CHAPTER 14

HIGH-TEMPERATURE SUPERCONDUCTORS

IN 1987 it was discovered that some metal oxide ceramics which are semiconductors at room temperature become superconducting at a relatively high temperature, around 100°K. Though the transition temperature of these ceramics is nearly 200°K below room temperature they have become known as 'high-temperature' superconductors because their transition temperatures are much higher than the 'traditional' metallic superconductors with critical temperatures of 23°K or less.

Examples of such high temperature superconducting ceramics are: $YBa_2Cu_3O_7$ (often called 'YBCO') with $T_c = 93°K$, $Bi_2(Sr_2Ca)Cu_2O_8$ (often called 'BSCCO') with $T_c = 110°K$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (which has the highest transition temperature, 125°K). To show superconductivity the oxygen content of these ceramics must be slightly less than 7, 8 or 10 respectively (i.e. there must be a small oxygen deficiency). These superconducting ceramics are of extreme interest, both from a scientific point of view because there is as yet no acceptable explanation of how superconductivity can occur at such high temperatures, and from a practical point of view because these temperatures can be achieved without difficulty by the use of easily-available liquid nitrogen. At the present time (1993), however, our understanding of the superconductivity of these materials has been hindered because it has not been possible to produce reasonably large single crystals which have superconducting properties. The fact that the individual crystallites in a polycrystalline sample have extremely anisotropic superconducting properties adds to the difficulty in understanding them.

The high-temperature superconducting ceramics have a layered crystal structure. In general there are several neighbouring layers of copper oxide separated from the next group of copper oxide layers by several layers of other metal oxides ('isolation planes', see Fig. 14.1). The electrical conductivity and superconductivity are associated with the copper oxide planes. For a given basic compound, the higher the number of

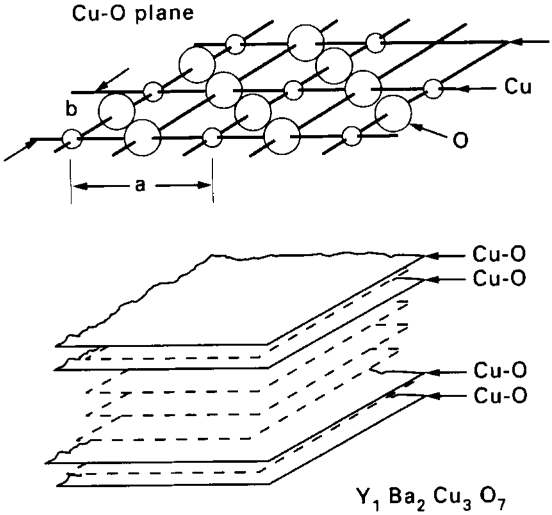

FIG. 14.1. Structure of typical high-temperature superconducting ceramic.

neighbouring copper oxide planes (up to a maximum of 3 or 4), the higher is the transition temperature.

The association of the superconductivity with the copper oxide planes is illustrated by the fact that the superconducting properties are little altered by changing the composition of the intermediate planes. For example, if in $YBa_2Cu_3O_7$ the yttrium, which lies between the copper oxide planes, is replaced by another rare earth the properties are scarcely affected. In particular, if the yttrium, which has no magnetic moment, is replaced by gadolinium, which has a large magnetic moment, the transition temperature is scarcely altered, although the introduction of magnetic atoms into a superconductor normally causes a dramatic decrease in the transition temperature (see § 9.3.8).

As would be expected from their high transition temperature, these ceramic superconductors have a very short coherence range, only a few atomic spacings long, and a very deep penetration depth. They are, consequently, extreme examples of type-II superconductors. Furthermore, because the atoms are arranged in parallel planes, their superconducting (and normal state) properties are very anisotropic, the superconducting properties being stronger in directions parallel to the atomic planes ('*ab*-planes') than in the perpendicular direction (the *c*-axis). For example, it seems that the coherence range parallel to the *c*-axis is about 0·2 nm but parallel to the *ab*-planes it is about 1·5 nm. As a result the Ginzburg–Landau constant, κ, is highly anisotropic varying in magnitude from a few tens parallel to the *c*-axis to a few hundred parallel to the atomic planes. Properties such as critical magnetic fields and critical currents can be an order of the magnitude greater when measured parallel to the atomic planes than in the perpendicular direction.

The upper critical magnetic field, H_{c2}, can be extremely high, as we would expect from the high value of κ. Just below the transition temperature the rate at which H_{c2} increases with decreasing temperature is about 10^7 A m^{-1} per degree when the field is applied parallel to the atomic planes, though considerably less when it is parallel to the perpendicular direction. This leads us to expect very high values of the upper critical field, H_{c2}, at low temperatures. For $YBa_2Cu_3O_7$, the upper critical field at liquid helium temperature (4·2°K) is estimated to be about 5×10^8 A m^{-1} when the magnetic field is applied parallel to the copper oxide planes and about 1×10^8 A m^{-1} when the field is in the perpendicular direction. These magnetic field strengths are too high to be achievable with existing magnets but pulsed magnetic field experiments have shown that H_{c2} is indeed greater than 8×10^7 A m^{-1}.

Apart from any scientific interest, the value of the critical current of superconductors is important for practical applications. At low, liquid helium, temperature the critical current density of superconducting ceramic is less than that of the best conventional superconductors if any applied magnetic field is weak. However, the resistanceless current-carrying capacity of the ceramics scarcely decreases when the magnetic field strength is increased, so that in high magnetic fields their critical current is much greater than that of conventional superconductors (Fig. 14.2).

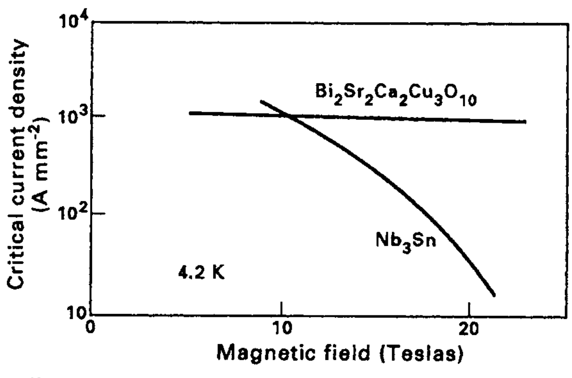

FIG. 14.2. Effect, at low temperature, of magnetic field on critical current of superconducting ceramic ($Bi_2Sr_2Ca_2Cu_3O_{10}$) compared with best 'conventional' superconductor (Nb_3Sn) (after Sato *et al.*).

At 'high' temperatures (i.e. at about 77°K, the temperature of liquid nitrogen, where conventional superconductors are not superconducting) the ceramic superconductors have disappointingly low critical currents. There appear to be several reasons for this: in the bulk material composed of many crystallites the current must cross many boundaries between the crystallites and each of these acts as a weak link; furthermore in some crystallites the current may be constrained to flow perpendicularly to the copper oxide planes. The critical current of long lengths can be considerably increased by treatments which align the crystallites so that the planes of copper oxide lie parallel to the axis of the wire or tape. Indeed, in tapes of BSCCO which have been processed so that the crystallites are aligned with their copper oxide planes roughly parallel to the plane of the tape, the interfaces between crystallites no longer act as weak links, and the critical current is determined by fluxon pinning within the crystallites. However, even in single crystals the critical current is low, because thermal excitation enables the fluxons to detach themselves from the pinning sites (see § 13.3). Furthermore, it seems that at these relatively high temperatures the fluxon lattice loses its rigidity so that those fluxons which are not themselves pinned can move under the Lorentz force exerted by a transport current.

The ability of the fluxons in high-temperature superconductors to move is revealed in the phenomenon of *flux creep*. Because of the pin-

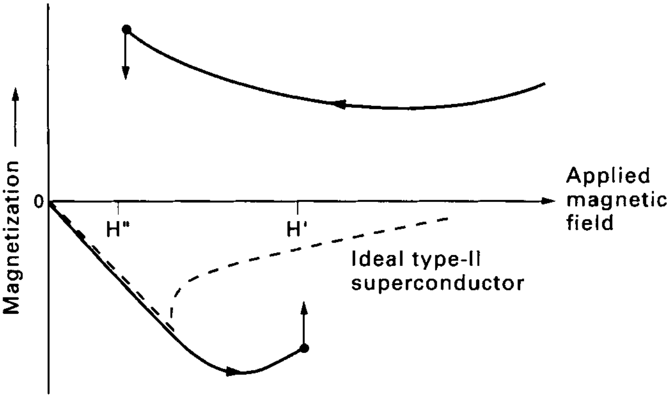

FIG. 14.3. Flux creep. If the applied magnetic field is increased from zero to a strength H' and then held steady at that value, the negative magnetization slowly decreases, as shown by the vertical line, showing that fluxons are entering into the sample. Similarly, if the magnetic field is decreased from a high value to some lower value H'' the magnetization slowly decreases as fluxons leave the sample.

ning centres, these type-II superconductors have irreversible magnetization (see § 12.5.2), but if the applied magnetic field is changed the new magnitude of the magnetization slowly decays towards its equilibrium value (see Fig. 14.3), this flux-creep motion decaying logarithmically with time. This shows that fluxons can enter into or leave the specimen in spite of the pinning.

Why superconductivity appears in these materials at such a high temperature is not at present (1993) understood. Quantum interference experiments (see Chapter 11) show that the supercurrent is carried by electron pairs, as in conventional metallic superconductors, but there is as yet no general agreement as to the mechanism which causes this pairing. There is some experimental evidence for an energy gap, but it is not yet clear whether a BCS-like mechanism is responsible for the superconductivity.