

## Point-contact tunneling in monophasic and polyphasic Y-Ba-Cu-O samples: Experiment and model

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Tunneling experiments using large-area point-contact structures have been performed on several monophasic polycrystalline  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$  samples and on polyphasic samples containing, mixed with the previous superconducting phase, also about 11% of the so-called green phase ( $\text{BaY}_2\text{CuO}_5$ ). Both niobium and Y-Ba-Cu-O tips were used as counterelectrodes and measurements were made at 4.2 and 77 K. Results obtained at different experimental conditions show great reproducibility, indicating the presence of a gap voltage at about 20 mV in the dynamic resistance curves. A phenomenological model was then developed to interpret in a quantitative way our data by means of a decomposition of the experimental conductance into a background component and a superconducting-tunneling component. The former results essentially in a parabolic contribution versus the bias voltage typical of a tunneling between normallike junction electrodes while the latter component is smeared out in voltage by a large amount of broadening. Using the model in a least-squares fit of the experimental data of Nb/Y-Ba-Cu-O junctions, values  $V_G = 21.3 \pm 0.8$  mV and  $V_G = 22.0 \pm 0.6$  mV for the voltage gaps at 4.2 K of monophasic and polyphasic materials, respectively, have been determined. These results have been well confirmed by measurements on Y-Ba-Cu-O/Y-Ba-Cu-O junctions while, at 77 K, there are no indications of superconducting tunneling. We obtained also the parameters of the background conductance, which indicates the presence of a nonsuperconducting layer at the surface of the material.

### I. INTRODUCTION

Research that aims at understanding the fundamental properties of the ceramic high- $T_c$  superconductors has involved tunneling measurements as a very effective probe.<sup>1-14</sup> It provides information on the energy gap  $\Delta$ , which compared to  $k_B T_c$  is a good indicator of strong "electron-electron" coupling.

The tunneling measurements already reported both on La-Sr-Cu-O and on Y-Ba-Cu-O systems support in general a strong-coupling superconductivity with a ratio  $2\Delta/k_B T_c$  higher than 3.53 predicted by Bardeen-Cooper-Schrieffer (BCS) theory.<sup>1-14</sup> Anisotropy in the tunneling has been tested with measurements on single crystals but it seems that there is no strong evidence of a relevant change of gap voltage with crystallographic planes.<sup>3</sup>

The so-called "background" conductance at voltages higher than the gap voltage is anomalous. In fact, it is not constant but begins to rise with voltage with either a linear<sup>2,3,6,11-13,15</sup> or parabolic<sup>1,16</sup> behavior. The linear behavior has usually been interpreted as a consequence of the Giaever-Zeller effect, but it has also been suggested that it is an intrinsic property which plays an important role in explaining the strong electron-electron correlation in high- $T_c$  materials.<sup>15</sup> However, in many measurements the background conductance has not been analyzed in detail.

In this paper we report point-contact tunneling measurements on polycrystalline, bulk samples of Y-Ba-Cu-O compounds, both monophasic ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ) and polyphasic (89 vol.%  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and 11 vol.% of the green phase  $\text{Y}_2\text{BaCuO}_5$ ). Repeated measurements have been carried out at different experimental conditions and on various samples in order to achieve an accurate determination of the gap voltage and of the background conductance of this material as produced.<sup>16</sup> Our tunneling measurements involve large area point contacts and, therefore, the  $I$ - $V$  characteristics result from an average over regions exhibiting various tunneling properties. This approach is different from the scanning tunneling microscopy (STM) technique which uses small area tips (0.1  $\mu\text{m}$  or less).<sup>2,3,9</sup> In fact, the latter offers the possibility to investigate the local superconducting properties of the material showing, in the best case, very pronounced gap features but with wide variations from point to point over the sample.<sup>9</sup>

In Sec. II of the paper, the preparation and chemical characterization of the samples is summarized. The critical temperature has been determined by four-wire standard technique.<sup>17</sup> Then the tunneling measurements are described in detail including the measurements of the first derivative of the  $I$ - $V$  characteristic, with particular attention to the common features observed in all the experiments.

From the observation that the background normal conductance predominates over the structures induced by the superconducting tunneling characteristics for voltages greater than 5 mV, a model is introduced in a phenomenological way which appears able to account for the behavior of experimental dynamic resistance and conductance curves with a high precision. The model is based on the decomposition of the experimental conductance into the contributions of two parallel channels: The background normal component, identified with a normal-insulator-normal (NIN) tunneling, and the superconducting tunneling component, identified with the superconducting-insulator-superconductor (SIS) or the superconductor-insulator-normal (SIN) tunneling and represented by means of a phenomenological equation.<sup>18</sup> The resulting fit to the experimental data is finally commented on, showing that it can determine both the gap voltage and the background-conductance parameters. This background conductance supports the presence of a nonsuperconducting layer at the Y-Ba-Cu-O surface.<sup>2,15</sup>

## II. EXPERIMENT

### A. Sample preparation

Samples were prepared by thermal decomposition (about 0.5 h at 900 °C) of mixtures of Ba(NO<sub>3</sub>)<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, and Cu<sub>2</sub>O in the proper atomic ratios. The so obtained solids, carefully homogenized in agate mortar, were pressed in pellets and sintered in flowing oxygen at 950 °C for 10 h, followed by an annealing at 850 °C for 2 h, and a slow cooling at 450 °C for 12 h in streaming oxygen.

The samples were x-ray analyzed by powder diffraction using a step-counting diffractometer using Cu *K*α radiation with  $\lambda = 1.5418 \text{ \AA}$ . The spectrograms of monophasic specimen showed only the reflections of the superconducting orthorhombic phase Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7- $\delta$</sub> . The cell parameters  $a_0 = 3.821$ ,  $b_0 = 3.885$ , and  $c_0 = 11.675 \text{ \AA}$  are in good agreement with Ref. 19. The oxygen stoichiometry, determined by iodometric titration technique, is  $6.93 \pm 0.02$  which agrees well with Ref. 20 and corresponds to a mean oxidation number 2.29 for Cu.

Polyphasic samples furnished an x-ray spectrogram on which, besides the lines of Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7- $\delta$</sub> , appeared only the reflections typical of the semiconducting compound Y<sub>2</sub>BaCuO<sub>5</sub> (the green phase). The volume percent of this latter phase, calculated on the base of the starting composition (Y = 20, Ba = 32.5, Cu = 47.5 at.%) and the theoretical densities of the two phases,<sup>21,22</sup> was 10.6.

Measurements of the critical temperature performed on these samples using the standard four-probe technique, with particular attention to the isothermal conditions of the samples, gave  $T_c = 90.5 \text{ K}$  with a transition amplitude of 4.5 K (10–90% of transition) for monophasic Y-Ba-Cu-O and  $T_c = 90.9 \text{ K}$  with a transition amplitude of 8.8 K for polyphasic samples.<sup>17</sup>

### B. Tunneling measurements

Tunneling experiments have been performed on the two types of Y-Ba-Cu-O samples with point-contact junctions

made by Y-Ba-Cu-O cylinder disks of 10 and 5 mm diam and niobium tips as counterelectrodes (estimated contact area  $250 \times 250 \mu\text{m}^2$ ), as well as by using Y-Ba-Cu-O samples for both electrodes (apparent contact area of about  $1 \text{ mm}^2$ ). For all the measurements a cryogenic probe was used, which features a fine adjustment of the contact pressure, low thermal emf, and the capability to radiate the samples with microwaves. Figure 1 shows a schematic picture of this cryogenic probe. The Y-Ba-Cu-O surface was polished by means of fine sandpaper while the Nb tip was chemically etched.

The measurements have been carried out at liquid-nitrogen (77 K) and at liquid-helium (4.2 K) temperatures in order to study the tunneling behavior in situations where one or both the electrodes are superconducting, i.e., with SIN or SIS junctions. At these temperatures the following measurements have been performed: (a) twenty measurements with different readjusted contacts on two Nb/Y-Ba-Cu-O (monophasic) junctions, (b) three measurements with different readjusted contacts on one Nb/Y-Ba-Cu-O (polyphasic) junction, (c) four measurements with different readjusted contacts on one Y-Ba-Cu-O/Y-Ba-Cu-O (both monophasic) junction.

The measurement of the different Y-Ba-Cu-O phases aimed to study in these samples the variation of the energy gap with critical temperature. Measurements have also been tried on Nb/Y-Ba-Cu-O (polyphasic, with 40% of green phase) junctions but, due to the poor surface structure which was easily damaged even for low-contact pressures, no reproducibility was observed. For all samples *I-V* characteristics and first derivative  $dV/dI$  vs *V* have been observed. An analog differentiator with a

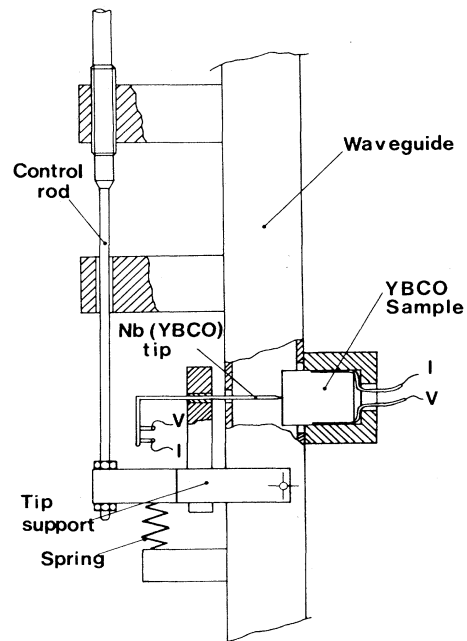


FIG. 1. Schematic view of the point-contact configuration of our probe. The pressure of the Nb or Y-Ba-Cu-O tip over the Y-Ba-Cu-O substrate is finely adjustable from outside the Dewar by the control rod.

differential input, an adjustable gain, and a signal-to-noise ratio at the operating frequency (5 Hz) of about 40 dB was used. The second derivative was also monitored.

One may distinguish two main regions of bias voltages in the conductance curves obtained from the experimental  $dV/dI$  data at 4.2 K.

(1) A "low-voltage" region ( $V < 12$  mV) where the prevalent effects are summarized as follows. (1a) Zero-voltage currents up to  $150 \mu\text{A}$  have been usually obtained in Nb/Y-Ba-Cu-O junctions depending on the contact pressure and the surface quality of the samples, while in Y-Ba-Cu-O/Y-Ba-Cu-O junctions zero-voltage currents with a maximum value of  $30 \mu\text{A}$  have been observed. (1b) In Nb/Y-Ba-Cu-O junctions a well-defined minimum in the  $dV/dI$  vs  $V$  curve, which corresponds to a zero crossing in the second derivative at about 2 mV, has been observed as shown in Fig. 2. This feature is usually ascribed to a SIN tunneling between Nb and normal-state Y-Ba-Cu-O.<sup>4-6,15</sup> The value of 2 mV is greater than the gap voltage of bulk Nb ( $\sim 1.5$  mV) at 4.2 K, but we calculated that it is in very good agreement with the shift of the minimum of the resistivity produced, according to the BCS theory, by the thermal broadening at 4.2 K for a Nb/normal junction.<sup>23</sup>

(2) An "intermediate voltage" region ( $12 \text{ mV} < V < 60$  mV for Nb/Y-Ba-Cu-O and  $V < 160$  mV for Y-Ba-Cu-O/Y-Ba-Cu-O) where a high background conductance is present. Its general behavior is well represented by a parabolic and asymmetric curve, typical of NIN contacts.<sup>24</sup> From our experimental data in this region of bias voltage the contribution of the superconducting tunneling appears as a deviation from the background conductance and it is noticeable at 4.2 K, but almost negligible at 77 K.

In fact, in Nb/Y-Ba-Cu-O junctions, a well pronounced change of slope in the first derivative characteristics, and in the best contact situations a plateau, has been detected for monophasic and polyphasic samples at about 20 mV with slight differences between the two. In Fig. 3 an example of a best contact situation for a Nb/Y-Ba-Cu-O (monophasic) junction is shown. A localized change of

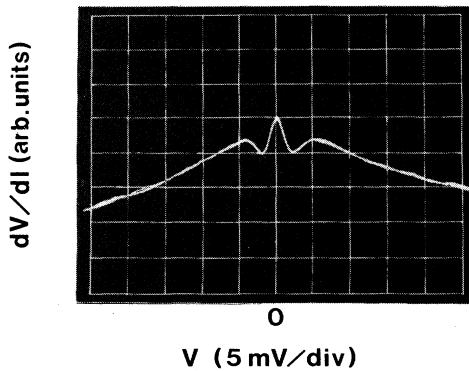


FIG. 2.  $dV/dI$  vs  $V$  of Nb/YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  point-contact junction at 4.2 K. The low-voltage range of the dynamic resistance of point-contact is examined and the minimum at about 2 mV is representative of SIN tunneling in the junction Nb/normal Y-Ba-Cu-O.

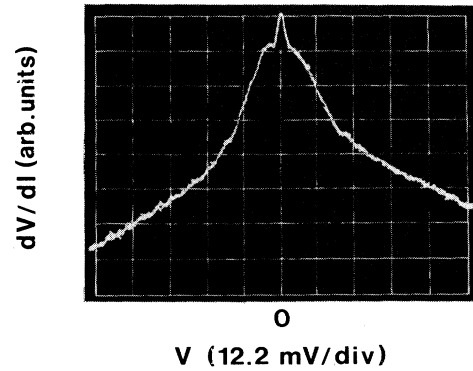


FIG. 3.  $dV/dI$  vs  $V$  of Nb/YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  point-contact junction at 4.2 K. The intermediate voltage range of the dynamic resistance of point contact is investigated. The sharp change of slope at about 20 mV is associated to the Y-Ba-Cu-O tunneling gap.

slope in the  $dV/dI$  vs  $V$  curve at about 40 mV was present in Y-Ba-Cu-O/Y-Ba-Cu-O junctions, but less pronounced compared with Nb/Y-Ba-Cu-O junctions. A typical example is shown in Fig. 4. We have related such slope changes to the contribution of the superconducting tunneling since, in any case, they are independent from the contact pressure. In Sec. III we will analyze these curves with an appropriate model in order to derive a value of the Y-Ba-Cu-O energy gap.

In this region of bias voltage, a series of secondary sharp peaks has been sometimes observed in the  $dV/dI$  vs  $V$  characteristics of both Nb/Y-Ba-Cu-O and Y-Ba-Cu-O/Y-Ba-Cu-O junctions. In some cases the voltage position of these structures appears to be a multiple of a particular voltage value. However, it depends on the contact pressure and the contact surface and changes also from sample to sample. Observation of the  $I$ - $V$  characteristics in correspondence with these peaks has shown the presence of hysteretic structures which could be ascribed ei-

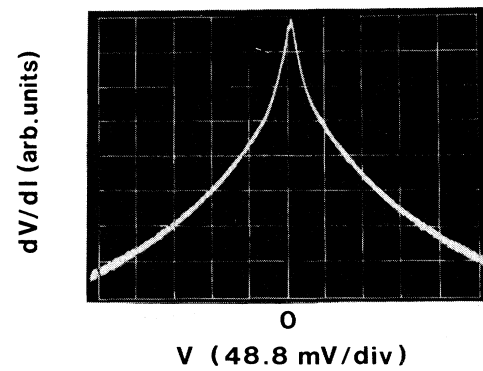


FIG. 4.  $dV/dI$  vs  $V$  of a YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> /YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  point-contact junction at 4.2 K. The smooth change of slope associated with Y-Ba-Cu-O gap, even if present, is not easily detectable. However, the model discussed in the text enabled it to be evaluated.

ther to heating effects of the currents circulating in the material grains or with resonances of small tunnel junctions.<sup>12</sup> Therefore, we believe that these peaks are not related to gap voltages of Y-Ba-Cu-O. In some contacts, for bias voltages higher than 160 mV, a “high-voltage” region has been observed, where the conductance seems to increase even faster than parabolic.

Measurements at 77 K have shown a  $V^{-2}$  behavior of the experimental  $dV/dI$  curves both for Nb/Y-Ba-Cu-O and for Y-Ba-Cu-O/Y-Ba-Cu-O junctions, and in no case were there appreciable deviations from this behavior.

### III. ANALYSIS OF THE TUNNELING MEASUREMENTS

#### A. Model

As we have seen in Sec. II, in a few cases a plateau at about 20 mV in the dynamic resistance curve for Nb/Y-Ba-Cu-O point contacts is present. All the remaining experimental  $dV/dI$  curves present only a sharp slope change at approximately the same value of voltage. This situation seems to be common with some previous papers on tunneling spectroscopy with large area junctions.<sup>5,6,9</sup>

One consequence is that the determination of the gap voltage by visual inspection of the resistance and conductance curves seems impractical for our measurements where the superconducting-tunneling features are not dominant. On the other hand, a thorough analysis of tunneling characteristics was looked for. For this reason, a model has been developed in order to account for, in a phenomenological way, the conductance behavior in our experiment with large area point contacts. Such a model is based on the analysis of what happens from the physical point of view in these contacts.

First of all, there are many hints that a noticeable part of Y-Ba-Cu-O samples behaves as normal, in some way, even at 4.2 K. In fact we observe SIN tunneling between Nb and normal-state Y-Ba-Cu-O at low bias voltages (see Fig. 2). Also susceptibility and Meissner effect measurements generally seem to confirm that part of the material is normal at liquid-helium temperature. All of this may be explained by the presence of a surface layer that is not superconducting<sup>2,15</sup> which may be caused by two possible phenomena: the very short coherence length (10–20 Å) which could result in a nonsuperconducting layer at grain surfaces and interfaces<sup>25</sup> and, in addition, an oxygen deficiency at the sample surface.<sup>2,26</sup>

When a large-area tip is pressed against the Y-Ba-Cu-O electrode one breaks through this nonsuperconducting surface layer at random positions generating a network of parallel conducting channels, a part of which are due to true superconducting tunneling and the rest are due to conduction through the nonsuperconducting layer. In this framework the normal material may produce NIN contacts in Y-Ba-Cu-O/Y-Ba-Cu-O junctions even at 4.2 K.

On the other hand, NIN-type tunneling is an effect seen in many configurations where two electrodes are separated by an oxide barrier when bias voltages are comparable to the barrier heights. In particular, it is also seen with su-

perconducting electrodes when the junction is biased at voltages much greater than the gap-induced structures. In fact, we observed this effect in Nb/Pb thin-film tunnel junctions at 4.2 K, where the conductance, instead of remaining constant after the minimum at  $V=12$  mV caused by the Nb phonon spectrum, increases following a  $V^2$  law up to at least 100 mV. Therefore, we also expect NIN tunneling in Nb/Y-Ba-Cu-O junctions at bias voltages greater than 12 mV. The surface-layer breaking mechanism does not prevent the thin nonsuperconducting layer at grain interfaces because the short coherence length contributes to the natural barrier in SIN or SIS contacts anyway, since it is an intrinsic property of the interfaces in this material. The complex range of tunneling phenomena which take place in parallel in large-area contact junctions according to the physical picture outlined above is summarized in Table I. The phenomena expected in principle but not observed in the experiments are reported in parentheses.

In this paper, we restrict our analysis to the intermediate voltage region where, according to our physical model, two main phenomena appear to be present: the background NIN tunneling, and, in parallel, the SIS or SIS' tunneling. The conductance of the point contact in this region of bias voltage is given, therefore, by two terms

$$\sigma = \sigma_b + \sigma_s, \quad (1)$$

where  $\sigma_b$  is the background conductance and  $\sigma_s$  is the superconducting-tunneling conductance.

The first term, describing the conductance of NIN tunneling in the voltage range lower than the barrier height, is given by<sup>24</sup>

$$\sigma_b(V) = a + 3bV^2, \quad (2)$$

TABLE I. Summary of the tunneling phenomena which take place in parallel in large-area contact junctions assuming a model of an array of small-scale different contacts. Phenomena expected in principle but not observed by us are shown in parentheses.

Temp. (K)	Low-voltage range ( $0 < V < 12$ mV)	Intermediate-voltage range ( $12 < V < 160$ mV)
	Nb/Y-Ba-Cu-O	
4.2	Supercurrents <sup>a</sup> SIN	SIS' NIN
77	NIN (NIS')	NIN (NIS')
	Y-Ba-Cu-O/Y-Ba-Cu-O	
4.2	Supercurrents <sup>a</sup> NIN	SIS' NIN (SIN and NIS')
77	NIN	NIN (SIS') (SIN and NIS')

<sup>a</sup>Zero-voltage currents are likely to be Josephson currents (Ref. 5).

where  $a$  (mho) and  $b$  ( $\text{mhoV}^{-2}$ ) are constants typical of each junction.

As for the second channel, i.e., tunneling from superconducting Nb to superconducting Y-Ba-Cu-O, we can observe in our point-contact measurements that its contribution to the total conductance is very spread in voltage. It may be compared with the peaked conductance observed in tunnel and sometimes also in point-contact junctions. This can be due to many causes, like Gaussian broadening of the gap values, thermal broadening, and pair-breaking phenomena. The former is caused essentially by the rather complex polycrystalline nature of these sintered materials, which may also include proximity effects between normal layers and superconducting cores of the grains. Surface oxygen deficiencies, locally changing the critical temperature of the sample,<sup>26</sup> can occur producing a high degree of gap broadening. Meanwhile, because of the very low value of  $T/T_c \approx 0.05$ , the thermal broadening at 4.2 K should have little influence.

The equation we adopted for describing the quasiparticle current  $I_N$  in superconducting tunneling is that proposed in Ref. 18 because of its ability to account for, in a simple way, a large gap conductance spreading. According to this model we have

$$I_N(V) = G_N V^{n+1} / (V^n + V_G^n) \quad \text{with } n \geq 1, \quad (3)$$

where  $G_N$  = conductance of the normal state,  $V_G$  = gap voltage, and  $n$  = parameter which quantifies how ideal is the tunnel junction. The superconducting-tunneling conductance is, therefore,

$$\sigma_s(V) = \frac{G_N V^n [(n+1)V_G^n + V^n]}{(V^n + V_G^n)^2} \quad \text{with } n \geq 1. \quad (4)$$

The relevant features of this model are the following.

(1) The parameter  $n$  accounts for, in a phenomenological way, the deviations of the experimental conductance curves from the ideal BCS behavior. Thus, at high values of the  $n$  parameter ( $n > 20$ ), Eq. (4) well represents the typical experimental  $\sigma_s$  vs  $V$  dependence of a tunnel junction. On the other hand, at lower values of  $n$  ( $1 < n < 5$ ), Eq. (4) seems to reasonably well represent the experimental  $\sigma_s$  vs  $V$  dependence of weak-link junctions or tunnel junctions with a large amount of broadening.

(2) This phenomenological model is very simple and Eq. (4) is suitable for numerical computations and curve fitting procedures. Contributions of the ac Josephson currents to the total current have been neglected since in all the experiments point contacts were adjusted so as to obtain a very small zero-voltage current.

### B. Least-squares fit results

The theoretical  $dV/dI$  vs  $V$  dependence derived from Eq. (1) proved to be very good in fitting sharp slope changes present in experimental dynamic resistance curves. We applied a least-squares fit to our experimental  $dV/dI$  curves using the theoretical resistance expression as a guess function. The five parameters of the fit ( $a, b, G_N, V_G, n$ ) were obtained by minimizing the standard

deviation of the fit under the typical physical constraints

$$a, b, G_N, V_G > 0, \quad n \geq 1.$$

Initial values for the fit parameters were chosen after visual inspection of the experimental  $I$  vs  $V$  and  $dV/dI$  vs  $V$  characteristics as well as by comparison of simulated and experimental dynamic resistance curves. Since  $dV/dI$  curves are expressed in arbitrary units, after the fitting procedure, parameters  $a$ ,  $b$ , and  $G_N$  were scaled by comparison of the calculated  $I$ - $V$  curves to the experimental ones.

Figures 5–8 show some of the results of the fit for different samples and temperatures. In all the figures, open circles represent experimental data while the continuous line represents the dynamic resistance obtained from Eq. (1) using the fitted values of the parameters. These values are reported in the caption of every figure.

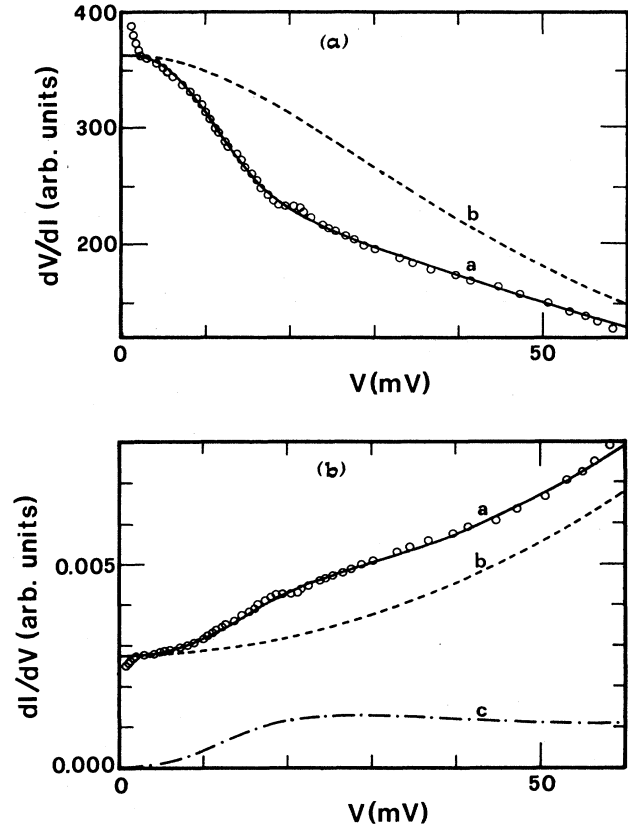


FIG. 5. (a) Dynamic resistance curve for a Nb/YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  junction at 4.2 K. Open circles are the experimental points while continuous line (curve *a*) represents the resistance obtained by the model using the fitted values of the parameters. Curve *b* is the contribution of the background resistance to the total  $dV/dI$ . Only voltage values greater than 10 mV have been used in the least-squares fit. Fitted parameters:  $a = 6.6 \times 10^{-2}$  mho,  $b = 9.0 \times 10^{-6}$  mhoV<sup>-2</sup>,  $G_N = 2.4 \times 10^{-2}$  mho,  $n = 2.9$ ,  $V_G = 22.0$  mV. (b) Same results of (a) shown in terms of conductance in order to better clarify the contribution of background conductance (curve *b*) and the superconducting-tunneling conductance (curve *c*) to the total one (curve *a*).

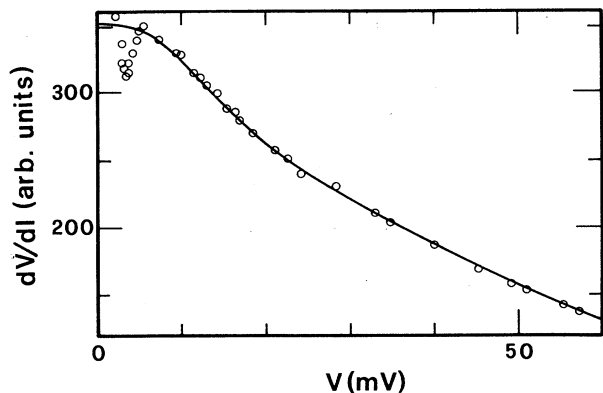


FIG. 6. Dynamic resistance of a Nb/Y-Ba-Cu-O (with 11% of green phase) junction at 4.2 K. Details are like in Fig. 5(a). Values of the fitted parameters are  $a=1.6 \times 10^{-1}$  mho,  $b=2.3 \times 10^{-5}$  mhoV $^{-2}$ ,  $G_N=2.5 \times 10^{-2}$  mho,  $n=3.1$ ,  $V_G=23.2$  mV.

In Fig. 5(a) the model has been applied to one of the best contacts obtained with a Nb tip and monophasic Y-Ba-Cu-O as the substrate. In this case of low-pressure contact, a plateau at about 20 mV was present in the dynamic resistance and the fitted value for the gap voltage is  $V_G=22.0$  mV while  $n$  parameter is 2.9 and the ratio  $G_N/a$  is 0.36.

The features of the model are analyzed in more detail in Fig. 5(b), which shows the  $\sigma$  vs  $V$  curve obtained from experimental data of resistivity reported in Fig. 5(a). Curve  $b$  is, in fact, the contribution of the background conductivity calculated from Eq. (2) while curve  $c$  is the contribution of the superconducting-tunneling conductivity obtained from Eq. (4). Curve  $a$  is the sum of the two according to Eq. (1).

One of the results obtained using a Nb tip and a po-

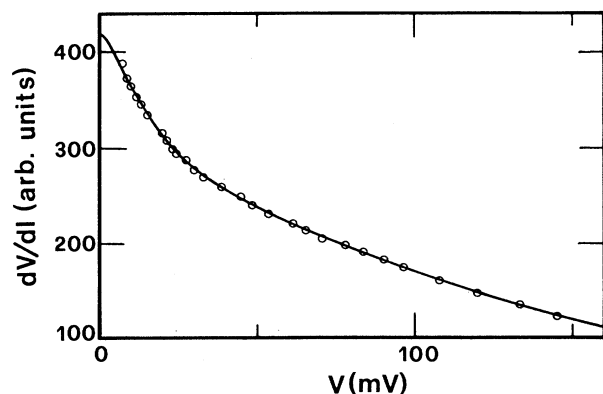


FIG. 7.  $dV/dI$  vs  $V$  curve for a YBa $_2$ Cu $_3$ O $_{7-\delta}$ /YBa $_2$ Cu $_3$ O $_{7-\delta}$  junction at 4.2 K showing a very smooth change of slope associated with Y-Ba-Cu-O gap. The model described in the text obtained the following parameters:  $a=7.1 \times 10^{-3}$  mho,  $b=2.0 \times 10^{-7}$  mhoV $^{-2}$ ,  $G_N=4.3 \times 10^{-3}$  mho,  $n=1.5$ ,  $V_G=42.1$  mV.

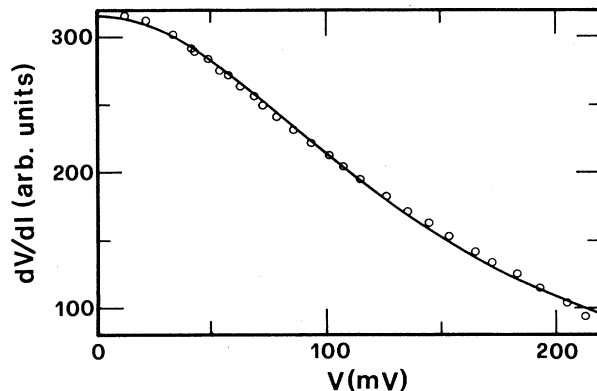


FIG. 8.  $dV/dI$  vs  $V$  curve for a YBa $_2$ Cu $_3$ O $_{7-\delta}$ /YBa $_2$ Cu $_3$ O $_{7-\delta}$  junction at 77 K. No evidence of contributions due to the superconducting tunnel is present. The adopted model confirms this observation. Values of the background conductance parameters obtained with both the complete model and the conductance of Eq. (2) alone are  $a=6.9 \times 10^{-2}$  mho,  $b=1.1 \times 10^{-6}$  mhoV $^{-2}$ .

lyphasic substrate (11% of green phase) is shown in Fig. 6. The visual determination of the characteristic voltage was rather difficult here because the  $dV/dI$  curve only presents a smooth slope change. The least-squares fit procedure gives a gap voltage of 23.2 mV with  $n=3.1$  and  $G_N/a=0.15$ . The average values of the gap voltages obtained in several experiments for monophasic and polyphasic Y-Ba-Cu-O samples were  $22.8 \pm 0.8$  mV and  $23.5 \pm 0.6$  mV, respectively. If we consider these values as the sum of gap voltages of Nb and Y-Ba-Cu-O, then subtracting the Nb voltage gap ( $\sim 1.5$  mV at 4.2 K) we obtain  $21.3 \pm 0.8$  mV for monophasic Y-Ba-Cu-O and  $22.0 \pm 0.6$  mV for the polyphasic one. As a consequence, ratios  $2\Delta/k_B T_c$  are  $5.46 \pm 0.20$  and  $5.62 \pm 0.15$ , respectively. These values are similar to already published results.<sup>2-6,10,12</sup> This result seems to also be consistent with measurements of critical temperature which indicate a little increase of  $T_c$  in polyphasic samples with increasing percentages of green phase.<sup>17</sup>

Figure 7 shows the results obtained in a Y-Ba-Cu-O/Y-Ba-Cu-O point-contact experiment at 4.2 K. Once again only a broad slope change was present in the original  $dV/dI$  data. Nevertheless, the value of the gap voltage obtained by fitting the measured data  $V_G=42.1$  mV is almost equal to twice the Y-Ba-Cu-O gap voltage obtained in Nb/Y-Ba-Cu-O experiments at the same temperature as expected in a symmetrical junction.

At 77 K, the fitting procedure gives consistent indications of very low values of  $G_N$  independent of the initial choice for  $V_G$  and  $n$  (see Fig. 8). Values of  $a$  and  $b$  parameters obtained by fitting the same data using only the background conductance expression are identical to those obtained by the complete model indicating the insignificant contribution of superconducting tunneling at this temperature. We performed a  $\chi^2$  test on our least-squares fits in order to obtain a statistical measure of their quality. In all cases the test was passed at 90% level of significance.

#### IV. DISCUSSIONS AND CONCLUSIONS

In this paper we have described tunneling measurements with point-contact junctions performed on several Y-Ba-Cu-O samples both monophasic and with 11% of green phase. We have obtained the main parameters of both the superconducting tunneling and of the normal background by fitting a phenomenological equation that models the differential resistance ( $dV/dI$ ) of tunneling in the junctions to experimental curves taken at the temperatures of 4.2 and 77 K.

The first result is the determination of the gap voltage  $21.3 \pm 0.8$  mV for the monophasic Y-Ba-Cu-O at 4.2 K. This value is consistently obtained both in Nb/Y-Ba-Cu-O and Y-Ba-Cu-O/Y-Ba-Cu-O junctions and seems in good agreement with the values previously published in the technical literature.<sup>2-6,10,12</sup> The determination of the gap voltage of the 11% green phase samples at 4.2 K,  $V_G = 22.0 \pm 0.6$  mV is in rather good accordance with the critical-temperature measurements.<sup>17</sup> It could be regarded as an indication of the sensitivity of the method, both model and fitting procedure, in determining the gap.

It should be noted that in Ref. 2 it has been suggested that the value of the gap obtained in tunneling experiments could be lower than the bulk value because of the presence of the oxygen-deficient surface layers with lower critical temperatures.<sup>26</sup> Our measurements confirm this hypothesis. In fact, the measurements taken on junctions at 77 K do not show superconducting-tunneling features on conductivity and thus indicate that the material of the surface layers involved in the contacts has an even lower critical temperature. On the other hand, the superconducting-tunneling conductivity observed at 4.2 K is typical of a largely broadened state density [see Fig. 5(b), curve c] and seems to be produced mainly by a broadening of Gaussian type related to both the oxygen-deficient layer<sup>26</sup> and the extremely short coherence length in these materials.<sup>25</sup> Moreover, these effects lowering the voltage gap at surfaces and interfaces can give rise to a Gaussian distribution of gap values in tunneling channels. The effect of coherence length is highly enhanced when the temperature is near  $T_c$  (Ref. 25).

Notwithstanding, we would like to observe that the adopted model is able to extract the superconducting-tunneling parameters from a predominant background also in the presence of a large amount of gap broadening. For these reasons such a model could be useful not only to test the presence of superconducting tunneling in highly anisotropic and gap-broadened situations but also to determine the correct gap voltage in SIN junctions with a great amount of thermal and Gaussian broadening where this value is not coincident with the position of the conductance maximum.<sup>23</sup>

As far as the background conductance is concerned, its determination is relevant to the theory. We have already said that in several experiments involving STM techniques where the normal material (Au,W) tips have dimensions comparable with superconducting grain size or even

less,<sup>2,9</sup> a linear behavior versus the bias voltage has been observed while the gap related features showed strong variations from point to point over the sample. On the contrary, our measurements constantly show a quadratic behavior of the background conductance versus  $V$  independently of the tip position. We first observe that the point-contact areas of our junctions are large compared with the typical dimensions of superconducting grains in such materials (10–50  $\mu\text{m}$ ) and thus it is likely that the tunneling results from an average of several superconducting and normal-state tunneling contributions over a relatively wide region of the surface material, according to the analysis of Sec. III summarized in Table I. Since the parabolic conductance comes both from SIN and NIN channels (in Nb/Y-Ba-Cu-O junctions) it is reasonable that it looks as the predominant effect. As a consequence, we cannot say that the observed background conductance is an intrinsic property of the superconducting material itself but in our large-area experiments it can constitute a proof of the presence of a nonsuperconducting layer at the surface of Y-Ba-Cu-O compounds and, probably, also at the grain interfaces up to 160 mV. The large-area contact may also explain the presence, in our measurements, of a large broadening of superconducting-tunneling characteristics (parameter  $n$  between 1.5 and 3).

The hypothesis of the presence of a thermodynamically stable<sup>2</sup> distribution of oxygen content increasing from the material surface to the bulk might explain both the existence of a nonsuperconducting surface layer and the presence in our point-contact experiments of superconducting-tunneling features typical of a critical temperature lower than 91 K.

Finally, examining closely the values of parameters  $a$  and  $b$  of the background conductance, in Nb/Y-Ba-Cu-O junctions, they can be used to calculate the height ( $\phi$ ) and the width ( $S$ ) of the potential barrier of the NIN tunneling.<sup>27</sup> The values  $\phi = 0.19 \pm 0.06$  V and  $S = 35.3 \pm 4.0$  Å are obtained. Notwithstanding that this method of determining  $\phi$  and  $S$  is not very sensitive, the obtained values are very similar to that ones of NbO<sub>x</sub> barriers.<sup>28</sup> On the other hand, from the chemical point of view, it is very likely that a NbO<sub>x</sub> barrier is present at the Nb/Y-Ba-Cu-O interface.

In conclusion, we believe that tunneling experiments should be pursued and improved and aimed at obtaining quantitative information not only on the gap voltages but also on the normal-state material at the surfaces and grain interfaces of oxide superconductors. This information could also be important for the development of the theory of high- $T_c$  superconductors.

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- <sup>1</sup>M. E. Hawley, K. E. Gray, D. W. Capone II, and D. G. Hinks, *Phys. Rev. B* **35**, 7224 (1987).
- <sup>2</sup>E. R. Moog, M. E. Hawley, K. E. Gray, J. Z. Liu, D. G. Hinks, D. W. Capone II, and J. Downey, *J. Low Temp. Phys.* (to be published).
- <sup>3</sup>J. R. Kirtley, R. T. Collins, Z. Schlesinger, W. J. Gallagher, R. L. Sandstrom, T. R. Dinger, and D. A. Chance, *Phys. Rev. B* **35**, 8846 (1987); J. R. Kirley, C. C. Tsuei, S. I. Park, C. C. Chi, J. Rozen, M. W. Shafer, W. J. Gallagher, R. L. Sandstrom, T. R. Dinger, and D. A. Chance, *Jpn. J. Appl. Phys.* **26**, Suppl. 26-3, 997 (1987).
- <sup>4</sup>Y. Katoh, K. Tanabe, H. Asano, and O. Michikami, *Jpn. J. Appl. Phys.* **26**, L1777 (1987).
- <sup>5</sup>A. Barone, A. Di Chiara, G. Peluso, V. Scotti di Uccio, A. M. Cucolo, R. Vaglio, F. C. Maticotta, and E. Olzi, *Phys. Rev. B* **36**, 7121 (1987).
- <sup>6</sup>H. Tao, Y. Chen, L. Lu, Q. Yang, B. Zhao, Y. Shi, Y. Lu, H. Wang, Y. Zheo, L. Li, Y. Fan, Y. Liu, L. Chen, D. Teng, and Q. Wu, *Int. J. Mod. Phys. B* **1**, 555 (1987).
- <sup>7</sup>T. Ekino and J. Akimitsu, *Jpn. J. Appl. Phys.* **26**, L452 (1987).
- <sup>8</sup>S. Pan, K. W. Ng, A. L. de Lozanne, J. M. Tarascon, and L. H. Greene, *Phys. Rev. B* **35**, 7220 (1987).
- <sup>9</sup>M. Naito, D. P. E. Smith, M. D. Kirk, B. Oh, M. R. Hahn, K. Char, D. B. Mitzi, J. Z. Sun, D. J. Webb, M. R. Beasley, O. Fischer, T. H. Geballe, R. H. Hammond, A. Kapitulnik, and C. F. Quate, *Phys. Rev. B* **35**, 7228 (1987); M. D. Kirk, D. P. E. Smith, D. B. Mitzi, J. Z. Sun, D. J. Webb, K. Char, M. R. Hahn, M. Naito, B. Oh, M. R. Beasley, T. H. Geballe, R. H. Hammond, A. Kapitulnik, and C. F. Quate, *ibid.* **35**, 8850 (1987).
- <sup>10</sup>I. Iguchi, H. Watanabe, Y. Kasai, T. Mochiku, A. Sugishita, and E. Yamaka, *Jpn. J. Appl. Phys.* **26**, L645 (1987).
- <sup>11</sup>M. F. Crommie, L. C. Bourne, A. Zettl, Marvin L. Cohen, and A. Stacy, *Phys. Rev. B* **35**, 8853 (1987).
- <sup>12</sup>J. Moreland, J. W. Ekin, L. F. Goldrich, T. E. Capobianco, A. F. Clark, J. Kwo, M. Mong, and S. H. Liou, *Phys. Rev. B* **35**, 8856 (1987); J. Moreland, L. F. Goodrich, J. W. Ekin, T. E. Capobianco, and A. F. Clark, *Jpn. J. Appl. Phys.* **26**, Suppl. 3, 999 (1987).
- <sup>13</sup>H. Koch, R. Cantor, J. F. March, H. Eickenbusch, and R. Schöllhorn, *Phys. Rev. B* **36**, 722 (1987).
- <sup>14</sup>P. J. M. van Bentum, L. E. C. van de Leemput, L. W. M. Schreurs, P. A. A. Teunissen, and H. van Kempen, *Phys. Rev. B* **36**, 843 (1987).
- <sup>15</sup>P. W. Anderson and Z. Zou, *Phys. Rev. Lett.* **60**, 132 (1988).
- <sup>16</sup>R. S. Gonnelli, D. Andreone, V. Lacquaniti, F. Abbattista, and M. Vallino, in *Centro Interuniversitario di Struttura della Materia and Gruppo Nazionale di Struttura della Materia Workshop on High-T<sub>c</sub> Superconductivity*, Vietri, Italy, 1988 (unpublished).
- <sup>17</sup>P. Brovotto (private communication).
- <sup>18</sup>K. Matsuo, *Prog. Theor. Phys.* **69**, 301 (1980).
- <sup>19</sup>J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyrou, J. L. Tholence, and R. Tournie, *Europhys. Lett.* **3**, 1301 (1987).
- <sup>20</sup>H. Takagi, S. Uchida, K. Kitazawa, K. Kishio, K. Fuchi, and S. Tana, in *Proceedings of the First European Workshop on High-T<sub>c</sub> Superconductors and Potential Applications, Genova, 1987*, edited by J. Vilain and S. Gregoli (Commission of the European Communities, Brussels, Belgium, 1987), p. 241.
- <sup>21</sup>R. J. Cava, B. Batlogg, R. V. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Esnosa, *Phys. Rev. Lett.* **58**, 1676 (1987).
- <sup>22</sup>C. Michel and B. Raveau, *J. Solid State Chem.* **43**, 73 (1982).
- <sup>23</sup>S. Hayashi and R. Aoki, *Jpn. J. Appl. Phys.* **26**, 1653 (1987).
- <sup>24</sup>J. G. Simons, *J. Appl. Phys.* **34**, 238 (1963); **34**, 1793 (1963); **34**, 2591 (1963); J. M. Rowell, in *Tunneling Phenomena in Solids*, edited by E. Burstein and S. Lundqvist (Plenum, New York, 1969), p. 385.
- <sup>25</sup>G. Deutscher and K. A. Müller, *Phys. Rev. Lett.* **59**, 1745 (1987).
- <sup>26</sup>W. K. Kwok, G. W. Crabtree, A. Umezawa, B. W. Veal, J. D. Jorgensen, S. K. Malik, L. J. Nowicki, A. P. Pauliksa, and L. Nunez, *Phys. Rev. B* **37**, 106 (1988).
- <sup>27</sup>J. M. Rowell, in *Tunneling Phenomena in Solids*, edited by E. Burstein and S. Lundqvist (Plenum, New York, 1969), p. 273.
- <sup>28</sup>D. G. Walmsley, E. L. Wolf, and J. W. Osmun, *Thin Solid Films* **62**, 61 (1979).