Reflectivity and Transmission of High T_c Superconductors *

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In the present communication we will review our results on the dependence of precursors of the superconducting gap in $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ doped with Zn ($0 \geq x \geq 0.10$). From the infrared difference spectrum, calculated from the difference between the transmission spectra taken at 80K and 300K, it is possible to infer that the presence of the gap in the pure compound comes with a process that affects carriers at frequencies much higher than those for the position of the gap. This last one is calculated from the peak position of the ratio of spectra T_s/T_n. The introduction of Zn^{2+} shifts this peaks, present even in the non-superconducting state, to lower frequencies in a fashion similar to results recently reported for iron doped $YBa_2Cu_3O_x$. It disappears for $x = 0.10$. This behavior suggests that the spin vacancy around copper would introduce a net moment that causes the destruction of the Cooper pair. We will also show results on the Raman scattering response of these compounds for the two-magnon excitation in the normal state.

I. Introduction

Far Infrared and Raman scattering techniques are natural probes for looking into electronic excitations, searching for spectral evidence on the behavior of high T_c superconductors. They imply direct measurement of the pair excitation energy, i.e., of the gap 2Δ. In addition, they also complement information retrieved by tunneling spectroscopy, photoemission and electron energy loss spectrometry.[1-3]

In this paper we will present infrared transmission and reflectivity data for a series of Bi based high T_c materials and will apply a qualitative argument from which to infer the gap frequencies. Although the analysis is not rigorous, it serves to understand the data on the light of BCS theory.

From the early days of spectroscopy, far infrared has been extensively used in studying conventional superconductors. Pioneering work by Tinkham and collaborators showed that in oriented thin films of classical superconductors such as Nb, V, Sn, Pb, this technique was successful in obtaining the ratio $2\Delta/kT_c$ and that the values thus obtained were an experimental corroboration for the Bardeen-Copper-Schreiffer-Eliashberg theory.[4,6]

The ratio of the transmission or reflectivity of spectra between the normal and the superconductor state yields a bell-shaped curve that peaks near the energy of the gap. Its frequency position suggests mechanisms that mediate in carrier pairing. Of them, electron-phonon interactions seem to play a fundamental, but not unique, role in cuprate superconductors in which

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*"Dedicated to Prof. P. J. Aymonino on occasion of his 65th anniversary"

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the intervention of high-frequency phonons would suggest a BCS behavior, $2\Delta/kT \approx 3.5$. It implies a weak coupling limit.

Transmission measurements are ideally done from oriented thin films not thicker than the penetration depth, that in high T_c superconductors is on the order of 100-200 *nm*. The difficulty lies in the fact that the ideal configurations is not easily met because of the inhomogeneities that introduce in the spectra contributions other than the pure response of two-dimensional CuO_2 planes, essential to superconductivity in high T_c cuprates. To our knowledge there are few relevant results reported in the literature mentioning transmission measurements of films using synchrotron radiation.[6] Superconducting and normal state transmission through a 100 nm thick film of Nb_3Ge results in a ratio that can be fitted with Tinkhams's approach[7] for transmission of films on a non-absorbing sbstrate (MgO). The same technique repeated on thin films of $YBa_2Cu_3O_{7-\delta}$ resulted in a curved bell-shaped spectrum distorted by phonon modes not present in the classical superconductor. Their analysis, using a Mattis-Bardeen theory, suggests a similar underlined contour for both compounds, and common to other superconducting thin films, although in the last one low-frequency phonons are superposed to the expected profile and unpaired normal carriers blur the gap position.

Reflectivity, on the other hand, corresponds to perfect reflectivity since in a perfect superconductor there is no energy loss below the gap and thus, the temperature dependence of its edge signals the onset of the gap. This is impaired by defects in real systems. The difficulty with both techniques - transmission and reflection - lies in obtaining absolute values. For that reason, as it is inferred from the above, the ratio of the spectra at the room-temperature normal state to the one taken in the superconductive state is used in searching for superconducting gap behavior.

Here we will focus on the phenomenum of superconductivity in high T_c superconductors. It depends heavily on the dynamics in the CuO_2 planes of which important manifestations are, among others, spectroscopical evidence of carrier-phonon interactions, low-frequency gap features, mid-infrared carrier features as well as the two-magnon Raman active band. Thus, we will show preliminary reflection and transmission measurements of sintered pellets of pure $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (Bi-2212), of those with Cu substituted by Zn, and with $Bi_{1.75}Pb_{0.25}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223).[8] Bi-2212 and Bi-2223 represent two components of the family of bismuth compounds with two ($T_c \approx 80K$) and three ($T_c \approx 110K$) CuO_2 planes respectively.

II. Results and discussion

The measurements were carried out in a Bruker 113v in the 10000 cm^{-1} to 20 cm^{-1} range using DTGS detectors. For transmission we used semi-transparent gray pellets made with spectroscopic grade CsI and minute quantities of the sample to be studied. All measurements were performed with the sample on a cold finger of an Oxford cryostat DN 1754 and of a Displex cryogenic system. We used an aluminum mirror as 100% reference for reflectivity measurements.

A typical low-temperature infrared transmission spectrum for *bismuth* cuprates *is shown* in Fig. 1 for $Bi_{1\,75}Pb_{0\,25}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) at 20K. As it can be seen, there is phonon structure at 610 cm^{-1}, 480 cm^{-1}, 362 cm^{-1} and 326 cm^{-1} superposed to electronic contributions. It is known from *polarized* measurements of single crystal that the contribution of carriers *in* the *CuO_2 layers completely screens all phonon* activity in the *ab* plane, while for vibrations in the configuration for E || c reveals strong structure.[9] Thus, the spectra from pellets made of high T_c cuprates, either pure or in a CsI matrix, are a superposition of spectra for three polarizations, in which the structure observed corresponds to E || c, i.e., the direction perpendicular to the CuO_2 planes.

We observe in Fig. 2(a) that when the difference spectrum is taken for Bi-2223 from the substraction of the spectra run at room temperature and at 100K, a clear edge is found that resembles the behavior espected for the real part of the dielectric function, c ~in the superconducting state. It signals the presence of the superconducting gap at the minimum of the profile. In addition, unscreened phonons are seen as weak peaks. The relatively flat trace in the lower part of the same figure is the spectrum difference between those taken at 20K and 100K. It is interpreted as evidence that the pairing process in this sample has already taken effect at near T_c while the other minority phases, mainly two-plane Bi-2212, might contribute to its slight slope. We also note that these difference spectra involve carrier processes at frequencies much higher than the nominal position of the gap. Within the same context, the ratio of the two spectra, T_nT_s, shown in Fig. 2b, peaks at about 500 cm^{-1}, i.e., $2\Delta/kT_c \sim 6.5$. The departure to the gap-shape profile suggested by measurements in Nb_3Ge is again attributed to, again, the presence of phonon and temperature-dependent electron-phonon interactions with normal residual carriers.

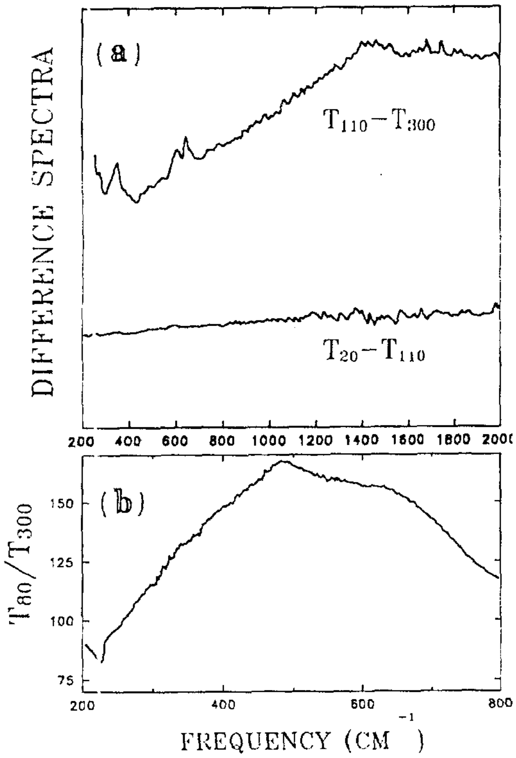

Figure 2: a) Difference spectrum T_{108} - T_{300} of $Bi_{1.75}$ $Pb_{0.25}$ Sr_2 Ca_2 Cu_3 $O_{10+\delta}$. b) Transmission ratio T_{108}/T_{300} for the same compound.

The same arguments can be used to analyze data from Bi-2212. As it is shown in Fig. 3a, the difference spectrum T_{80}-T_{300} shows the same profile as in the case of Bi-2223 and the ratio of the two has the expected bell contour. However, since now $T_c \sim 80K$, we find the picture shifted down to lower energies. In addition, since the microcrystals are incorporated in CsI, it is necessary to note that the transmission experiment has a cut-off frequency at 200 cm^{-1}. Nonetheless, that peak value of the curve at $2\Delta \sim 330$ cm^{-1}, i.e., $2\Delta/kT_c \approx 6.$ is in full agreement with several reports for this compound.[1,10] It also strongly suggests that Bi-2212 and Bi-2223 share the superconducting mechanism.

To further test the spectroscopical response in this region, it is then of interest to alter the content of the two-dimensional CuO_2 plane by introduction of impurities. In particular, we discuss the effects of replacement of Cu by Zn ($3d^{10}4s^2$). Its 3d band being completely full, it eliminates 3d holes at Cu sites and produces spin vacancies in the antiferromagnetic correlation of the planes. As pointed out in several publications,[11] Zn is known to be a stronger T_c suppressor in all cuprates. Resistivity measurements in $Bi_2Sr_2Ca_1(Cu_{1-x}Zn_x)_2O_{8+\delta}$, $0.00 \leq x \leq 0.10$ indicate a $T_c \sim 25K$ for $x = 0.02$ while ten percent of Zn replacement, in which some nucleation may occur, yields a semiconductor-like behavior down to 4 K.[12]

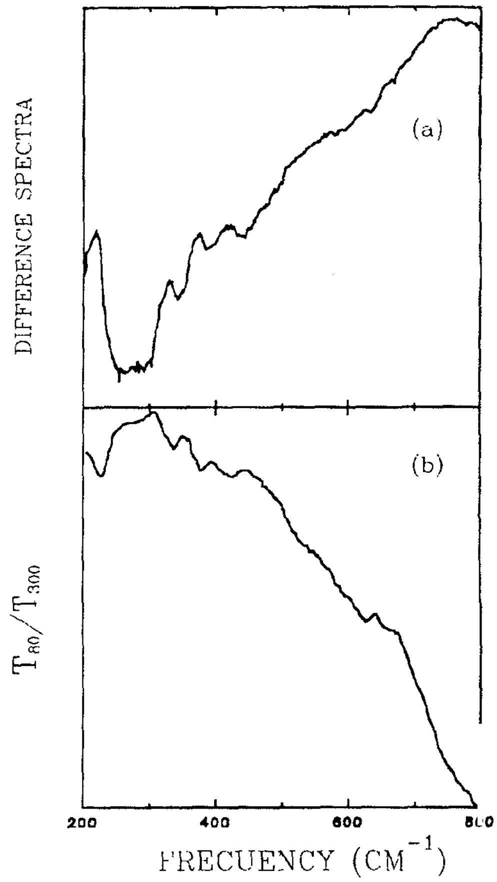

Figure 3: a) Difference spectrum T_{80} - T_{300} for Bi_2 Sr_2 Ca_1 Cu_2 $O_{8+\delta}$. b) Transmission ratio T_{80}/T_{300} for the same compound.

In what follows, we discuss the infrared response of these samples at the onset temperature at which pure Bi-2212 becomes a superconductor ($T_c \sim 80K$). Figures 4a, b, c and d show the ratio of spectra T_{80}/T_{300}

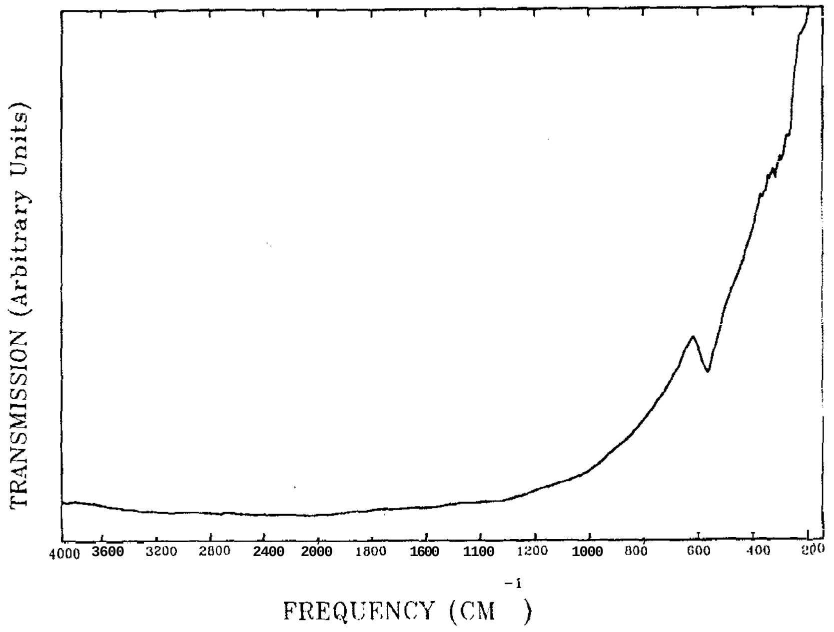

Figure 1: Infrared transmission spectrum of $Bi_{1.75}Pb_{0.25}Sr_2Ca_2Cu_3O_{10+\delta}$ at 20K

for x = 0.01, 0.03, 0.05 and 0.10 respectively. As it can be seen, 4d has almost the same profile as the curve for pure Bi-2212 indicating that the gaps or its precusors as expected for sintered material, have a finite distribution of values. When x is increased to 0.03 and 0.05 this feature shifts down in frequency and, although part of the bell-shaped curve is missing, it is still possible to infer its presence, in spite of the CsI cut-off. With x = 0.10, in Fig. 4a, the picture is radically altered and there is no structure that we may associate with the gap. By expanding the vertical scale, we see sharper structure that might be, tentatively, assigned to phonons.

We see, that in doped samples that have T_c at lower temperature than for pure Bi-2212, there are excitations in the infrared region acting as precursors that we might associate with the eventual appearance of the gap. Then, additional measurements at lower frequencies than the CsI cut-off at 200 cm^{-1} are clearly needed. For that purpose we have done reflectivity measurements. Figure 5a shows the spectra for the pellet with x = 0.05 at 300K and 80K in the region between 300 cm^{-1} and 20 cm^{-1}. The ratio, Fig. 5b, yields a structure peaking at about 100 cm^{-1} implying a precursor of the gap in a material for which, using the ratio 6.5 $\approx 2\Delta/kT_c$, we can estimate a $T_c \approx$ 20K in reasonable agreement with what is expected from resistivity measurements. We can then conclude that gap precursors in sintered light Zn doped 131-2212 indicate a shift of the gap to lower energies.

There have been a few studies on the alteration of superconducting and normal state properties due of the presence of Zn in $YBa_2Cu_3O_{x+\delta}$, $7 \leq x \leq 8$, $0 \leq \delta \leq 1$. [13-16] In agreement with our observations in $Bi_2Sr_2Ca_1(Cu_{1-x},Zn_x)_2O_{8+\delta}$, $0.00 \leq x \leq 0.10$, it is inferred that local distortions in the sublattice and, mainly, the destruction of antiferromagnetic correlations are closely related to the supression of T_c with Zn doping.

Moreover, recent spectroscopic studies[17,18] on the effect of paramagnetic impurities indicate that the observation of the gap in the far-infrared spectra of iron-doped $YBa_2Cu_3O_x$ roughly follows a BCS behavior and is in agreement with theoretical predictions on superconductors with paramagnetic impurities[19]. Thus, although our quantitative analysis of the present data is only in progress, this preliminary report on the experimental measurements favors a similar interpretation. As in those cases, the remanent spin, now due to spin fluctuations of the impairement of antiferromagnetic order, flips one spin of the Cooper pair, causing its destruction and broadening of the electronic states on both sides of the gap.

Another temperature dependent feature, that in

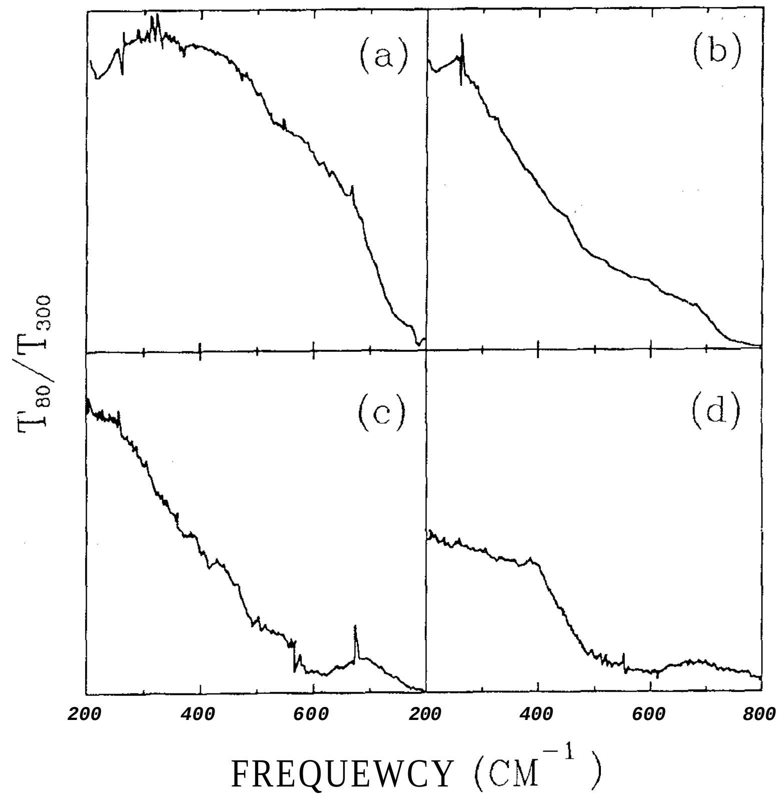

Figure 4: Transmission ratio T_{80}-T_{300} for $Bi_2Sr_2Ca_1(Cu_{1-x},Zn_x)_2O_{8+\delta}$, $0.00 \leq x \leq 0.10$; (a) x = 0.01, (b) x = 0.03, (c) x = 0.05, (d) $x = 0.10$..

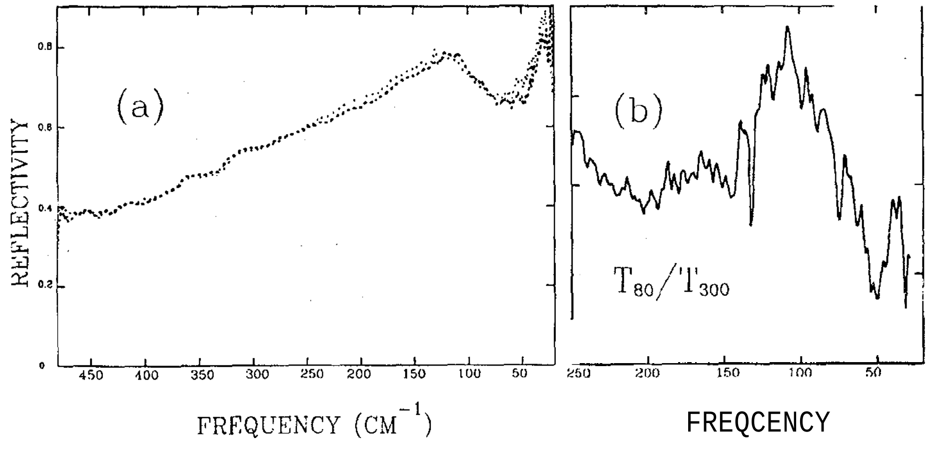

Figure 5: a) Reflectivity spectra for $Bi_2Sr_2Ca_1(Cu_{0.95},Zn_{0.05})_2O_{8+\delta}$ at 300 K and 80 K. b) Reflectivity ratio T_{80}/T_{300} for the same compound.

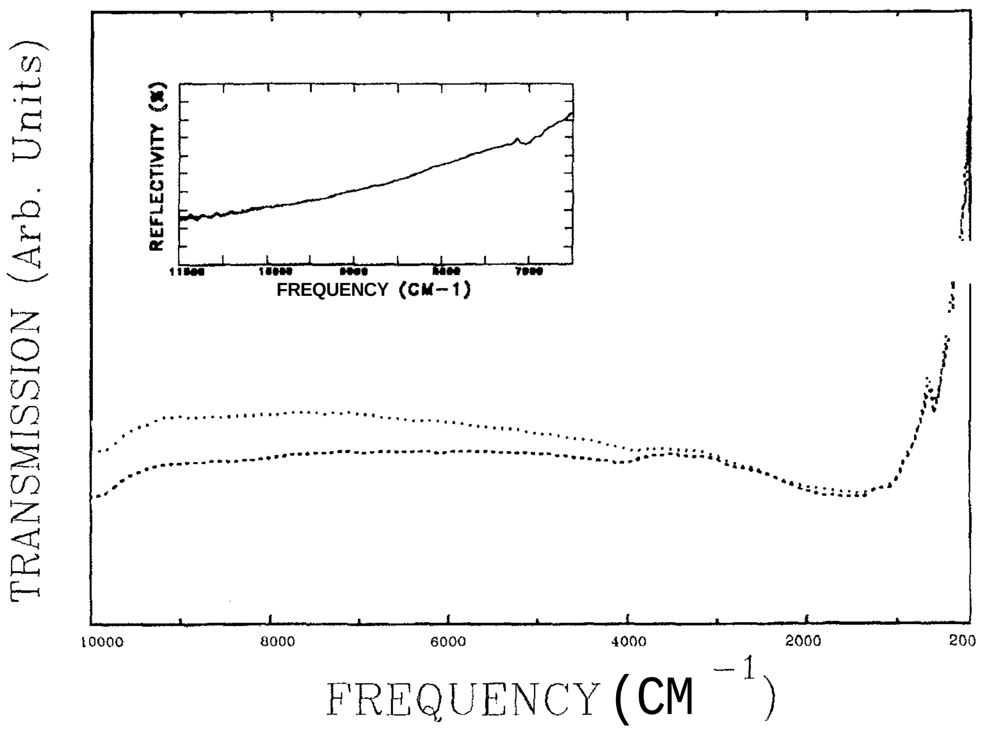

Figure 6: Typical transmission spectra of $Bi_2Sr_2Ca_1(Cu_{0.95},Zn_{0.05})_2O_{8+\delta}$ at 300 K and 80 K. The inset shows its reflectivity at room temperature.

early measurements has been identified with a gap, accompanies indeed its detection by spectroscopic means. It is registered in most cuprates in the 500 cm^{-1}-800 cm^{-1} ($\approx 8kT_c$ to $\approx 12kT_c$) spectral range. Our measurements, either of Bi-2223 or Bi-2212, do not alter the picture already reported in the literature[18,20] in which it is associated with a Holstein process, a phonon difference band, a disorder effect or regarded as a polaronic feature. However, of all of them, we favor a polaronic-related explanation because of its close temperature behavior to gap detection in which carrier pairing effects and spin fluctuations might not be absent.

At higher frequencies, the spectra up to 10000 cm^{-1} are featureless for Bi-2212 doped with Zn. They have, with small variations, an edge at about 9500 cm^{-1}. A typical result is shown in figure 6 for Bi-2212 doped with x = 0.05.

From the above it is been concluded that Zn impurities, in addition to hindering carrier hopping, introduce net spin fluctuations in the two dimensional CuO_2 plane sublattice. Thus, it is also of interest to investigate the two-magnon Raman response of this system. This is detected as an asymmetric strong band centered at about 2300 cm^{-1} in double layer $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ whose origin is mainly due to two-magnon scattering. Figure 7 shows our low temperature normal state two-magnon Raman spectra as recorded in increments of 10 cm^{-1} in a Spex-Ramalog spectrophotometer with conventional photon counting techniques. We used the 5145 Å and 4880 Å Ar^+ ion lines with 20 mW at the sample.

For x = 0.00, the spectra reproduce the known results, i.e., resonant dependent band profiles with R $\approx$ 2.7*J yielding a superexchange interaction $J \approx 1000$ cm^{-1}. Single[21] and multiphoton scattering[22,23] is superposed on the lower frequency side of the bell-shaped band, and the distinctive asymmetry on the higher frequency side of the spectrum recorded with the 4850 Å line is explained in terms of higher order spin correlations.[24] The spectra for $x = 0.02$ show similar characteristics but the two spectra have more differentiated cross sections. At x = 0.10 our results do not change much, i.e., although for the 4550 Å spectra there is a minute increase in the band half width at half maximum in passing from x = 0.02 to $x = 0.10$. We can state that broadening and shifting to lower frequencies due to Zn dilution, as in the case of $(Mn_{1-x},Zn_x)F_2$

(ref. 25), are not present.

As pointed out above, in our doped cuprates, 3d holes are prevented from hopping hindering antiferromagnetic correlations. Thus, with the exchange interaction J on the order of t^2/U in the Hubbard approximation, t being the hopping integral and U the on-site Coulomb repulsion, one would expect changes in the magnetic Raman response, even at low dopant concentrations. As shown in Fig. 7 b, c they are not observed.

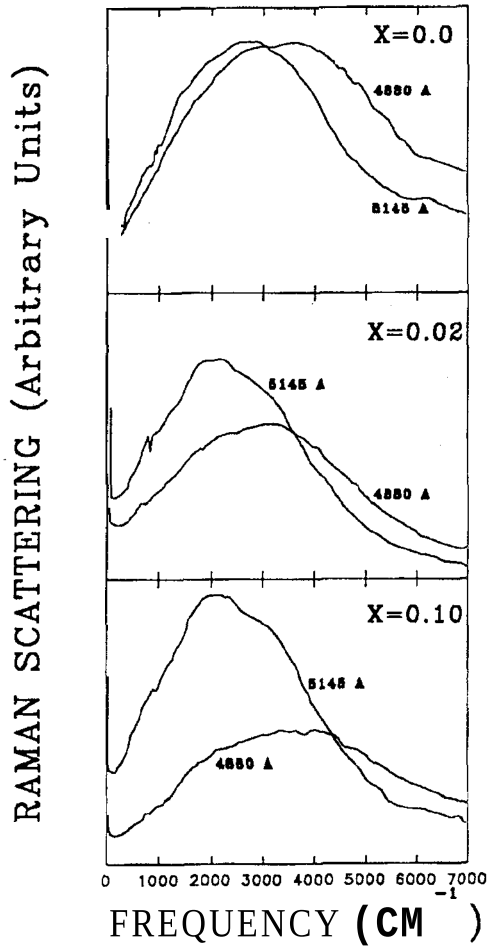

Figure 7: Normal state two-magnon Raman spectra of $Bi_2Sr_2Ca_1(Cu_{1-x},Zn_x)_2O_{8+\delta}$, (a) x = 0.00, (b) x = 0.02, (c) X = 0.10.

It is, however, worth noting that we were able to fit the broad band in the 4880 Å spectra of the doped samples with only one gaussian. This indicates that higher order spin correlations found in the frequency region between 4J and 5J, and unlike spectra of iron-doped pellets,[26] are strongly suppressed and may not be present at all for x = 0.10.

Concluding. our preliminary data on Zn-doped Bi-2212 points to unpaired spin fluctuations as the reason for the detriment of T_c. However, it remains uncertain the origin of the band observed in our measurements, common to all high T_c cuprates, at $\approx 8kT_c$ to $\approx 12kT_c$. Moreover, the explanation for the failure of the Hubbard approach, for predicting the behavior of the magnon pair Raman response in doped samples as deduced from our measurements, is not intuitive.

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