



# Charged magnons and magneto-elastic polarons in the mid-infrared spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_6$

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## Abstract

The optical conductivity of undoped and low-doped  $\text{YBa}_2\text{Cu}_3\text{O}_6$  is studied in detail in the mid-infrared range. Full isotope substitution of  $^{16}\text{O}$  with  $^{18}\text{O}$  is used to (a) study the optical phonons in the far-infrared and (b) identify the rich structure emerging in the mid-infrared from multiphonon and bimagnon-plus-phonon absorption. Substitution of Zn in the  $\text{CuO}_2$  planes allows *direct* observation of bimagnon excitations. Very light chemical doping with oxygen introduces localized charge carriers in the form of magneto-elastic polarons, i.e., holes which are strongly coupled both to the vibrational and magnetic degrees of freedom. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The low-energy dynamics and in particular the infrared optical conductivity  $\sigma_1(\omega)$  of holes doped into a 2D antiferromagnet have been the subject of intensive theoretical investigations (for recent reviews, see Refs. [1,2,28,29]). But experimentally, the influence of very low levels of doping on the optical conductivity of the cuprates has not been studied so far. In the undoped parent compounds a contribution of magnetic excitations to the mid-infrared (MIR) optical conductivity has been established. The main

absorption peak at about 0.4 eV in the MIR transmission spectra of  $\text{La}_2\text{CuO}_4$  and other single layer cuprates [3] has been interpreted by Lorenzana and Sawatzky [4,5] in terms of bimagnon-plus-phonon absorption. A similar feature was reported in the bilayer system  $\text{YBa}_2\text{Cu}_3\text{O}_6$  [6], in the 2D  $S=1$  system  $\text{La}_2\text{NiO}_4$  [5,7] and in 1D  $S=1/2$   $\text{Sr}_2\text{CuO}_3$  [8,9]. In these compounds, direct bimagnon absorption is not dipole active due to symmetry, which can be broken by exciting a phonon simultaneously.

Here, we use full  $^{18}\text{O}$  substitution to identify the prominent resonances in the MIR spectrum of  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . In particular we use this to distinguish vibrational from electronic degrees of freedom and to give direct experimental evidence for the exis-

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tence of bimagnon-plus-phonon absorption. Symmetry breaking also occurs if Zn is substituted into the  $\text{CuO}_2$  planes. We report the observation of direct bimagnon absorption in a sample with 3% of Zn substitution. Recently, similar ‘charged magnons’ have been observed in the two-leg ladder compound [10]  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . In order to study the influence of low chemical doping we will compare spectra of eight different samples of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  with  $6.0 \leq x \ll 6.1$ , corresponding to an effective number of carriers of  $\leq 5 \times 10^{19} \text{ cm}^{-3}$ . In this paper, we will concentrate on the experimental results; a more detailed theoretical analysis will be given elsewhere.

## 2. Experimental

Single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  were grown using the recently developed  $\text{BaZrO}_3$  (BZO) crucibles [11,12], which in contrast to other container materials do not pollute the resulting crystals. Crystals grown using this technique exhibit therefore a superior purity ( $> 99.995 \text{ at.}\%$ ) [13]. To exchange the oxygen isotope, the crystals were annealed at  $600^\circ\text{C}$  in a sealed quartz ampoule containing a 99.5% isotope pure  $^{18}\text{O}$  atmosphere. The obtained weight gain corresponded to a complete exchange of the oxygen isotope. For comparison, single crystals grown in  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  (YSZ) crucibles have been studied as well. In one of these the oxygen content was fixed to O6 by annealing the sample in UHV at  $700^\circ\text{C}$  for several days. For all other samples an oxygen content close to O6 was obtained by annealing the crystals in a flow of high-purity argon (99.998%) at temperatures between  $650^\circ$  and  $750^\circ\text{C}$  for 2 to 7 days. In the case of  $\text{YBa}_2\text{Cu}_{3-y}\text{Zn}_y\text{O}_6$  [14], the melt nominally contained 5% of Zn. After oxygenation a  $T_c$  of 67 K was measured, and hence we obtain [30]  $0.05 \leq y \leq 0.07$ . Assuming that Zn prefers the planar  $\text{Cu}(2)$  sites this corresponds to a substitution of  $\approx 3\%$ . The samples had typical dimensions of  $1 \times 1 \text{ mm}^2$  in the  $ab$ -plane. For the transmission measurements the samples need to be thin in the  $c$ -direction. The Zn-free crystals were between 155 and  $18 \mu\text{m}$  thick, whereas the  $\text{YBa}_2(\text{Cu,Zn})_3\text{O}_6$  sample was polished down to  $35 \mu\text{m}$ . Infrared reflection and transmission measurements were carried out on two Fourier transform spectrometers between 4 meV and 1 eV for tempera-

tures between 4 and 300 K. All measurements were carried out with  $k \parallel c$  and the electric field vector parallel to the  $ab$ -plane.  $\sigma_1(\omega)$  has been calculated directly from the experimentally measured mid-infrared transmission and reflection data. The small remnants of interference fringes in some of the calculated spectra of  $\sigma_1(\omega)$  are artifacts caused by deviations of the measured data from the assumed ideal case of absolutely flat and plane parallel surfaces.

## 3. Results

In Fig. 1 we display the optical conductivity  $\sigma_1(\omega)$  in the mid-infrared for frequencies just above

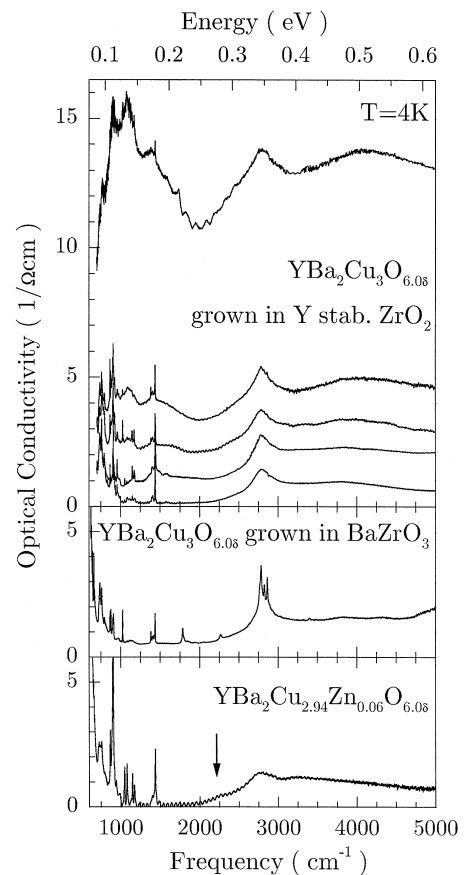


Fig. 1.  $\sigma_1(\omega)$  at  $T = 4 \text{ K}$  for  $E \parallel ab$ . Top panel: Five samples of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  grown in YSZ crucibles with very small differences in oxygen content,  $6.0 \leq x \ll 6.1$ . Mid panel: Sample grown in BZO. Lower panel: Zn-substituted sample. The arrow indicates direct bimagnon absorption.

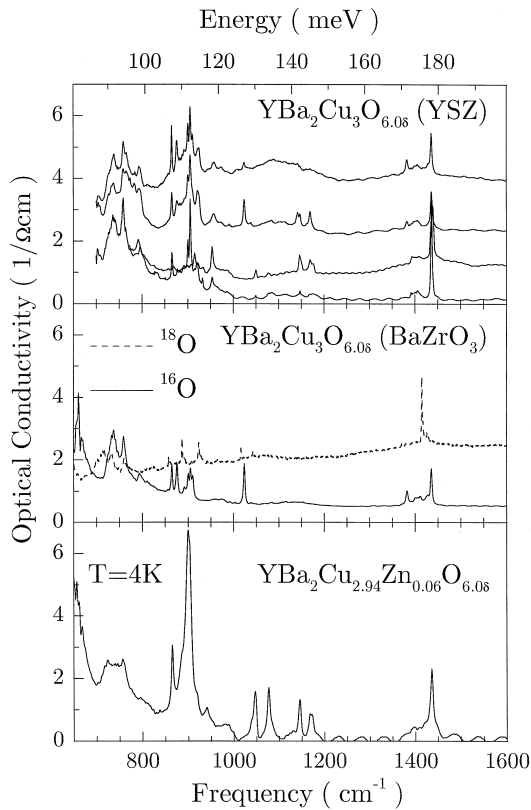


Fig. 2. Enlarged view of Fig. 1, displaying also the spectrum of a sample with full oxygen-18 substitution.

the highest phonon. Please note the very low values of  $\sigma_1(\omega)$ . The three panels show spectra of (from top to bottom): (a) five samples with zero to very little hole doping grown in YSZ crucibles, (b) a sample grown in a BZO crucible, (c) a sample with  $\approx 3\%$  of Zn substitution. At low frequencies the spectra are dominated by two-phonon absorption processes. Taking twice the highest phonon frequency measured in inelastic neutron scattering [15] we infer an upper cut-off for two-phonon absorption at about  $1360 \text{ cm}^{-1}$ . An enlarged view of this range is given in Fig. 2. We observe a strong sample dependence of multiphonon absorption, indicating that most of these processes are actually forbidden but made weakly dipole active due to, e.g., impurities. It is obvious that the spectral weight of these features increases if impurities are added, i.e., the spectral weight increases from the pure samples

grown in BZO crucibles to the samples grown in YSZ crucibles to the Zn-substituted sample.

The sharp line at  $1436 \text{ cm}^{-1}$ , i.e., above the upper two-phonon cut-off, is present in all samples. In an earlier paper this peak had been tentatively interpreted as a single optical magnon excitation [16] being weakly infrared active due to spin-orbit coupling. This interpretation was later contradicted by (i) the observation of this bilayer optical magnon at an energy of  $540 \pm 40 \text{ cm}^{-1}$  in inelastic neutron scattering spectra [16,17] and (ii) the absence of a magnetic-field induced shift of the sharp  $1436 \text{ cm}^{-1}$  line [18].

In order to clarify the nature of the  $1436 \text{ cm}^{-1}$  line we measured a fully oxygen isotope substituted sample. The isotope substitution was checked by (a) the weight gain after annealing as described above and (b) a comparison of the far-infrared phonon spectra (Fig. 3). The three oxygen phonon modes show isotope shifts of about 5%, which reflects some

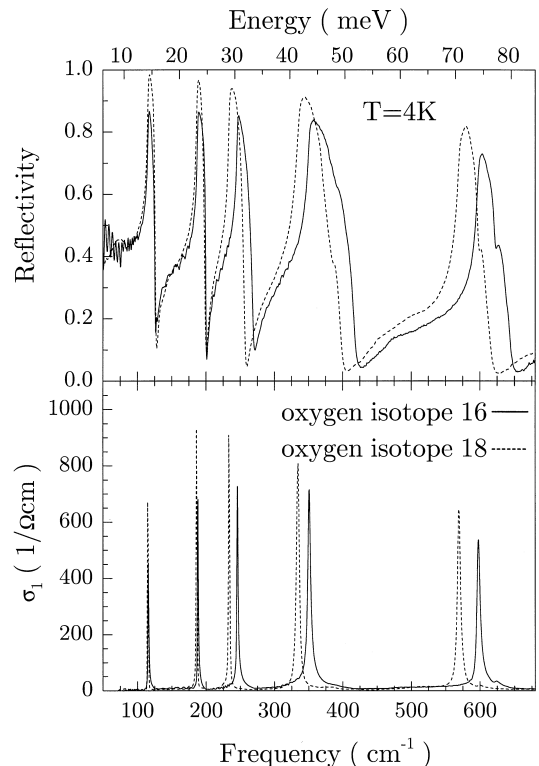


Fig. 3. FIR reflectivity and  $\sigma_1(\omega)$  of two samples of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  with different oxygen isotopes at  $T = 4 \text{ K}$  for  $E||ab$ . Both samples grown in BZO.

finite amount of copper character of these modes, as a pure oxygen mode should shift by about  $1 - \sqrt{16/18} \approx 5.7\%$ . Taking into account the finite oxygen contribution to the character of the other modes we conclude that the oxygen isotope indeed has been substituted completely. Details will be published elsewhere.

The sharp peak at  $1436 \text{ cm}^{-1}$  has a 1.46% isotope shift down to  $1415 \text{ cm}^{-1}$  in the  $^{18}\text{O}$  substituted sample (mid panel of Fig. 2). If this mode would be of pure vibrational (multiphonon) character, the shift should be about three to four times larger. Instead, the peak frequency and the isotope shift correspond to a combination tone of an electronic (or spin) excitation of  $\approx 1050 \text{ cm}^{-1}$  (with no isotope shift) and a phonon of about  $400 \text{ cm}^{-1}$ , with the corresponding isotope shift of about  $20 \text{ cm}^{-1}$ . Hence we suggest that this line is related to the bimagnon-plus-phonon absorption features observed at  $2800 \text{ cm}^{-1}$  and above. In this range,  $\sigma_1(\omega)$  of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  looks similar in shape and oscillator strength to the mid-infrared spectra of the single layer compounds [3] like  $\text{La}_2\text{CuO}_4$ . There this spectrum has been explained [4,5] as a combination tone involving bimagnons coupled to the in-plane stretching phonon mode. In  $\text{YBa}_2\text{Cu}_3\text{O}_6$  we observe an isotope shift of the main peak at  $2795 \text{ cm}^{-1}$  of  $28 \pm 8 \text{ cm}^{-1}$ , in agreement with the eigenfrequency of the longitudinal stretching phonon mode of about  $550$  to  $600 \text{ cm}^{-1}$ . This serves as a direct experimental test for the validity of the bimagnon-plus-phonon interpretation. The large error bars are due to the large linewidth of this peak. An extensive theoretical analysis of the bimagnon-plus-phonon spectrum of a bilayer system will be presented elsewhere.

Direct bimagnon absorption is not infrared active in the cuprate parent compounds due to inversion symmetry. Bimagnon-plus-phonon absorption processes obtain a finite spectral weight if the phonon involved breaks this symmetry. Substituting Zn into the  $\text{CuO}_2$  planes has a similar symmetry breaking effect, i.e., it should be possible to observe *direct* bimagnon absorption in the sample containing approximately 3% of Zn. But phonons are not only breaking the symmetry, they also contribute momentum. Only the combined  $\vec{k} = \vec{k}_{\text{phonon}} + \vec{k}_{\text{bimagnon}}$  has to be zero in order to be infrared active. Hence the infrared bimagnon-plus-phonon spectrum is a

weighted average over the Brillouin zone. In the case of a localized impurity,  $\vec{k}$  is not a good quantum number any more. Again we have to average over the whole Brillouin zone, only with a slightly different form factor. Therefore, the peak frequencies of charged bimagnon absorption can be inferred by subtracting the appropriate phonon frequency from the bimagnon-plus-phonon peaks. This yields about  $2200 \text{ cm}^{-1}$  for the main peak, which indeed corresponds to a broad absorption feature present only in the sample containing Zn (see arrow in Fig. 1).

In this spirit, the doublet at  $1060 \pm 20 \text{ cm}^{-1}$  which is only present in the Zn-substituted sample (Fig. 2) can tentatively be attributed to direct bimagnon absorption, possibly of two magnons at the Brillouin zone center. Results from inelastic neutron scattering [16,17] indicate a frequency of the optical magnon branch at  $\vec{k} = 0$  of  $540 \pm 40 \text{ cm}^{-1}$ , as mentioned above. At first sight, this seems to agree with our observation that the sharp line at  $1436 \text{ cm}^{-1}$  can be explained as a combination tone of a spin excitation of  $\approx 1050 \text{ cm}^{-1}$  and a phonon of about  $400 \text{ cm}^{-1}$ . But this still needs to be checked in a careful theoretical analysis. However, the temperature dependence of the doublet points in the same direction, as argued in an earlier paper [19].

For higher frequencies the situation is less clear. The undoped sample (lowest curve in the top panel of Fig. 1) shows a maximum at about  $\omega_1 = 3800 \text{ cm}^{-1}$ , and there is a second maximum at about  $\omega_2 = 4300 \text{ cm}^{-1}$  in the sample grown in a BZO crucible (mid panel of Fig. 1). With increasing hole doping the spectra first show both broad structures and finally there is only one broad peak centered between  $\omega_1$  and  $\omega_2$  for the highest doping value studied. After substituting Zn there is no clear maximum any more at these frequencies, but a new one appears at about  $3200 \text{ cm}^{-1}$ . Regarding the frequency, this could again be direct magnon absorption. However, the strong broadening of the spectrum due to scattering of magnons by the Zn impurities makes a definite assignment impossible. We want to mention that in single layer cuprates the interpretation of the structures above the main bimagnon-plus-phonon peak is still controversial. An assignment to higher order magnon-plus-phonon contributions [4,5] has been suggested, but in this scenario it is difficult to explain the relatively large

oscillator strength observed [20,21]. However, it is possible that strong quantum fluctuations would enhance the oscillator strength. A comparison with data of  $S = 1$   $\text{La}_2\text{NiO}_4$  led Perkins et al. to the conclusion that these higher energy features have to be viewed as a  $d-d$  exciton with sidebands [7,22]. However, this exciton should not be IR active, it should also be present in the Raman spectrum and there is theoretical [23,24] and experimental [25] evidence that its actual energy is a factor of two to three higher. Recent measurements of the pressure dependence of the IR and Raman spectra [26] of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  favor a magnetic origin for the peak at about  $4000\text{ cm}^{-1}$ .

The additional sharp structures between  $1800$  and  $3000\text{ cm}^{-1}$  which are only present in the sample grown in a BZO crucible are not understood at this moment.

Let us finally discuss the changes in  $\sigma_1(\omega)$  when of the order of  $10^{19}\text{ cm}^{-3}$  carriers have been added. Most prominent are the following.

(1) An increase in oscillator strength, both for multiphonons and bimagnon-plus-phonons.

(2) A very broad, flat background, which can be identified with the incoherent contribution from a magnetic polaron.

(3) A strong peak at about  $1000\text{ cm}^{-1}$ . A similar feature in  $\text{La}_2\text{CuO}_{4+y}$  has been previously attributed to a dielectric polaron [27]. This assignment is supported by the temperature dependence, indicated in the upper panel of Fig. 4: At low temperatures, the polaron is being formed, whereas at elevated temperatures activated phonons wash out the potential well and the peak vanishes.

The observation of a polaron involving both magnetic and vibrational degrees of freedom indicates that the electron–phonon interaction is dominated by the electron–spin interaction: The doped hole oscillates rapidly on the scale of the hopping parameter  $t$  within a small region of reduced staggered magnetization, which gives rise to the broad absorption of point (2). Without an interaction with phonons this spin-polaron moves on a scale of the exchange constant  $J$ . As this motion is slow, already a moderate coupling  $\lambda$  to the lattice is sufficient to distort the lattice around the *spin-polaron*, i.e., to form a *magneto-elastic* polaron (point (3)). But if  $\lambda$  is not too big, the rapid oscillatory movement on the scale of  $t$

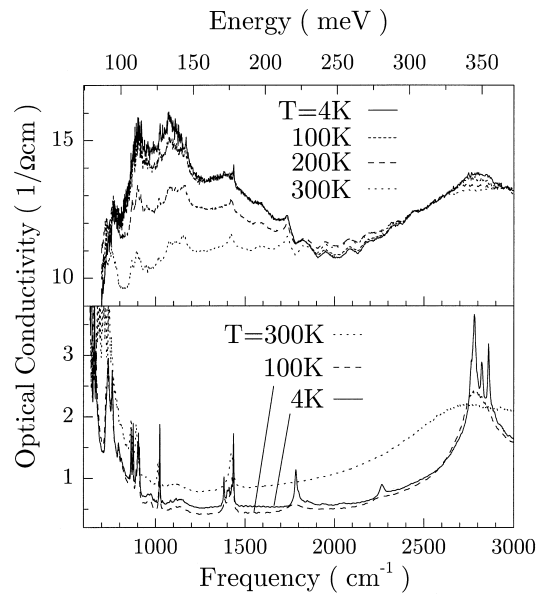


Fig. 4. Temperature dependence of  $\sigma_1(\omega)$  for  $E\parallel ab$  for  $\text{YBa}_2\text{Cu}_3\text{O}_x$  with different oxygen contents in the range  $6.0 < x \ll 6.1$ . Sample in lower (upper) panel grown in BZO (YSZ).

will still be possible. In terms of  $\sigma_1(\omega)$  this means that a finite  $\lambda$  suppresses the Drude contribution centered at  $\omega = 0$  and shifts the spectral weight to finite frequencies (point (3)), but hardly affects the broad contribution of point (2) to  $\sigma_1(\omega)$  in the MIR.

In conclusion, we have shown that the interactions between lattice and spin degrees of freedom are crucial to understand  $\sigma_1(\omega)$  in undoped and low doped  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .

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