CHAPTER 1

INTRODUCTION

1.1 High-Temperature Superconductors

In 1986 a revolution occurred in the field of superconductivity. After a three-year search for high-temperature superconductivity in oxide materials, J.Georg Bednorz and K.Alex Müller were rewarded with the discovery of a complex Ba-doped La–Cu oxide that had a transition temperature (T_c) of 30 K[*]. C.W.Chu replaced La with Y and produced a material with a staggering critical temperature of 92 K - overturning a widely held belief, substantiated by theoretical arguments, that the previous highest T_c of 23.2 K was close to a physical upper bound. There followed an explosion of interest in high-temperature superconductivity with huge world-wide effort directed towards raising T_c still further and understanding the properties of these materials.

The many high-temperature superconductors that are now known (table 1.1) have a common basic structure consisting of stacked layers of square-planar CuO_2[†]. These are partitioned into groups of *n* closely spaced planes with larger distances between groups. CuO_2 planes within a group are separated by a sparsely occupied layer of metal atoms whilst the inter-group space is occupied by denser oxide 'isolation layers' (figure 1.1). This highly anisotropic structure is reflected in anisotropy of many physical properties - suggesting a quasi-two-dimensional character in which the charge carriers and superconductivity are confined to the CuO_2 planes.

A second common property is that superconductivity occurs in the cuprate materials close to a metal–insulator transition, with the Cu ion magnetic moments antiferromagnetically ordered in the insulating phase. The superconducting metallic phase is obtained by doping the insulator with excess charge, for example by adding oxygen to $YBa_2Cu_3O_6$, or by replacing La^{3+} with Sr^{2+} in $La_{2-x}Sr_xCuO_{4-y}$.

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[*] The full story was told in the 1987 Nobel prize in Physics award speech, see Bednorz and Müller (1988) for a transcript.

[†] In this dissertation the classification 'high-temperature superconductor' refers only to the layered cuprate materials. In particular, it does not include the bismuthate or buckminsterfullerene superconductors (e.g., $Ba_{1-x}K_xBiO_3$ with $T_c \approx 30$ or $Rb_{2.7}Tl_{2.2}C_{60}$ with $T_c = 42.5$ K). 'Conventional superconductors' include the elemental and metal-alloy superconductors.

Material	T_c / K	n	Notation
$La_{2-x}Sr_xCuO_4$	38	1	LSCO or 214
$La_{2-x}Sr_xCaCu_2O_6$	60	2	
$Nd_{2-x}Ce_xCuO_4$	30	1	NCCO
$YBa_2Cu_3O_7$	92	2	YBCO or 123
$YBa_2Cu_4O_8$	80	2	124
$Y_2Ba_4Cu_7O_{14}$	40	2	247
$Bi_2Sr_2CuO_6$	0–20	1	Bi-2201
$Bi_2Sr_2CaCu_2O_8$	85	2	BSCCO or Bi-2212
$Bi_2Sr_2Ca_2Cu_3O_{10}$	110	3	Bi-2223
$TlBa_2CuO_5$	0–50	1	Tl-1201
$TlBa_2CaCu_2O_7$	80	2	Tl-1212
$TlBa_2Ca_2Cu_3O_9$	110	3	Tl-1223
$TlBa_2Ca_3Cu_4O_{11}$	122	4	Tl-1234
$Tl_2Ba_2CuO_6$	0–80	1	Tl-2201
$Tl_2Ba_2CaCu_2O_8$	108	2	Tl-2212
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125	3	Tl-2223
$HgBa_2CuO_5$	94	1	Hg-1201 †
$HgBa_2CaCu_2O_7$	112 ?	2	Hg-1212 †
$HgBa_2Ca_2Cu_3O_9$	133.5	3	Hg-1223 †
$Sr_{1-y}Nd_yCuO$	40	∞	all-layer phase ‡

Table 1.1. Transition temperatures of the principal high-T_c superconductors. Note that T_c generally increases with n. Also shown are commonly used names for these materials. Where T_c depends on stoichiometry, higher values are shown. After Burns (1992) except † (Edwards 1993) and ‡ (Cava 1991).

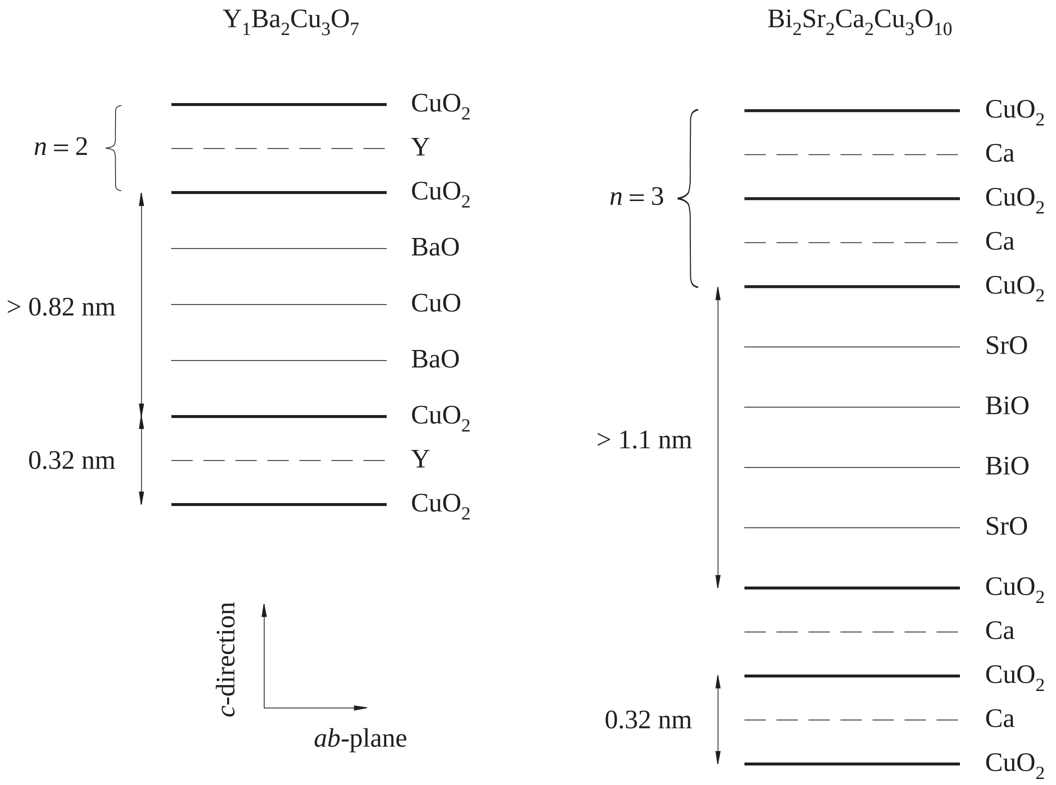

Fig. 1.1. Schematic illustration of the layered structure of high-T_c superconductors.

The existence of very high transition temperatures immediately oppugned the well established BCS theory of superconductivity with phonon-mediated electron pairing. To account for the observed high T_c values BCS-like theories with higher-energy bosonic interactions (e.g., magnons) were proposed or brought out of mothballs. Other more exotic theories also flourished amidst the excitement and lack of clear guidance from experimental data; it was often said that there were ‘as many theories as theorists’. This chaotic situation highlights the importance of experimental results that are able to place constraints on possible theories (Little 1988). An important class of such experiments are those that measure the *energy gap*, Δ, in the excitation spectrum of a new superconductor. The most sensitive (and historically the most important) method for measuring this gap is by electron tunnelling.

1.2 Electron Tunnelling

Tunnelling is a phenomenon of quantum mechanics whereby an electron, as a consequence of its wave-like character, may pass from one conducting electrode to another through a thin ($\lesssim 1$ nm) intervening potential barrier that would confine a classical particle. An artificial structure in which the conductance is predominantly due to tunnelling electrons is called a ‘tunnel junction’. The voltage applied to a junction determines the range of energies of tunnelling electrons whilst the current depends on properties of the barrier and electrode materials. This forms the basis of a simple but powerful energy spectroscopy, with high resolution of order $k_B T$, which is only 0.36 meV at the temperature of liquid helium. In particular, when one of the electrodes is superconducting the tunnelling electrons probe important low-lying excitations and the dynamic conductance is proportional to the density of excitation states.

The importance of electron tunnelling as a tool for investigating the origin of superconductivity in conventional metals and alloys may be illustrated by reference to its role in the progress of BCS theory. Tunnelling was first used to investigate the superconducting state in the early 1960s. These experiments demonstrated in a very direct way the existence of an energy gap and verified detailed predictions of the 1957 BCS theory of superconductivity. Many materials were found to have a *gap ratio*, $2\Delta/k_B T_c$, in agreement with the BCS value of 3.52. Further work, however, revealed anomalous behaviour in Pb and Hg, manifested as a larger gap ratio (≈ 4.6) and structure in the tunnelling conductance ‘above the gap’ (i.e., at energies in the range 4–8Δ). It was soon realised that these deviations occurred at phonon energies, supporting the idea of a phonon-mediated pairing interaction, and a modified BCS theory was developed that took into account the effects of strong electron–phonon coupling.

With this distinguished record it was hoped that electron tunnelling would prove equally successful in revealing the mechanism of high-T_c superconductivity. However, formidable problems due to the short coherence length in these materials and their propensity to form a non-conducting surface layer have hindered progress. The tunnelling characteristics of cuprate superconductors contain many non-ideal features when compared with conventional superconductor tunnel junctions (e.g., voltage-dependent background, broadening, ‘multiple’ energy gaps). Most of these have been observed (to a lesser degree) with conventional materials and have usually been explained as extrinsic effects. Their presence complicates estimation of the energy gap and precludes measurement of more subtle properties such as gap anisotropy or the effective phonon spectrum, $\alpha^2 F$. Despite an enormous amount of experimental work over the last six years the interpretation of tunnelling results and the mechanism of high-T_c superconductivity remain controversial.