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Point contact tunnelling studies on ceramic YBCO with scanning tunnelling microscope tips

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Abstract. A detailed study of point contact tunnelling into ceramic YBCO with electrochemically etched tips of Pt, Nb and W is reported. The superconducting gap parameter (Δ) has been extracted from $I-V$ and $\mathrm{d}I/\mathrm{d}V-V$ curves using various procedures. Our results indicate a gap value of about 20 meV. We observe that the zero bias conductance is strongly dependent on the junction resistance. The normal state conductance varies linearly with bias voltage and the conductance curves are asymmetric with respect to polarity of the bias voltage. With contacts of very high junction resistance, we observe G(0)/G(100 mV) has a value as low as 1/6. This may be the lowest value reported so far.

Keywords. Point contact; tunnelling; superconducting gap; oxide superconductors; scanning tunnelling microscope.

PACS No. 74·50

1. Introduction

Quasiparticle tunnelling is a powerful technique to study gap structures in superconductors (Wolf 1985). The single particle excitation density of states in a superconductor according to the BCS weak coupling limit is given by

$$N_S = N_0(E^2/E^2 - \Delta^2)^{1/2} \tag{1}$$

where N_0 is the normal state density of states, Δ the superconducting gap parameter and E the energy of excitation measured from the fermi energy in the normal state.

The expression for tunnel current between a normal metal and a superconductor in an S–I–N junction is given by (Wolf 1985):

$$I_{NS} = C_N \int^{\infty} \{|E|/(E^2 - \Delta^2)^{1/2}\}[f(E) - f(E + eV)]\mathrm{d}E \tag{2}$$

where $f(E)$ is the Fermi distribution function, 2Δ the energy gap and C_N the normal state conductance. From the above equation we obtain at absolute zero:

$$\begin{aligned} \mathrm{d}I/\mathrm{d}V &= C_N(eV)/[(eV)^2 - \Delta^2]^{1/2}, \quad eV > \Delta \\ &= 0 \qquad\qquad\qquad\qquad\qquad eV < \Delta. \end{aligned} \tag{3}$$

A schematic of a typical BCS-type tunnelling curve is shown in figure 1. It represents the ideal case. The actual shape of the $\mathrm{d}I/\mathrm{d}V-V$ curve depends on factors like

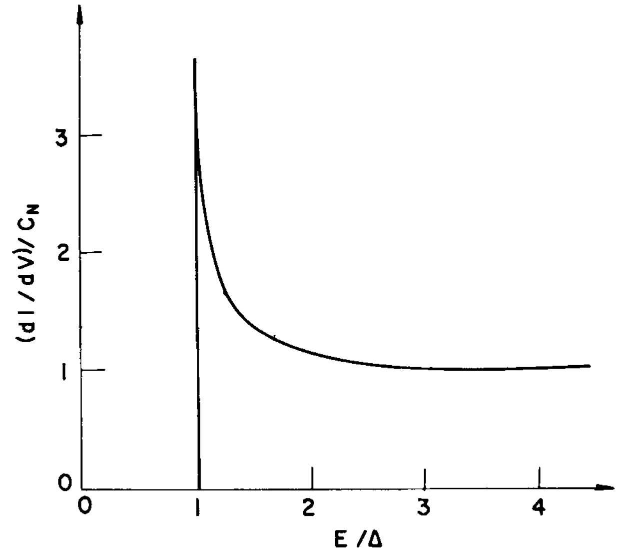

Figure 1. Schematic of ideal BCS tunnelling curve.

thermal smearing due to finite temperature, lifetime broadening effects (Dynes *et al* 1978) or strong phonon coupling (Wolf 1985).

Tunnelling measurements can be done with different geometries. In the high temperature oxide superconductors tunnelling in various geometries like planar, point contact, break junction have been reported (Srinivasan 1990). Scanning tunnelling microscopes (STM) are widely used to implement point contact tunnelling geometry. In the ceramic superconductors vacuum tunnelling with STM tips is very difficult because of an insulating oxide layer on the surface. In order to reduce (if not totally eliminate) the effect of the native oxide, the tips have to be pressed hard on to the surface thereby piercing the oxide layer and then slowly move back. The advantage of using sharply etched metal tips (typical tip diameter 100 to 1000 Å) lies in the fact that in polycrystalline pellets there is a good chance of making contact only with a single superconducting grain as the grain sizes in these superconductors are of the order of a few microns.

A large number of gap measurements on YBCO (both single crystals and ceramics) have been reported (Kirtley 1990). These reports show a wide variation in the BCS ratio ($2\Delta/k_B T_c$) from 3–11 with $2\Delta/k_B T_c \cong 5{\cdot}5$ as the most probable value. In fact point contact tunnelling measurements show lot of variety in the $I-V$ and conductance curves as compared to tunnelling measurements in the planar geometry. The general consensus is that data obtained from point contact measurements are not reproducible. Our objective is to make a thorough study of $I-V$ and $\mathrm{d}I/\mathrm{d}V-V$ characteristics of point contact junctions using a STM type set-up on ceramic YBCO with different tip materials and junction resistances. It is hoped that the inter comparison of data taken with different tips and different junction resistances (i) will enable us to extract reproducible gap parameters and (ii) will also help us understand why different types of curves are often observed.

In this paper we report our point contact measurements on ceramic YBCO pellets with electrochemically etched tips of Pt, Nb, W. We have used a STM type set-up with differential screw for coarse motion and a piezo tube for fine motion. We have also carried out similar experiments on BiSrCaCuO single crystals and related oxides. For the sake of keeping the report focussed on one aspect, we present our data on YBCO only. We have also given a brief description of our apparatus to illustrate how exactly we carried out the experiments.

2. Experiment

2.1 *Cryogenics and electronics*

Junctions are made in liquid helium by pressing an electrochemically etched metal tip against the YBCO pellet. Samples were prepared using the standard solid state reaction and subsequent oxygen treatment. The measured resistivity showed a T_c onset of 90 K. The contact resistance can be adjusted by means of a differential screw and applying voltage across a piezoelectric transducer (PZT5H). The entire assembly is rigidly mounted in a liquid helium dewar capable of going down to 1·5 K.

To measure the dc $I-V$ characteristics of the junction, the junction is current biased by a programmable current source (Keithley 220). The voltage is measured by a Keithley 181 nanovoltmeter. Four terminal measurement is done in all cases. The current is ramped in steps and both current and voltage are stored in a computer. A typical scan lasts for about 2 minutes and has about 200 points. A large number of scans are made to check for reproducibility in the $I-V$ curves. The conductance (dI/dV) plots are numerically obtained from these $I-V$ data using standard numerical recipes.

In addition to numerical differentiation of $I-V$ data we also employed a modulation technique to measure dI/dV (Srikanth *et al* 1990). A small amplitude ac modulating signal ($\delta V \cos \omega t$) is mixed with the dc bias voltage (V) which could be ramped up or down. ($\delta V \ll V$ typical δV value is 100 μV).

A feedback circuit with current boosters maintains the ac signal constant across the junction irrespective of even large or sharp changes in junction resistances. The dI/dV is measured by an SR530 lock-in-amplifier. Both dc and modulation techniques are completely computer automated. A schematic of the modulation circuit is shown in figure 2.

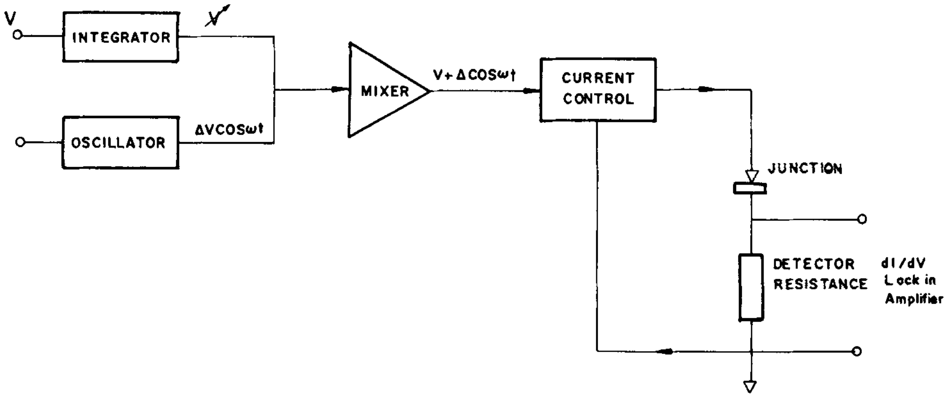

Figure 2. Block diagram of the modulation circuit employed to measure the dI/dV directly. The lock-in amplifier output is proportional to dI/dV and is recorded by a computer.

2.2 *TIP preparation*

The Pt, Nb and W tips were prepared by electrochemical etching. For Pt and Nb the etchant solution was an acid mixture HF + HNO_3 + HCl mixed in the ratio 1:2:3. Concentrated NaOH solution was the electrolyte used for etching W. In all the cases 0·2 mm thick wires were mechanically ground initially before being subjected to electrochemical etching. A carbon rod salvaged from an ordinary dry cell served as the counter electrode and an ac voltage at line frequency of about 5–10 V was applied between the electrodes. Before making contact with the sample the tips are cleaned with acid and alkali solutions. We find that the above technique gives sharp tips in a reproducible way.

2.3 *Data taking procedure*

The surface of the YBCO sample is scratched with a rough emery paper and thin Cu leads are attached using conductive Ag paint. The tip is driven hard into the sample to get as low a junction resistance as possible and then pulled back slowly with the help of the differential screw and the piezo tube for getting higher junction resistance. The $I-V$ and $dI/dV-V$ are measured for each contact resistance as described in §2.1. The junctions are made and all adjustments of junction resistance are done only in liquid helium environment.

3. Results

The $dI/dV-V$ plots for three different junctions formed with Pt, W and Nb tips pressed into the same YBCO pellet are shown in figures 3a, 3b and 3c. All the dI/dV data reported here are taken by the modulation technique except the figure 9.

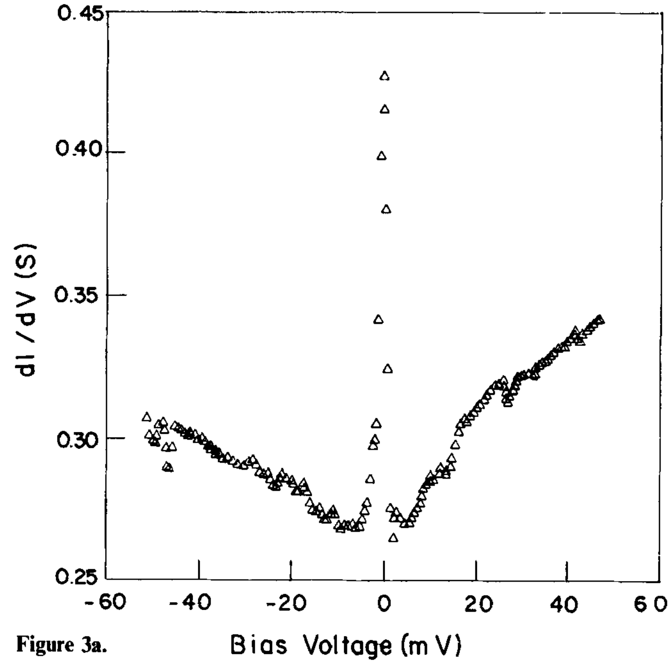

Figure 3a.

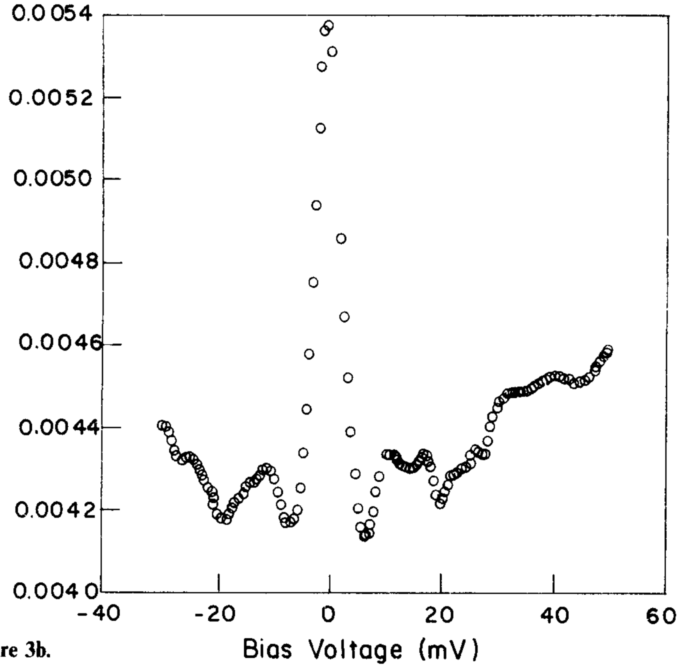

Figure 3b.

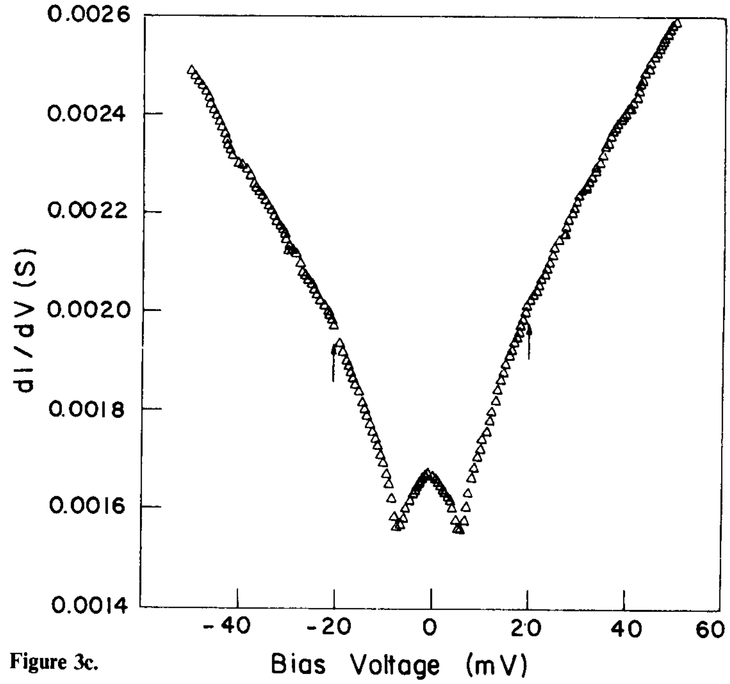

Figure 3c.

Figure 3. Point contact tunnelling conductance curves (dI/dV – V) taken at 1·5 K for (**a**) Pt–YBCO junction (**b**) W–YBCO junction (**c**) Nb–YBCO junction. Note the small slope change in dI/dV at 20 mV for Nb–YBCO case.

One can notice quite a few similarities which are listed below:

1) A distinct feature around 20 mV has been observed in $dI/dV - V$ curves of junctions with low resistance ($< 1\,k\Omega$). For $V > 20\,mV$ the curves are more or less featureless and varies linearly. Once in a while we see additional features too, above and below 20 mV. As can be seen in figure 3b, there are small smeared out features around 40 mV.
2) For high resistance junctions the conductance is more or less linear with a distinct change in slope at or near 20 mV. (Figures 4a and 4b).
3) For low resistance junctions there is a peak in conductance at zero bias with a spread of approximately 10 mV. This peak depends sensitively on the junction resistance. It is interesting to note that at high junction resistances (typically $> 1\,k\Omega$) this central feature vanishes. The central feature does not depend on whether the tip is normal (W and Pt) or superconducting (Nb). Also this central peak can be removed by applying a magnetic field.
4) We observe an approximately linear $G(V)$ at higher bias voltages (say above 40 mV).
5) A distinct asymmetry in the differential conductance curves with respect to the polarity of bias voltage has been observed. Note that in all cases polarity of voltage is with respect to tip bias. In other words a positive voltage implies the electron going from material into the tip.

There is not much difference in the tunnelling curves for different tip materials except for the fact that we do not see a sharp feature at 20 mV in Nb-YBCO contacts. Please note that this difference is quantitative in nature and not qualitative. For example we could consistently get a contact resistance as low as $10\,\Omega$ with Pt tip whereas the lowest contact resistance we got with Nb tip was about $600\,\Omega$. This is most likely due to a native oxide layer in the case of Nb.

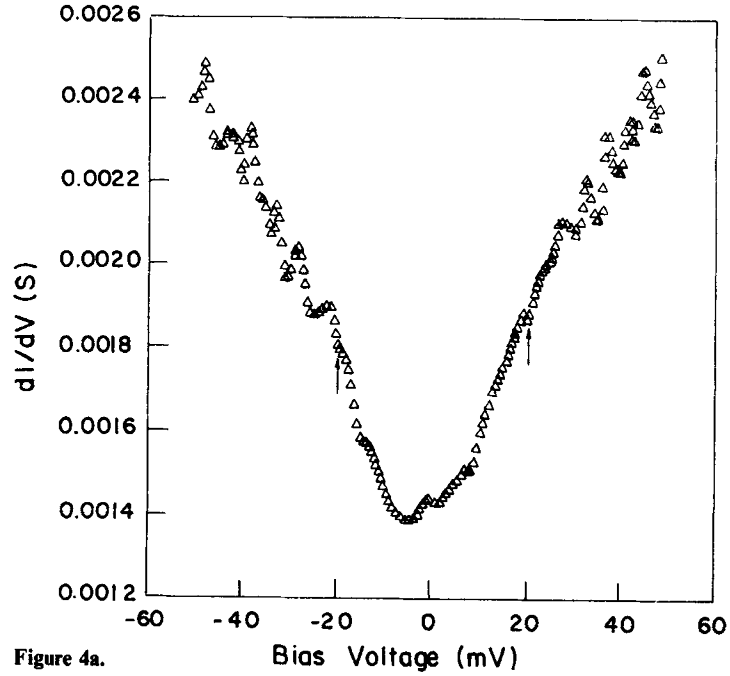

Figure 4a.

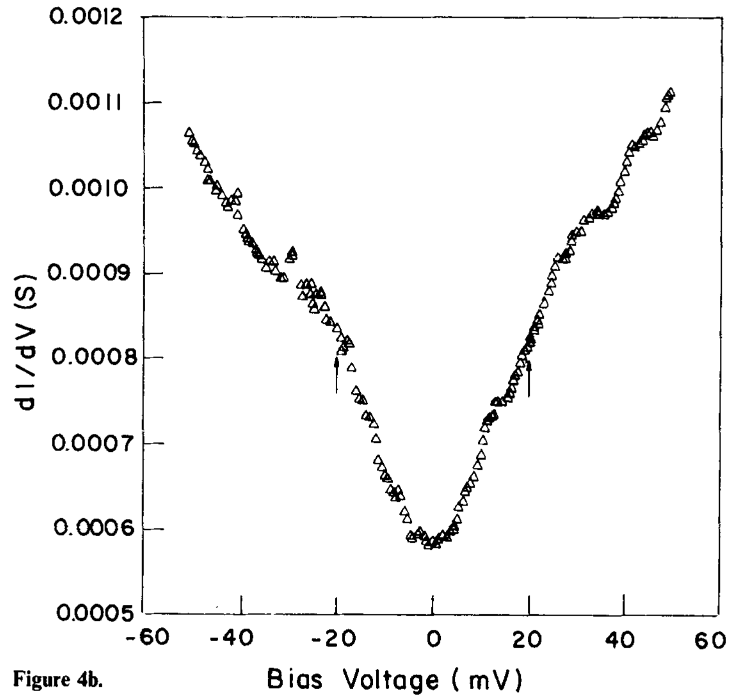

Figure 4b.

Figure 4. $dI/dV - V$ at 1·5 K for high resistance junctions formed on YBCO with (a) Pt tip (b) Nb tip. Compare 4(a) with 3(a) to appreciate the fact that zero bias peak vanishes as junction resistance increases.

4. Discussion

In this section we would like to comment on the above basic observations.

4.1 *Gap structure*

Distinct features are seen around 20 mV in figures 3a and 3b corresponding to Pt–YBCO and W–YBCO contacts. A slope change is seen around the same voltage in Nb–YBCO contact (figure 3c). We associate this with the gap parameter (Δ) in YBCO. We have studied a large number of contacts and the feature at 20 mV is extremely reproducible. Our deduction is that the gap is clearly seen in the $dI/dV - V$ plot at low junction resistance and as a slope change at high junction resistance (compare figures 3a and 4a). We have also elucidated the gap parameter by different procedures from $I^2 - V^2$ plots (Ekino and Akimitsu 1989) and from G_S/G_N vs V plots (see figures 5 and 6). In $I^2 - V^2$ plots we have considered the leakage current also by postulating that at $V = 0$ there is a leakage conductance $a = G(V) \neq 0$ and compensated the excess current at zero voltage by plotting $(I - aV)^2 - V^2$ where 'a' is the zero bias conductance (Srinivasan 1990). This is shown in figure 7. In table 1 we have listed the Δ values obtained from junctions with different tips using different procedures. The uncertainty in the gap value estimated by various methods is around 3–4 mV.

Point contact tunnelling measurements on YBCO with different tips and different junction resistances seem to indicate a gap value of about 20 mV.

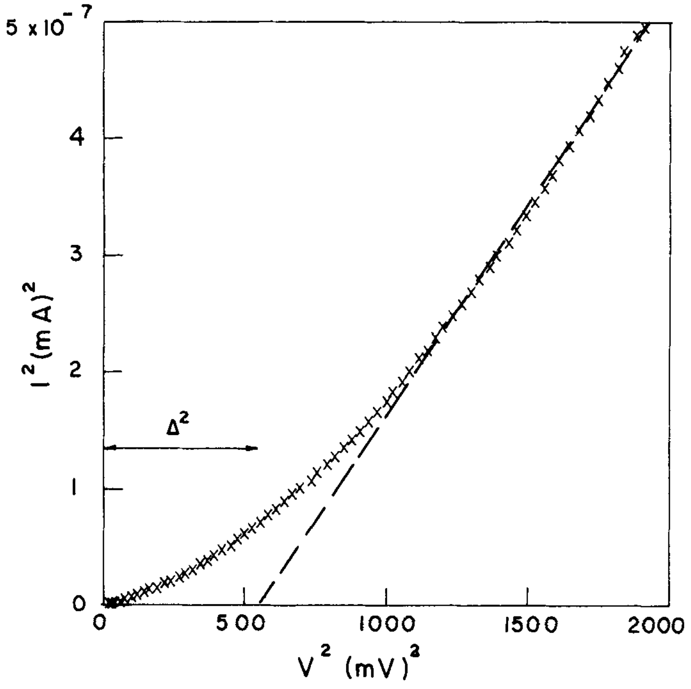

Figure 5. $I^2 - V^2$ plot for Nb–YBCO junction at 4·2 K. Gap value (Δ) elucidated is 23·5 mV.

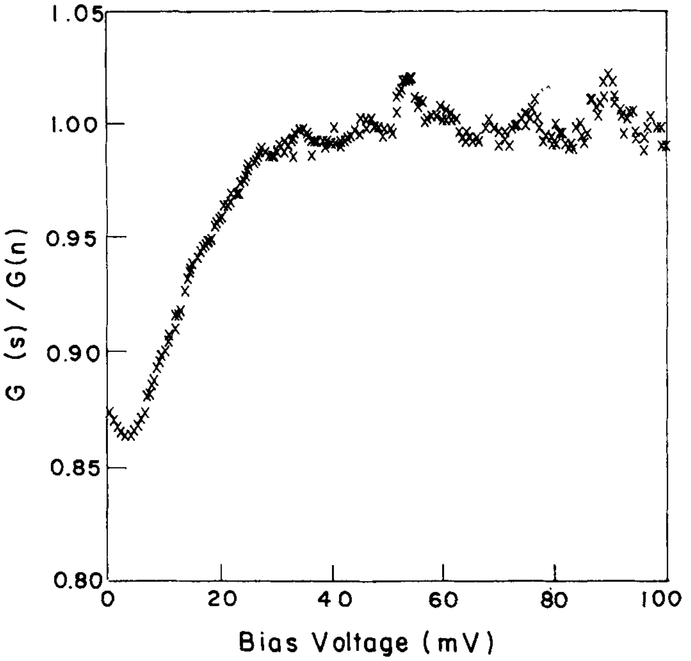

Figure 6. $G(s)/G(n)$ vs V plot for Nb–YBCO junction at 4·2 K. According to BCS theory this represents the tunnelling density of states.

Table 1. This table shows the superconducting gap (Δ) value elucidated from 3 different procedures for point contacts with 3 different tips.

Tips	$I^2 - V^2$	$(I - aV)^2 - V^2$	(G_S/G_N)
Nb	24 mV	23 mV	22 mV
Pt	19 mV	19 mV	20 mV
W	20 mV	20 mV	21 mV

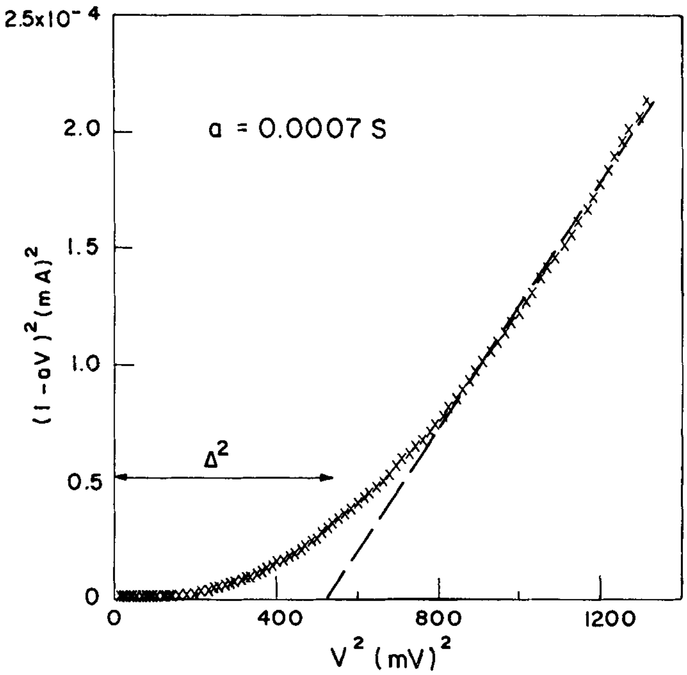

Figure 7. $(I - aV)^2 - V^2$ plot where "a" is the leakage conductance at zero bias. The junction is Nb–YBCO at 4·2 K. Gap value elucidated is 23 mV.

We would like to comment on the extra features sometimes observed at voltages other than 20 mV in the low resistance junctions. These can be particularly seen in figures 3(a) to 3(c). However, these features are not as reproducible as the feature at 20 mV. These types of multiple features in the tunnelling conductance curves have been observed before both in high T_c superconductors (Kirtley 1990) and in conventional superconductors (Wolf 1985). Various explanations have been suggested by different authors for these features. For structures occurring at voltages higher than the gap value some of the likely reasons are gap anisotropy, multiple sheets in the Fermi surface etc. For sub harmonic gap structures the likely causes are multiparticle tunnelling, microcontact, multiple Andreev reflection etc (Wolf 1985). However, there seems to be no universally accepted explanations for these extra features. It should be noted that these features are absent in high resistance junctions.

4.2 *Zero bias conductance*

A finite conductance at zero bias is present in all our tunnelling measurements. Ideally for a tunnel junction one expects the current to be zero at zero bias. The fact that it is not so raises the question of whether there is a non-vanishing density of states in the gap (Valles Jr. and Dynes 1990). Moreover in junctions of low resistance there is a peak in conductance at zero bias which rapidly falls with increasing bias till a bias of approximately 10 mV. This central peak has been observed before and is considered an anomaly and various interpretations have been given. Some of the suggested reasons are excess current due to Josephson-like weak links between grains in polycrystalline samples, microshorts formed due to pin-holes on the oxide, Andreev reflection and existence of local magnetic impurities. Our observations clearly show that at high junction resistance the central peak at zero bias disappears and good tunnelling behaviour is seen although with $G(V=0) \neq 0$. This occurs irrespective of the tip material. We believe that the low junction resistance $\mathrm{d}I/\mathrm{d}V - V$ curves can be modelled on the basis of a parallel combination of microshorts and tunnelling (Ya Divin and Nad 1979). This is shown in figure 8. For "metallic" contacts the conductance $G(V)$ decreases as V increases because of opening up of more inelastic scattering channels. The fact that zero bias peak disappears at high junction resistance is strongly in favour of this model. The observations that the central peak vanishes with (a) increasing magnetic field and (b) increasing temperature indicate that the superconductivity of YBCO has a role to play too. Continuous evolution from a microshort to a tunnelling regime by pulling the tip away is possible and we have observed this with Nb–Nb point contact junctions (Blonder *et al* 1982).

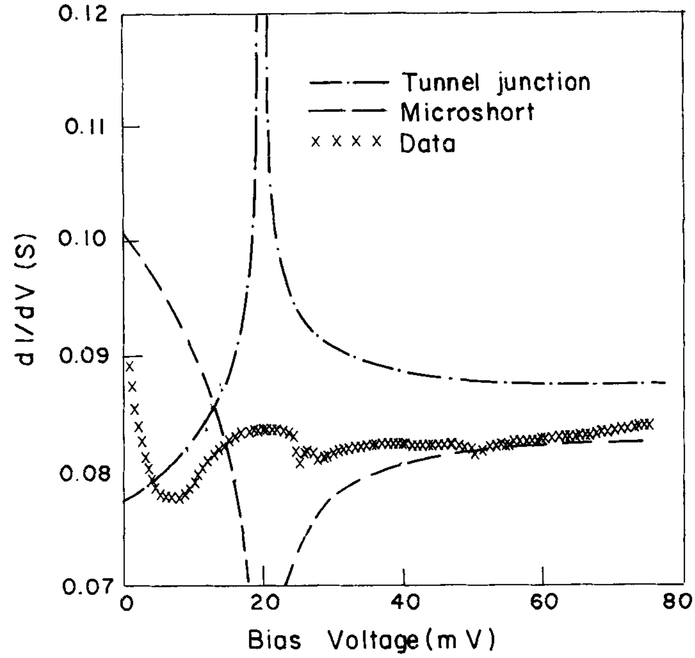

Figure 8. $\mathrm{d}I/\mathrm{d}V - V$ plot for Pt–YBCO junction at 4·2 K with ideal microshort and tunnelling behaviours superimposed on it. The junction can be thought of as a parallel combination of microshorts and tunnel junctions.

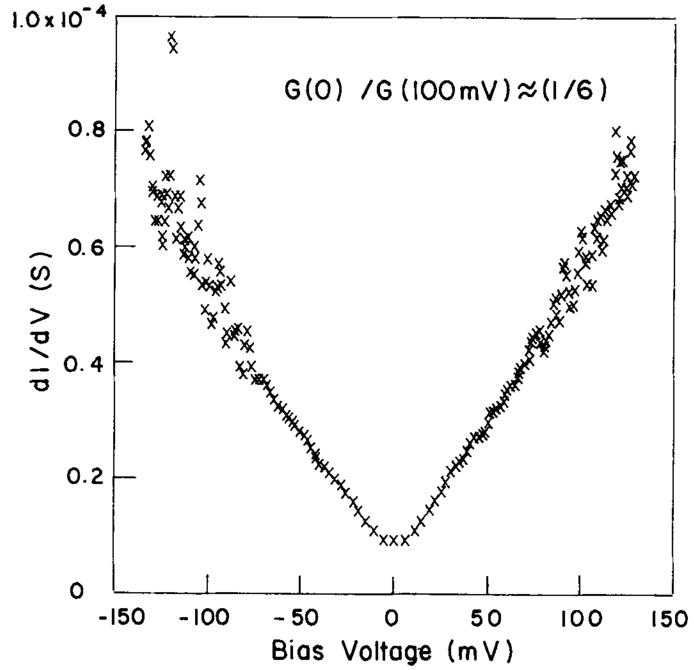

Figure 9. High resistance Nb–YBCO junction at 4·2 K showing $G(0)/G(100\,\mathrm{mV})$ value to be 1/6.

For high resistance junctions (of the order of a few kΩs) the peak at $V = 0$ vanishes but even then $G(V = 0) \neq 0$. Results from tunnelling in planar junction and thin film junction geometries indicate an appreciable zero bias conductance $G(V = 0)/G(V = 100\,\mathrm{mV}) = 1/2$ (Gurvitch *et al* 1989; Cucolo *et al* 1989). However with sharp metallic tips and at high junction resistance $G(V = 0)/G(V = 100\,\mathrm{mV})$ is comparatively much lower. We have observed with Nb–YBCO contacts of very high resistance, this conductance ratio can be as low as 1/6 (see figure 9). This may be the lowest value reported so far. We also find that $G(V = 0)/G(V = 100\,\mathrm{mV})$ decreases with increasing junction resistance irrespective of the tip material. The implication of this observation seems to be that we have pierced the native oxide layer while making first the low resistance contact and while going to a high resistance region by retracting the tip slowly we may have reached the vacuum tunnelling regime. If it is truly vacuum tunnelling, the tunnelling current should depend exponentially on the distance separating the tip and the sample (Binnig and Rohrer 1982). We are yet to verify this on 123 material at helium temperature. But from earlier room temperature studies done on STM one can show that when junction resistance > 100 kΩ one does see the current $I \propto e^{-\alpha d}$ where d is the distance between tip and the material (Shivashankar and Raychaudhuri 1990). We are currently conducting a detailed check to find out if the high junction resistance range is truly a vacuum tunnelling regime or not.

4.3 *Linear conductance background*

The tunnelling conductance has a parabolic dependence on voltage in M–I–M junctions (Wolf 1985). So in conventional M–I–S tunnel junctions a parabola is fitted

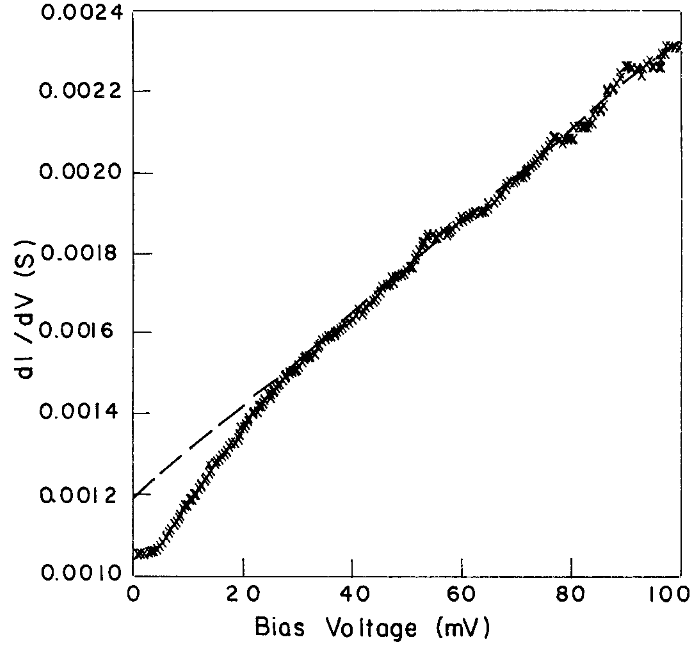

Figure 10. Straight line fitted to Nb–YBCO junction data at 4·2 K. Indicates clearly that the normal state conductance is linear.

to the conductance curve at $V \gg \Delta$ to get the normal state conductance. But in YBCO the background is clearly linear. This has been observed also with planar tunnel junctions. A straight line fitted to the $\mathrm{d}I/\mathrm{d}V - V$ curve for higher bias range and extrapolated to intercept the ordinate for zero bias is shown in figure 10. In fact in the $(\mathrm{d}I/\mathrm{d}V)_S/(\mathrm{d}I/\mathrm{d}V)_N$ plot shown earlier in figure 6 the normal state conductance $(\mathrm{d}I/\mathrm{d}V)_N$ is obtained by fitting a straight line. Since the ratio G_S/G_N reflects the density of states, in YBCO the linear conductance would suggest that the density of states is predominantly flat with a singularity near the Fermi level. Such a singularity has been observed due to electron–electron interaction in materials undergoing metal-insulator transition (Mcmillan and Mochel 1981; White *et al* 1985; Rajeev *et al* 1990).

4.4 *Asymmetry in tunnelling curves*

The point contact tunnelling conductance curves are asymmetric with respect to the polarity of the bias voltage. This asymmetry is more pronounced for low junction resistance contacts than for high junction resistance contacts. In tunnel junctions, asymmetry in conductance can be due to barrier shape being different from the ideal approximation of a rectangular barrier. Suggestions like a semiconducting oxide layer between tip and YBCO forming a Schottky barrier have been given to explain the asymmetry in $\mathrm{d}I/\mathrm{d}V - V$ curves (Kirk *et al* 1987). At this juncture we do not have any comments on the asymmetry.

5. Conclusion

We have made point contact tunnelling studies on polycrystalline YBCO high temperature oxide superconductors with normal (Pt, W) and superconducting (Nb) tips. We have carefully looked at the $I-V$ and $\mathrm{d}I/\mathrm{d}V-V$ characteristics for low and high junction resistances. Our observations and subsequent analysis sets the superconducting gap in YBCO around 20 mV. We find that the observed $G(V)$ vs V curves depend primarily on the junction resistance with very little qualitative difference between the tips. For low resistance junctions showing a central peak at zero bias ($|V| < 10\,\mathrm{mV}$) we tried to use a model of microshort and tunnel junction in parallel. This particular feature (peak at zero bias) vanishes for higher junction resistances ($> 1\,\mathrm{k}\Omega$) but $G(V=0)$ is not zero. It appears that $G(V=0)$ in high resistance junctions may be a function of junction resistance itself as we find that $G(V=0)/G(V=100\,\mathrm{mV})$ decreases with increasing junction resistance. We also find that the normal state conductance of these oxide materials is a linear function of voltage with a cusp expected at zero bias at very low T.

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