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LETTER TO THE EDITOR

Electron tunnelling spectroscopy of $YBa_2Cu_3O_{7-x}$ ceramics

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Abstract. Electron tunnelling measurements on $YBa_2Cu_3O_{7-x}$ superconducting ceramics are reported. A surface layer on the grains prevents observation of superconducting tunnelling characteristics with simple evaporated electrodes. However, point contacts between a variety of metal electrodes and the ceramic surface show a conductance characteristic with a broadened gap-like feature whose magnitude diminishes smoothly with temperature and disappears near the measured T_c of 91.7 K. The separation between conductance peaks varied between 28 and 65 mV over a sample of some 30 contacts, with a marked peak in the frequency distribution at 40 mV. The overall results are interpreted in a model where the spectra arise from proximity-induced superconductivity in a surface layer on underlying superconducting $YBa_2Cu_3O_{7-x}$ with a gap of $2\Delta \simeq 40$ mV, corresponding to $2\Delta/kT_c \simeq 5$. Peak separations larger than 40 meV are ascribed to the effects of finite inter-grain resistance.

There have been several recent reports of electron tunnelling measurements for the new high-temperature superconductors La–Sr–Cu–O and $YBa_2Cu_3O_{7-x}$, and features have been observed in the conductance spectra for both materials that have been associated with a superconducting gap. For the 123 material ($YBa_2Cu_3O_{7-x}$), which is the subject of this Letter, the measured gap energies vary over a wide range, from $2\Delta \simeq 23$ meV (van Bentum *et al* 1987) to values around 100 meV (Kirk *et al* 1987), with several other reported measurements between these extremes (for example, Crommie *et al* 1987, Moreland *et al* 1987, Kirtley *et al* 1987). These values have been obtained with a variety of junction types, including evaporated electrodes, STM-type point contact probes and 123–123 break junctions, but even when the same technique is used, widely varying gap values have been reported. For example, using STM methods, Kirk *et al* (1987) obtain $2\Delta \simeq 100$ meV from ceramic samples whilst Kirtley *et al* (1987) obtain $2\Delta \simeq 36$ meV from single crystals. Clearly there is a need for additional experimental data before any consensus on the interpretation of tunnelling experiments on $YBa_2Cu_3O_{7-x}$ will emerge.

In this Letter, we describe tunnelling measurements on ceramic discs of 123 material using evaporated and simple point-contact electrodes, and we report the temperature dependence of the spectra we observe. Our results enable us to put forward an explanation for the variety of behaviour reported in the literature.

Ceramic discs of 123 material with a grain size of 5–20 μm were prepared using the well known solid state reaction process. The DC resistance–temperature characteristics

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of the samples were recorded using a four-terminal configuration with silver paint electrodes. From room temperature downwards, a linearly decreasing resistivity was observed, with a sharp transition to the superconducting state centred at 91.7 (±0.2) K for a 50% resistance drop, with a 10–90% width of 1.7 K. To within the noise level of the measuring equipment, the fully superconducting state was achieved at 89.0 K.

Evaporated metal electrodes of lead or indium were deposited on both as-prepared and ground surfaces of 123 discs using conventional vacuum-deposition apparatus. The conductance–voltage characteristics were determined at 4.2 K in a four-terminal configuration, using two silver paint contacts to the back surface of the 123 discs. In all cases, the conductance spectra comprised a broad conductance minimum on which several sharp features were usually superposed. For both indium and lead, most of these features took the form of narrow dips in conductance at bias voltages that were approximately symmetrically disposed about zero. The positions of these peaks varied from sample to sample and also varied for a single sample with thermal cycling. With increasing temperature, they showed a general tendency to collapse towards zero bias as T_c was approached. We interpret them as critical current transitions at the interfaces of small 123 particles in the bulk which constitute part of the overall conduction path. Peaked structures have also been observed in resistance spectra by Iguchi *et al* (1987) for evaporated Pb–123 junctions, but they interpret the dips between what appear to be successive resistance peaks as conductance peaks and attribute them to harmonically related 123 gaps based on a $2\Delta \simeq 42$ meV fundamental.

In some of our samples with evaporated lead electrodes, a pronounced BCS-like dip occurred near zero bias. The width and temperature dependence of the latter feature was measured carefully and the assignment to the superconducting gap of lead confirmed. In one sample the zero-bias to above-gap resistance ratio at 4.2 K was greater than 4:1, implying that most of the current was due to tunnelling from the lead rather than to some other conduction mechanism. We observed no features in these spectra that can clearly be associated with the superconducting state of the 123 material. Since true tunnelling is being observed, we conclude that the surface of the 123 material is different from the underlying bulk. We have attempted to remove or modify the surface layer by argon-ion-beam milling and plasma anodisation respectively. However, the original black surface became powdery and took on a ferrite-brown coloration, implying a further surface modification rather than the desired result.

Since this non-superconducting surface layer appears to thwart tunnelling measurements on superconducting 123 using evaporated electrodes, we have attempted to expose fresh material by grinding the surface of a 123 disc whilst holding it under liquid helium and subsequently making contact through point contact electrodes. In initial experiments, the abrasive was a second piece of 123 material, but similar results were later obtained using a cleaned steel drill bit. The 123 material was quite weak mechanically and grains were easily broken away from the surface using this procedure. The surface was cleaned of loose material by swirling in liquid helium followed by light pressure from a lead probe which embedded any remaining loose grains. The probes used for tunnelling included aluminium, lead, indium, tungsten and niobium, all in the form of mechanically sharpened wires. In the case of aluminium both thermally oxidised and anodised probes were used. The finest wire used was 90 μm diameter aluminium, with an estimated tip radius of curvature of no less than 10 μm. However, similar results were obtained with much coarser tips.

The measured conductance spectra depended upon the initial pressure applied to the contact. With light pressure, high-resistance junctions were obtained whose conductance resembled the shape of an asymmetric, rounded V centred on zero bias, without any evidence for a superconducting gap. This suggests that a surface layer is still present on the crystallite surfaces that were originally internal to the porous 123 disc but that were exposed by the grinding. However, when sufficient pressure was applied to give junction resistances of between 20 and 100 Ω, a broadened superconducting gap characteristic superposed on the background was observed. In this case, the surface layer and any existing oxide layer on the metal probe are presumably being deformed mechanically and the metal brought into closer contact with the superconducting 123 material.

Figure 1 shows the clearest such spectra, obtained with an aluminium electrode at different places on a freshly prepared and abraded disc of 123 material. The conductance calculated for a BCS density of states with similar gap is also shown. By comparison, the gap-like feature we observe is considerably broadened and superimposed on a dominant background conductivity. The change in conductance between the peak and trough of the observed gap feature is about 30% of the background for spectrum (*a*) which is considerably larger than the ~1% features reported in a recent paper (Crommie *et al* 1987). Similar but less pronounced gap-like spectra were obtained in a large number of measurements with aluminium and all the other probe types, and from material whose surface had not previously been ground. However, the shape of the spectra and the width between the conductance peaks varied from one contact to another. Selecting those recordings where the change in conductance was sufficiently large for the peak positions to be clearly defined, we obtain the histogram for the observed peak separations shown in figure 2. Earlier work has generally reported only the largest of measured separations.

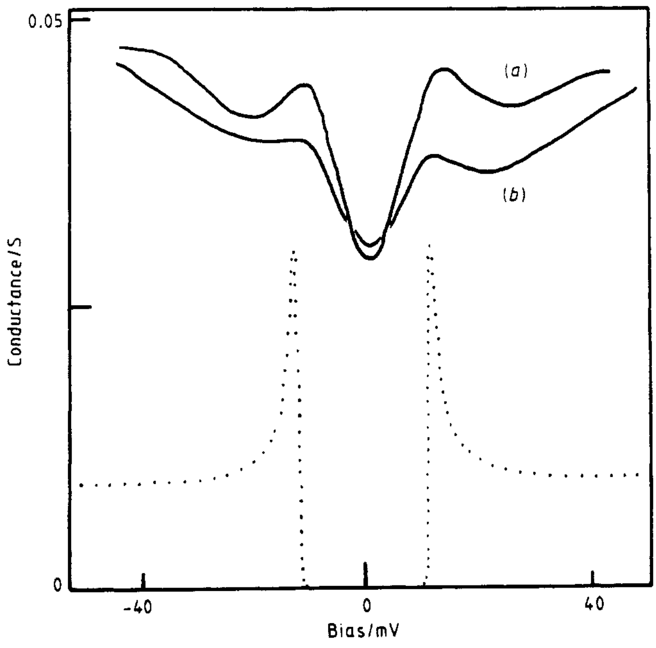

Figure 1. Conductance spectra recorded near 4.2 K for two Al–$YBa_2Cu_3O_{7-x}$ point contact junctions. The dotted curve shows the conductance for a BCS density of states with a similar gap for $T/T_c = 0.05$.

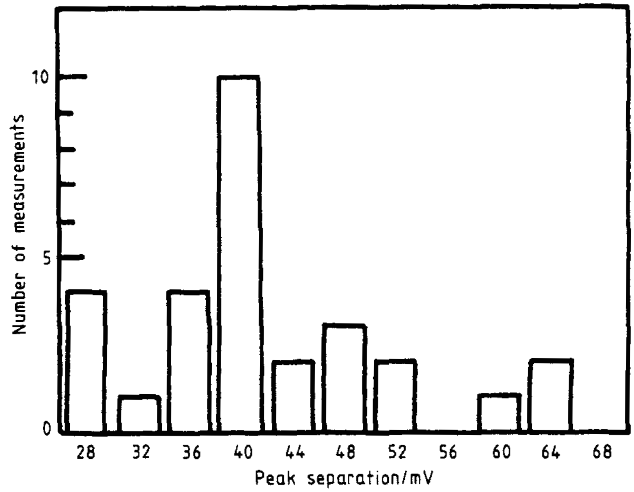

Figure 2. A histogram giving the number of measurements of peak separations lying within each 4 mV range for a total of 29 contacts where the conductance peaks could be clearly resolved.

The distribution of peak separations and the shape of the conductance curves clearly show that a simple BCS interpretation is not possible. Indeed, association of this gap-like feature with 123 superconductivity has been implicitly assumed here and in previous work, but other interpretations are possible; for example, the superposition of two zero-bias anomalies of opposite sense and different widths. To check this association, we have

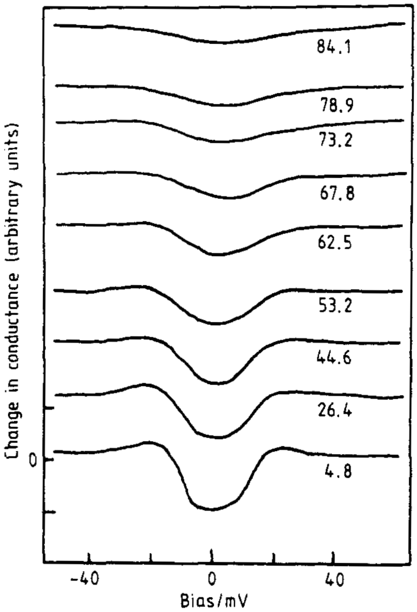

Figure 3. The difference of conductance data and polynomial fitted curves for various temperatures given on curves (in K). The origin for each curve other than the lowest has been displaced for clarity.

examined the temperature dependence of the spectra. This experiment was difficult with our simple experimental arrangement because of thermally induced mechanical instabilities, as manifested by abrupt jumps in the conductance. However, one set of spectra was successfully recorded up to temperatures just below T_c from a contact that showed a low-temperature peak separation of 42 mV. The problem of subtracting the dominant background to obtain the superconducting component is not trivial since the background curvature must be pronounced near zero bias and any interpolation from the above-gap regions is likely to be unreliable. In an attempt to extract the feature of interest from the background, we have used two procedures.

(i) We have fitted a fifth-order polynomial to each complete data set in the voltage range ±150 mV. This follows closely the spectra outside the central region but cannot follow the central gap-like feature. The polynomial therefore provides a satisfactory background that can be subtracted from the data to reveal the shape of the central feature. The results are shown in figure 3.

(ii) In recognition of the near-linear form of the conductance beyond the gap region, we fitted the even part of the conductance with a quadratic. The two forms chosen for the fitted curve differ markedly in their curvature near zero bias, and in a sense represent extreme choices.

Defining the amplitude of the spectra as the difference between extreme values of conductivity obtained after background subtraction, we plot in figure 4 the amplitude as a function of temperature. Clearly the amplitude estimated using either fitting procedure vanishes close to the measured transition temperature of 91.7 K, and so we may confidently associate the gap-like structure with the 123 superconductivity.

Our overall interpretation of the results, of which the key features are (i) the distribution of peak separations, (ii) the presence of background conduction, and (iii) a broadened structure as compared with a BCS density of states, is as follows.

The grains and crystallites of which the 123 ceramic consists all have a semiconducting

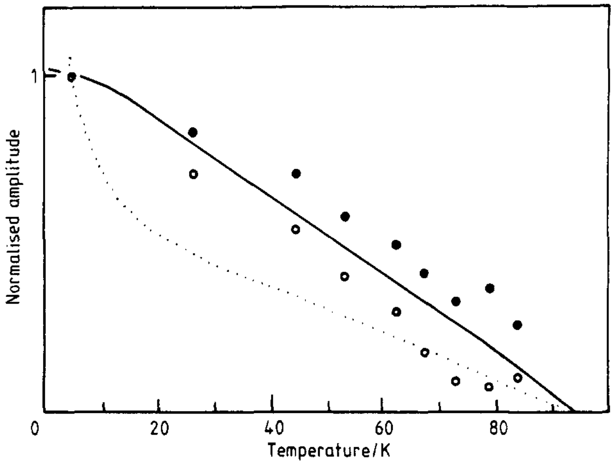

Figure 4. Amplitudes of the difference spectra derived from a fifth-order polynomial fit to the conductance (full circles), and from fitting the even part of the observed conductance with a quadratic (open circles), as functions of temperature. The dotted curve gives the BCS prediction, whilst the full curve is based on a broadened density of states (see the text). All the curves are normalised to their values at 4.8 K.

or semimetallic surface layer that forms Schottky tunnelling barriers with evaporated or impressed metal electrodes. Superconductivity is induced into the surface layer from the underlying superconducting 123 material by the proximity effect (Wolf 1985). When superconducting features are observed in the characteristics they correspond to penetration of the superconductivity to the edge of the tunnelling barrier. With evaporated electrodes, the surface layer is so thick that deviations from normal-state tunnelling are negligible and no gap-like structure is observed. With point contacts, however, the surface layer is plastically deformed and thinned by the pressure of the contacting electrode, so superconductivity penetrates to the tunnelling barrier and is observed in the tunnelling characteristic. It is immediately obvious that the mechanism by which coupling to the underlying superconducting material is achieved explains the variability of both the strength and the energy scale of superconducting features observed in tunnelling spectra. It also explains the smoothing of the gap structure as compared with a BCS density of states since there will be a distribution of surface layer thicknesses over the contacting area of any one tunnelling contact so that the conductance characteristic consists of a sum of contributions with gap structures differently attenuated by the varying proximity effect. Only when conduction is dominated by strongly thinned layers will the observed peak separation correspond to the true energy gap of the underlying material. Similarly, most contacts will involve significant contributions from areas where the surface layer is not thinned and these will contribute to what appears in the characteristics as the smooth background conductivity.

On the basis of this explanation of the observed behaviour, we associate the maximum at about 40 mV in the distribution of observed peak separations in figure 2 with the true energy gap of the superconducting 123 material. Lower values of peak separation, down to 28 mV found here and the 23 mV reported by van Bentum *et al* (1987), are due to thicker surface layers, and the broadening to a distribution of surface thicknesses over each contact area. The larger values of peak separation that are sometimes observed here, and by others, we attribute to the effects of finite inter-grain resistance in the bulk. If such resistive links occur in the current percolation path away from the tunnelling region, then the potential drop across them will be added to the potential across the tunnelling barrier and features will be displaced to higher voltages. This explanation is supported by our observation that the separation of the conductivity peaks corresponding to the superconductivity of lead electrodes at 4.2 K can become as large as 10 mV for some contacts, demonstrating clearly that large potential drops are occurring away from the tunnelling region.

Our association of the peak in the histogram distribution at 40 mV with the gap energy is based on the qualitative argument that the subset of contacts with no inter-grain resistance broadening will give rise to an abrupt drop in the distribution above the gap energy. The only evidence for such a feature in figure 2 is the sharp fall between 40 and 44 mV. A true energy gap of approximately 40 meV is also supported by the observation of a maximum peak separation of 39 mV by Kirtley *et al* (1987) for single crystals, where the effects of inter-grain resistance are presumably absent.

In figure 4 we compare the temperature dependence of the strength of the superconducting gap structure in our results with predictions (i) for a BCS density of states and (ii) for a broadened density of states whose energy scale follows the BCS temperature dependence. The broadened density of states used is the *observed* gap structure in the low-temperature limit where thermal broadening is negligible. We find much better agreement with the temperature variation of the broadened structure. The temperature dependence is thus consistent with our model. It does not, of course, prove that it is the correct explanation of the low-temperature broadening. Other possible mechanisms would include lifetime and anisotropy broadening, but these could not easily account for the observed distribution of peak separations.

Unfortunately, the temperature dependence of the energy separation of the peaks in figure 3 cannot be followed beyond $T/T_c \simeq 0.6$ because the structure becomes too weak and the peaks are not sufficiently defined. Below $T/T_c \simeq 0.6$ the peak separation increases gradually with temperature, as would be expected on our model. It is only at higher temperatures that the collapse of the gap would be observed.

Our explanation for the tunnelling results depends on the presence of surface layers on the grains of the 123 material. Other experiments have implied the presence of such layers. Critical currents deduced from magnetisation measurements are very much greater than can be supported by the bulk material and electron microscope studies show evidence for up to 40% of the grain boundaries having a composition and structure different from the bulk (Camps *et al* 1987). Also, the microwave impedance measurements of Cohen *et al* (1987) show considerable inter-grain resistance in the bulk.

In conclusion, we have observed gap-like characteristics in the tunnelling spectra of tunnel junctions between various metals and $YBa_2Cu_3O_{7-x}$ from which we estimate an intrinsic energy gap of $2\Delta \simeq 40$ meV corresponding to $2\Delta/kT_c \simeq 5$, compared with a BCS value of 3.53. Our results indicate the presence of non-superconducting surface layers on all grains of the material whether they be on the surface or internal to a bulk sample. There is also evidence for inter-grain resistance in the bulk. Our results emphasise the need for a detailed study of the grain surfaces, and the desirability of working with single crystals to isolate grain boundary problems.

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