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Origin of the A_{1g} and B_{1g} electronic Raman scattering peaks in the superconducting state of $YBa_2Cu_3O_{7-\delta}$

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The electronic Raman scattering was investigated in optimally oxygen-doped $YBa_2Cu_3O_{7-\delta}$ single crystals as well in crystals doped with nonmagnetic, Zn^{2+} and magnetic Ni^{2+} impurities. We found that the intensity of the A_{1g} peak is impurity independent and its energy to T_c ratio is nearly constant $(2\Delta/k_B T_c \sim 5)$. Moreover, the signal at the B_{1g} channel is completely smeared out when nonmagnetic Zn^{2+} impurities are present. These results are discussed in terms of the current models of Devereaux *et al.*, Venturini *et al.*, and Zeyher and Greco.

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The phenomenon of high-T_c superconductivity in the cuprates has been related to an unconventional pairing mechanism.[1] It is widely accepted that this mechanism is closely related to their normal-state properties, e.g., the non-Fermi-liquid behavior,[2] in spite of the lack of consensus about the correct description of this state. The presence of fluctuations, such as spin, flux phases, stripes, or charge-density waves (CDW), are additional complications[3] and many models considering one or more of these fluctuations have been proposed. However, there is still a large amount of experimental results that these models cannot explain (see, e.g., Secs. 5.4 and 6.4 of Refs. 1 and 2, respectively). Among these results we can mention the absence of a convincing explanation for the electronic Raman scattering (ERS) of many cuprates in the superconducting state.

The redistribution of the ERS in the superconducting state has been used to study the gap order parameter in many superconductors, both conventional and unconventional, such as Nb_3Sn,[4] cuprates,[5] borocarbides,[6] and, recently, MgB_2.[7] In general, the ERS of the superconducting cuprates presents two characteristic peaks seen in the B_{1g} and $A_{1g}+B_{2g}$ channels in the superconducting phase. In the optimally oxygen-doped crystals of $YBa_2Cu_3O_{7-\delta}$ (Y123) the ERS shows the A_{1g} peak stronger than the B_{1g} counterpart. Also, the maximum intensity of the A_{1g} peak lies at a lower energy than that of the B_{1g} one.[8] In the overdoped state, the B_{1g} peak shifts down converging approximately to the position of the A_{1g} peak[8] while in the strongly underdoped regime neither A_{1g} nor B_{1g} peak is observed.

The appearance of these peaks just below T_c suggests that they may be related to the superconductivity, being interpreted as pair-breaking peaks in several works in the literature. Some reports[9] have already shown that for a gap with nodes and $d_{x^2-y^2}$ order parameter, the ERS efficiency obeys the $\sim\omega^3$ and $\sim\omega$ power laws at low energies in the B_{1g} and $A_{1g}+B_{2g}$ channels, respectively. Also, these works have predicted that the A_{1g} peak should be weaker than the B_{1g} component with their maxima appearing at the same energy 2Δ. In spite of the good agreement between the theory and the experimentally observed power laws, the relative position and intensity of the ERS peaks are in disagreement with the theoretically expected results for the pair-breaking ERS response. Hence, the origin of the A_{1g} and B_{1g} peaks remains unclear.

In this communication we make an attempt to clarify this question by means of ERS measurements in Y123 single crystals doped with a small amount, 5%, of either magnetic Ni^{2+} (Y123:Ni) or nonmagnetic Zn^{2+} (Y123:Zn) impurities in the copper planes. It is known that substituting Cu by Zn or Ni in Y123 preserves the oxygen doping level and the crystal structure is only slightly modified.[10,11] Moreover, the nonmagnetic Zn^{2+} impurities, instead of the magnetic Ni^{2+} ones, restore significant spin fluctuations in the normal state.[10,11] Since the presence of impurities in the CuO_2 planes are known to induce a pair-breaking effect,[10,11] the investigation of the change in the electronic properties by introducing magnetic and nonmagnetic impurities can give important insights into the open questions related to the superconductivity in the cuprates.

Single crystals of Y123, Y123:Ni, and Y123:Zn were prepared as previously described.[12] After thermal annealing, the transition temperatures, measured by *dc*-magnetization, were 91, 76, and 72 K for the Y123, Y123:Ni, and Y123:Zn samples, respectively. In terms of the oxygen level, all samples are in the optimally doped state. The Raman measurements were carried out using a triple spectrometer equipped with a charge-coupled device detector. The spectrometer response was corrected by measuring the emission of a tungsten lamp and comparing it with the emissivity of a blackbody at same temperature. The 514.5 nm line of an Ar^+ ion laser was used as excitation source. The laser power at the sample was kept below 8 mW on a spot diameter of about 50 μm. The samples were cooled in an exchange He gas variable temperature cryostat, and measured in a near-backscattering configuration on the ab plane. For the tetragonal D_{4h} point group, the choice of the (x',x') geometry probes a combination of the A_{1g} and B_{2g} channels, while choosing the (x',y') geometry couples to excitations in the B_{1g} channel. x' (y') denote axes rotated by 45° from the crystallographic $a(b)$ axes.

In Fig. 1 we present the Raman spectra in the $A_{1g}+B_{2g}$ channel at different temperatures for the Y123, Y123:Ni, and

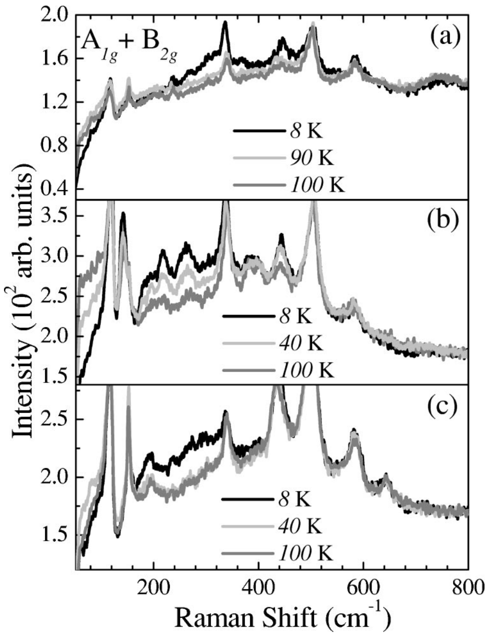

FIG. 1. Temperature dependence of the Raman spectra in the $A_{1g}+B_{2g}$ channel showing the redistribution of the ERS below T_c for (a) Y123 with $T_c=91$ K, (b) Y123:Ni with $T_c=76$ K, and (c) Y123:Zn with $T_c=72$ K single crystals.

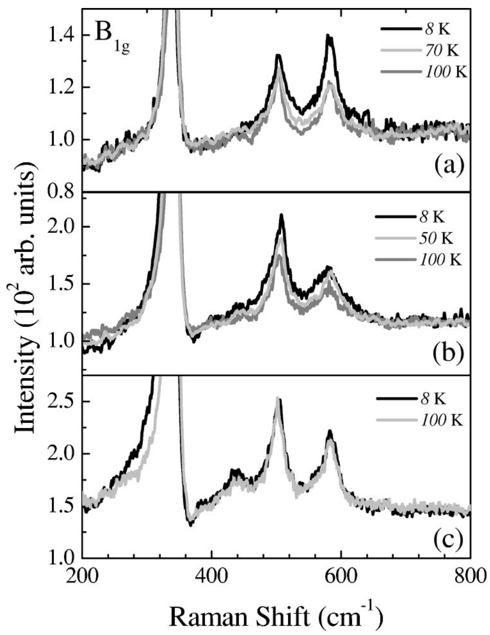

FIG. 2. Temperature dependence of the polarized Raman spectra in B_{1g} channel for (a) Y123, (b) Y123:Ni, and (c) Y123:Zn.

Y123:Zn samples, corrected by the thermal Bose-Einstein factor. In Fig. 1(a), the spectrum for Y123 at 100 K displays a flat background. Just below $T_c\sim 91$ K the rearrangement of the electronic background starts, resulting in a broad peak in the spectral range between 200 and 400 cm^{-1}. The same behavior is also found in Fig. 1(b) for Y123:Ni. However, in this case the rearrangement of the ERS starts only below 50 K, producing a broad peak located in the same spectral range as that for the pure sample. For Y123:Zn, Fig. 1(c), the gain of spectral weight in the superconducting state is also present in the $A_{1g}+B_{2g}$ channel; although it starts to appear at 40 K ($T_c\sim 72$ K), it is also located in the same spectral range as for the other two samples.

In the B_{1g} channel, Fig. 2, the rearrangement of the ERS is also displayed for Y123 and Y123:Ni. For Y123, Fig. 2(a), it starts below 70 K and it appears in the 450–650 cm^{-1} spectral range. For Y123:Ni, Fig. 2(b), the broad peak first appears below 60 K and it is also located in the 450–650 cm^{-1} spectral range. Surprisingly, for Y123:Zn, Fig. 2(c), the rearrangement of the ERS is absent below T_c. The only observed effect of lowering the temperature was the broadening of ~ 3 cm^{-1} of the B_{1g} phonon at 330 cm^{-1}.

In order to determine the energy of the broad peaks appearing in the superconducting phase in $A_{1g}+B_{2g}$ and B_{1g} channels, the pure ERS response function has been obtained by subtracting the contribution of the phonons fitted to Lorentzian or Fano profiles to the Bose-Einstein corrected raw data. We follow the currently used method of ERS analysis outlined by Boch in Ref. 13.

In Fig. 3 we present the pure ERS response for the $A_{1g}+B_{2g}$ channel at 8 and 100 K. At 8 K we found the A_{1g} response peaks around 320, 250, and 300 cm^{-1} for Y123 (3a), Y123:Ni (3b), and Y123:Zn (3c), respectively. We notice that the A_{1g} energy to T_c ratio $\hbar\omega_{A_{1g}}/k_BT_c$ is ~ 5.0 for Y123, ~ 4.7 for Y123:Ni, and ~ 5.8 for Y123:Zn. As commented above, at 100 K, the rearrangement of the ERS is absent and the Raman spectra present no pronounced peak.

Figure 4 shows the pure ERS for the B_{1g} channel at 8 and 100 K. The dramatic difference between the response of Y123:Zn compared to the other crystals is evident. The peak is absent in Y123:Zn but it appears centered around 480 cm^{-1} in Y123 and Y123:Ni. The ratio $\hbar\omega_{B_{1g}}/k_BT_c$ is

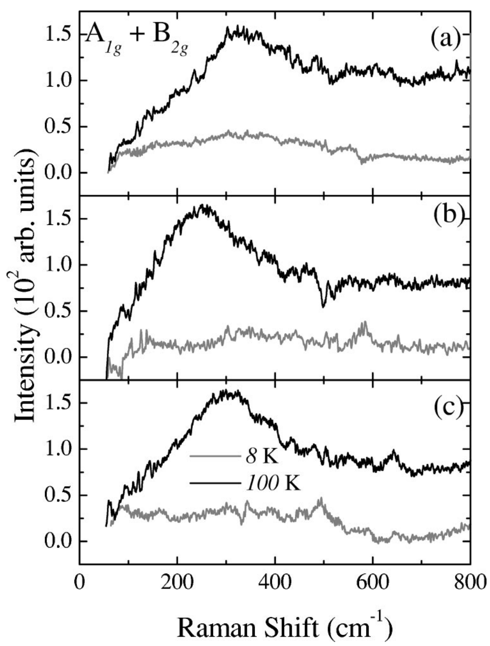

FIG. 3. Electronic Raman response at 8 K (black lines) and 100 K (gray lines) for (a) Y123, (b) Y123:Ni, and (c) Y123:Zn single crystals in $A_{1g}+B_{2g}$ channel.

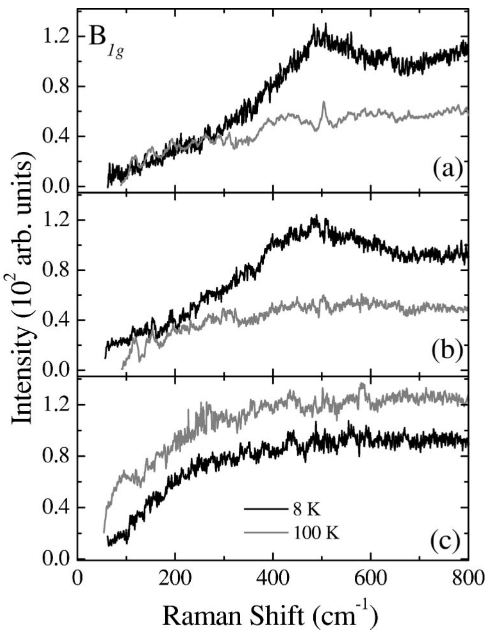

FIG. 4. Electronic Raman response at 8 K (black lines) and 100 K (gray lines) for (a) Y123, (b) Y123:Ni, and (c) Y123:Zn in the B_{1g} channel.

$\sim$7.7 for Y123 and $\sim$9.2 for Y123:Ni. Moreover, the ERS spectrum in Y123:Zn is almost the same at 8 and 100 K being also quite similar to those in Y123 and Y123:Ni above T_c, except for a constant offset in Y123:Zn. The origin of this offset is not clear.

The data of Figs. 3 and 4 indicate that the Zn substitution affects the $A_{1g}+B_{2g}$ and B_{1g} channels in a different way. While in the $A_{1g}+B_{2g}$ channel the intensities of the peaks are unaffected by the impurities, in the B_{1g} channel the peak is smeared out in the Zn-doped sample. The comparison between the B_{1g} channel signals at 8 and 100 K in Y123:Zn indicates that the ERS in the superconducting and normal states are nearly the same. This unusual effect of Zn substitution on the B_{1g} Raman response is surprising and has not been predicted by any theoretical model neither been observed by other systematic comparative experimental work. Another relevant result is the almost constant energy to T_c ratio $\sim$5 for the A_{1g} peak for all samples. This value is in agreement with previous values obtained for the A_{1g} peak[14,15] and for the superconducting gap measured by electron tunneling spectroscopy in Y123.[16]

Venturini *et al.*[17] developed a model suggesting that the observed peak in the $A_{1g}+B_{2g}$ channel is produced by collective spin fluctuations, being a two-magnon Raman peak. In the same model, the B_{1g} peak is related to pair breaking. They were able to fit the experimental Raman spectrum of Bi2212 to their model and obtained the correct relative position of the A_{1g} and B_{1g} peaks.[17] Moreover, Gallais *et al.*[15] have shown that the A_{1g} peak tracks the magnetic resonance peak observed by inelastic neutron scattering[10] at 40 meV in Ni-substituted $YBa_2Cu_3O_{6.95}$. These authors have interpreted this fact as an evidence for the magnetic origin of the A_{1g} peak.

However, our results cannot be interpreted in terms of the works of Venturini *et al.*[17] and Gallais *et al.*[15] The main reason is the strong Zn-impurity dependence observed in the B_{1g} spectra. In the Venturini's framework the B_{1g} peak is related to pair-breaking process with their maximum at 2Δ energy. Thus, the complete smearing out of the B_{1g} peak observed in our experiments [see Fig. 4(c)] would imply that $2\Delta\rightarrow 0$ for the Zn-substituted crystal. However, T_c does not go to zero in this system and, assuming the absence of any anomalous behavior in the $2\Delta/k_BT_c$ ratio, 2Δ cannot go to zero. Furthermore, the $\hbar\omega_{A_{1g}}/k_BT_c$ ratio for the A_{1g} peak presents better agreement to the gap energy measured by other groups (see, e.g., Ref. 15) than the B_{1g} one, indicating that the A_{1g} peak is a better candidate to pair breaking.

Another model, by Zeyher and Greco,[18] used the superconducting model of Cappelluti and Zeyher[19] to explain the ERS in cuprates. The model of Cappelluti and Zeyher proposed that the superconductivity in cuprates is originated by the competition between the superconducting and the *d*-CDW order parameters. Zeyher and Greco[18] suggested that the A_{1g} and B_{1g} peaks are originated by amplitude fluctuations of the superconducting and *d*-CDW order parameters, respectively. The *d*-CDW phase corresponds to a flux phase where current flows around each CuO_2 square alternatively clockwise and counterclockwise[20] giving rise to orbital antiferromagnetism where the only interaction present in the order parameter is the Heisenberg exchange coupling between the Cu^{2+} ions.[18]

As mentioned above, our experimental data indicate that the A_{1g} peak is related to pair breaking. In this sense, our experimental ERS results give support to the Zeyher and Greco's theory. However, this theory does not include the impurity effects on its formulation. Intuitively, both magnetic and nonmagnetic impurities should affect in some extent the orbital antiferromagnetism. It is interesting to mention that Cappelluti and Zeyher[21] have shown that the Zn impurities do not have appreciable influence on the oxygen doping phase diagram of the cuprates. Therefore, the theory to explain the subtle effect of impurities on the ERS of cuprates needs more ingredients.

Nevertheless we can elaborate, at least qualitatively, about the impurity effect on the B_{1g} signal as follows. It is known that the main interaction originating the *d*-CDW is the Heisenberg coupling between the Cu^{2+} spins.[21] Thus, it is reasonable to expect that the Cu^{2+} $(S=1/2)$ substitution by nonmagnetic Zn^{2+} $(S=0)$ impurity would strongly affect the long-range coherence of the orbital antiferromagnetism and smear out the *d*-CDW order parameter fluctuations. This may be consistent with the large depletion of T_c produced by the presence of Zn^{2+} impurities.[10,11] On the other hand, the magnetic Ni^{2+} $(S=1)$ impurities are probably less effective in smearing out the orbital antiferromagnetism order parameter fluctuations, notwithstanding also decreasing T_c. Besides, as shown by Gupta and Gupta,[22] the charge-density redistribution due to the Ni^{2+} ions is localized while the Zn^{2+} perform an extended perturbation. On these bases, one might expect that the Zn^{2+} ions would be more effective on reducing the *d*-CDW order parameter fluctuations.

In conclusion, our results show that the A_{1g} ERS peak presents a constant gap to T_c ratio ~ 5 regardless of the presence of magnetic or nonmagnetic impurities. The B_{1g} ERS peak is smeared out in the Y123 when the Cu^{2+} is substituted by small amount of nonmagnetic Zn impurities whereas the $A_{1g}+B_{2g}$ spectra remain insensitive to both kinds of impurities. These results are incompatible with the models of Devereaux *et al.*[9] and Venturini *et al.*[17] and were qualitatively discussed in terms of the Zeyher and Greco's[18] theory that relates the ERS in the $A_{1g}+B_{2g}$ and B_{1g} channels to superconducting and *d*-CDW order parameters fluctuations, respectively.

However, it is clear that more theoretical work is needed to explain the impurity effects on the ERS of cuprates and that Zeyher and Greco's theory should be extended to explicitly incorporate the impurities effects.

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