold, H.P. Geserich, and T. Kopp, Europhys. Lett. **35**, 55 (1996).

[11] J.D. Perkins, D.S. Kleinberg, M.A. Kastner, R.J. Birgeneau, Y. Endoh, K. Yamada, and S. Hosoya, Phys. Rev. B **52**, R9863 (1995).

[12] H. Suzuura, H. Yasuhara, A. Furusaki, N. Nagaosa, and Y. Tokura, Phys. Rev. Lett. **76**, 2579 (1996).

[13] J. Lorenzana and R. Eder, Phys. Rev. B **55**, R3358 (1997).

[14] Y.Y. Wang, F.C. Zhang, V.P. Dravid, K.K. Ng, M.V. Klein, S.E. Schnatterly, and L.L. Miller, Phys. Rev. Lett. **77**, 1809 (1996); F.C. Zhang and K.K. Ng, Phys. Rev. B **58**, 13 520 (1998).

[15] A.V. Chubukov and D.K. Morr, Phys. Rev. B **57**, 5298 (1998).

[16] R.B. Laughlin, Phys. Rev. Lett. **79**, 1726 (1997).

[17] A. Erb, T. Traulsen, and G. Müller-Vogt, J. Cryst. Growth **137**, 487 (1994).

[18] A. Erb, E. Walker, and R. Flükiger, Physica C **245**, 245 (1995); **258**, 9 (1996).

[19] M. Grüninger, D. van der Marel, A. Damascelli, A. Zibold, H.P. Geserich, A. Erb, M. Kläser, Th. Wolf, T. Nunner, and T. Kopp, Physica C **317-318**, 286 (1999).

[20] A. Zibold, H.L. Liu, S.W. Moore, J.M. Graybeal, and D.B. Tanner, Phys. Rev. B **53**, 11 734 (1996).

[21] Direct excitation of two magnons in bilayers via spin-orbit coupling was suggested (Ref. 10) to reproduce the MIR line shape in $YBCO_6$ up to 4000 cm^{-1}. However, a spin exchange of $J_{12}=0.5J$ had to be assumed, which is not anymore consistent with neutron scattering (Refs. 30 and 31).

[22] H. Eskes, L.H. Tjeng, and G.A. Sawatzky, Phys. Rev. B **41**, 288 (1990).

[23] R.L. Martin and P.J. Hay, J. Chem. Phys. **98**, 8680 (1993).

[24] P. Kuiper, J.-H. Guo, C. Såthe, L.-C. Duda, J. Nordgren, J.J.M.

Pothuizen, F.M.F. de Groot, and G.A. Sawatzky, Phys. Rev. Lett. **80**, 5204 (1998).

[25] M. Grüninger, Ph.D. thesis, University of Groningen, 1999 (http://www.ub.rug.nl/eldoc/dis/science/m.u.grueninger).

[26] C. de Graaf and R. Broer (private communication).

[27] M. Yoshida, N. Koshizuka, and S. Tanaka, Phys. Rev. B **42**, 8760 (1990).

[28] S.L. Cooper, G.A. Thomas, A.J. Millis, P.E. Sulewski, J. Orenstein, D.H. Rapkine, S.-W. Cheong, and P.L. Trevor, Phys. Rev. B **42**, 10 785 (1990).

[29] T. Nunner, T. Kopp, M. Grüninger, and D. van der Marel (unpublished).

[30] D. Reznik, P. Bourges, H.F. Fong, L.P. Regnault, J. Bossy, C. Vettier, D.L. Milius, I.A. Aksay, and B. Keimer, Phys. Rev. B **53**, R14 741 (1996).

[31] S.M. Hayden, G. Aeppli, T.G. Perring, H.A. Mook, and F. Dogan, Phys. Rev. B **54**, R6905 (1996).

[32] S.L. Chaplot, W. Reichardt, L. Pintschovius, and N. Pyka, Phys. Rev. B **52**, 7230 (1995).

[33] Due to the dependence of the peak frequency on λ_{p2M}, we used $J=770\ \mathrm{cm}^{-1}$ in this case.

[34] The deviation is somewhat larger than given in Ref. 9, as a realistic estimate of $q_A/e=-6JU_{pd}/\Delta^2$ (see Ref. 9) yields $q_A/e \approx -0.025\ldots-0.08$ for both $\mathrm{La_2CuO_4}$ and $\mathrm{YBCO_6}$ (Ref. 25).

[35] W.A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[36] This is derived from Harrison's $t_{pd}(u)\approx t\times(1+u/a_{pd})^{7/2}$ (Ref. 35) and modulations of the on-site potentials.

[37] M.C. Aronson, S.B. Dierker, B.S. Dennis, S.-W. Cheong, and Z. Fisk, Phys. Rev. B **44**, 4657 (1991).

[38] S. Sugai, M. Sato, T. Kobayashi, J. Akimitsu, T. Ito, H. Takagi, S. Uchida, S. Hosoya, T. Kajitani, and T. Fukuda, Phys. Rev. B **42**, 1045 (1990).

[39] Y. Endoh, G. Shirane, R.J. Birgeneau, P.M. Richards, and S.L. Holt, Phys. Rev. Lett. **32**, 170 (1974).

[40] J. Lorenzana, J. Eroles, and S. Sorella, Phys. Rev. Lett. **83**, 5122 (1999).

[41] A.H. MacDonald, S.M. Girvin, and D. Yoshioka, Phys. Rev. B **37**, 9753 (1988); **41**, 2565 (1990).

[42] A.W. Sandvik, S. Capponi, D. Poilblanc, and E. Dagotto, Phys. Rev. B **57**, 8478 (1998).