APPENDIX B

LOW-T_c OXIDE SUPERCONDUCTORS

B.1 Bismuthate Superconductors

Prior to 1986 the highest known transition temperature in an oxide superconductor was 13 K in $BaPb_{1-x}Bi_xO_3$ with $x = 0.75$. The discovery of high-temperature superconductivity in the cuprates stimulated further investigation of bismuthate materials culminating in the discovery (in 1988) of $T_c \approx 30$ K in $Ba_{1-x}K_xBiO_3$ with $x \approx 0.4$.

The 'parent' compounds of both the cuprate and bismuthate superconductors (e.g., $BaBiO_3$) have half-filled bands so would be metallic according to simple band theory; however, these are energetically unstable so a phase transition to an insulating state occurs (Hinks 1990). In the cuprates this is an antiferromagnetic ordering; however, the bismuthates are non-magnetic and the change is structural. As doping of the parent compounds is increased they remain insulating until at a critical level there is a transition to a superconducting metallic state. In the bismuthates the highest transition temperature occurs at this point and further doping reduces T_c.

Bismuthate superconductors lack the CuO_2 layers that are widely believed to play a role in the origin of high-T_c superconductivity. In addition, they are three-dimensional in comparison with the quasi-2D cuprates, having a cubic crystal structure and more isotropic properties. Being chemically simpler than the cuprates, sample preparation has improved more rapidly and pure materials are now available even in ceramic form - resulting in elimination of extrinsic effects that led to anomalous results from early experiments. This is particularly true of tunnelling, where the much larger coherence length (≈ 4 nm) also reduces sensitivity to sample inhomogeneity and surface layers.

Early tunnelling results on bismuthate superconductors were similar to those still observed in the cuprates, with excessive broadening, a wide range of voltage-dependent backgrounds and scattered energy gap values. Zasadzinski *et al.* (1989) prepared planar junctions by evaporating indium onto ceramic $Ba_{1-x}K_xBiO_3$, with the tunnelling barrier provided by an intrinsic surface layer. The conductance–voltage characteristics were much broader than the BCS result and had a large zero-bias conductance of 50% of the above the gap value. Dyne's lifetime-broadening model with $\Delta = 7.0$ meV and $\Gamma = 5.0$ meV was used to explain these features.

The same sample was later investigated using a gold point contact (Huang *et al.* 1990*b*), yielding normalised conductance–voltage characteristics in perfect agreement with a thermally smeared BCS result. No additional broadening was necessary and there was no leakage current in the gap region. A large variation in energy gap measured at different points on the sample's surface (3.6–4.6 mV) and a broadened superconducting transition (28.5–27.5 K) were attributed to inhomogeneity in potassium doping within the sample. Evidently, the point contact was able to tunnel into individual grains whilst the planar junction could only measure averaged properties. Similar results have been obtained by several other groups, e.g., Valles and Dynes (1990).

Sample quality has improved still further. Hou *et al*. (1992) recently fabricated large-area planar SIN junctions on thin films of $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}Rb_xBiO_3$. Their narrow superconducting transition widths and near-ideal BCS-like tunnelling characteristics (with $2\Delta/k_BT_c = 3.5 \pm 0.2$) indicate a very homogeneous material.

Attempts have been made to invert the tunnelling data from $Ba_{1-x}K_xBiO_3$ to obtain the effective phonon spectrum, $\alpha^2F(\omega)$. Huang *et al*. (1990*c*) claim that structure in their tunnelling spectrum correlates with the phonon spectrum determined by inelastic neutron scattering. Moreover, the transition temperature calculated from α^2F (24.5 K) was in good agreement with the measured T_c (20 K). To obtain this agreement however, it was necessary to use a modified McMillan–Rowell procedure that includes the effect of a thin surface proximity layer. The electron–phonon coupling strength ($\lambda = 1.2 \pm 0.3$) and reduced gap value ($2\Delta/k_BT_c \approx 3.6$–$4.3$) determined by this analysis are consistent with trends found in conventional superconductors and suggest that superconductivity in these materials may be explained by a conventional phonon-mediated pairing interaction. Hinks (1990) draws the same conclusion in his review of the properties of $Ba_{1-x}K_xBiO_3$. Although λ is low, indicating that $Ba_{1-x}K_xBiO_3$ is weakly coupled, electrons appear to be coupled to high-energy phonons, resulting in a large average frequency of about 40 meV and a high T_c. Although the tunnelling-inversion results from $Ba_{1-x}K_xBiO_3$ are more reproducible than those of the cuprates, some experimenters remain unconvinced that the bismuthates are conventional, phonon-coupled BCS superconductors (Dynes *et al*. 1991).

One anomalous feature that persists even in 'ideal' bismuthate tunnelling characteristics is a V-shaped conductance background - identical to that seen with the cuprates. The presence of this phenomenon in the non-magnetic and cubic bismuthates casts doubt on explanations invoking spin fluctuations (section 4.2.3) or reduced dimensionality, unless one is prepared to ignore Occam's razor. Because high-quality tunnel junctions can be prepared on bismuthate materials with a wide range of transition temperatures (1 K–30 K), Sharifi *et al*. (1991) used them to investigate the T_c dependence of the linear conductance.

Firstly, using $Ba_{1-x}K_xBiO_3$ junctions with fixed area and T_c but with barriers prepared under different conditions[*], they found that the linear conductance slope was proportional to the zero-bias conductance. This indicates that

$$G(V) = G(0)(1 + kV)$$

where $G(V)$ is the dynamic conductance, $\mathrm{d}I/\mathrm{d}V$, and k is a constant. Secondly, using junctions made from different bismuthate superconductors, with transition temperatures ranging from 1 K to 30 K, they observed a remarkable linear correlation between the slope of $G(V)/G(0)$ and T_c, i.e.,

$$\frac{1}{G(0)}\left(\frac{\mathrm{d}G(V)}{\mathrm{d}V}\right)_{V>0} = k \propto T_c$$

They also noted a consistent asymmetry in the conductance slope of all the junctions studied, i.e.,

$$\left|\frac{\mathrm{d}G(V)}{\mathrm{d}V}\right|_{V>0} \approx \frac{1}{2}\left|\frac{\mathrm{d}G(V)}{\mathrm{d}V}\right|_{V<0}$$

These results have been spelt out here because this T_c dependence has been misinterpreted by some authors (see sections 4.2.5 and 4.8).

B.2 $Nd_{2-x}Ce_xCuO_{4-y}$

This is a relatively low-T_c cuprate with a maximum value of 25 K when $x \approx 0.15$ and $y \approx 0.02$. $Nd_{2-x}Ce_xCuO_{4-y}$ is discussed in this appendix because, as with $Ba_{1-x}K_xBiO_3$, high-quality BCS-like tunnelling characteristics have been obtained and inversion has yielded an effective phonon spectrum in reasonable agreement with neutron-scattering data (Zasadzinski *et al*. 1992). Reduced gap values estimated from the tunnelling data are lower than in other cuprates and similar to the BCS weak-coupled value (e.g., $2\Delta/k_BT_c \approx 3.9$, Huang *et al*. 1990*c*).

Although this material does contain CuO_2 layers, several properties distinguish it from other cuprates. Most importantly the antiferromagnetic insulating parent compound, $Nd_{2-x}CuO_{4-y}$ is *electron* doped by Ce substitution. Secondly, although the coherence lengths are small ($\xi_c \approx 1.5$ nm, $\xi_{ab} \approx 7$ nm) they are larger than in other cuprates - possibly explaining the superior tunnelling results. Other differences are discussed in the review by Maple (1990).

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[*] By ion-milling damage to the film's surface. Junction resistance could be controlled by changing the beam voltage, current and milling time.