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THE NEW SUPERCONDUCTORS

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SUMMARY

Recent developments in superconductivity, which have pushed the superconducting transition temperature up above the boiling point of liquid nitrogen (-196 C), are described. At first sight, the new materials, which are metal oxides, look extremely attractive for applications. However, fabricating them in usable form presents major problems.

The applications of conventional superconductors to both resistance-less current carrying, as in superconducting magnets and cables, and to devices, such as SQUIDs, are described. The possibilities for the replacement of conventional superconductors, or of conventional conductors, by the new materials are examined. It may well be that superconducting devices made from them are easier to achieve than, for example, high temperature superconducting magnets. These devices would be a lot more portable than those using conventional superconductors, and could find application in, for example, magnetic surveying.

Although there have been reports of superconductivity at yet higher temperatures, none of them have so far been substantiated.

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1 INTRODUCTION

Since the early months of 1987, the world's newspapers have carried headlines promising cheaper electricity, to be brought about by the new breed of superconductors. It is most certainly true that the science of superconductivity has taken a sudden, and totally unexpected, leap forward with the discovery of materials that retain their superconductivity to much higher temperatures than were previously thought possible. Indeed, in recognition of this watershed, which has stimulated thousands of scientists in practically every country of the world to work on superconductivity, the 1987 Nobel Prize for Physics was awarded to Georg Bednorz and Karl Müller for their discoveries at the IBM Laboratories in Zürich.

Solid state physicists, who had thought that the fundamental science of superconductivity was pretty well sorted out, have been presented with a new and exciting problem: how to understand what is going on in these novel superconductors. But the excitement has spread into industry and commerce too, where the prospect of electrical conductors without any electrical resistance has led to claims of revolutionary prospects for power generation, transport and so on.

The purpose of this article is to describe what superconductivity is about, why it is intrinsically a low temperature phenomenon, to outline the progress of the last year, and to examine in some detail the prospects for technological application of the new superconductors.

2 CONVENTIONAL SUPERCONDUCTORS

Superconductivity has been known for nearly eighty years. It was discovered during the systematic exploration of the behaviour of matter at ultra-low temperatures by the Dutch physicist Kamerlingh Onnes. His work was connected closely with the problem of liquefaction of gases, first oxygen and nitrogen, and later neon, hydrogen, and finally helium. At these low temperatures, it

is more natural to work with the absolute temperature scale, denoted by K to commemorate the 19th century physicist Lord Kelvin. On the absolute scale, absolute zero (which is at -273 C on the Centigrade or Celsius scale) is 0 K , so that there are no negative temperatures; the ice point (0 C) becomes 273 K . The boiling points of some common gases are listed in Table I.

Kamerlingh Onnes had been following the behaviour of the electrical resistivity of metals as they are cooled down. As is well known, the resistivity of pure metals is approximately linear in temperature at ambient temperatures (figure 1); when the temperature is lowered, the thermal vibrations of the atoms diminish, and so reduce the scattering of the conduction electrons. At low enough temperatures, only scattering from chemical impurities and crystalline defects remains, and the resistivity levels off to a constant value (the residual resistivity). Thus, ordinary copper conductor that is used for electrical cable has a resistivity that drops from $1.7 \times 10^{-8}\text{ ohm m}$ at room temperature to $2 \times 10^{-8}\text{ ohm m}$ at 77 K , and typically to $2 \times 10^{-10}\text{ ohm m}$ at 20 K or below. If extreme care is taken in purifying the copper, the residual resistivity can be reduced by a further factor of 100 or so. Other metals, such as aluminium and silver, show similar behaviour.

Kamerlingh Onnes' discovery in 1911 was the extraordinary one that the resistivity of mercury dropped sharply to zero at 4.1 K (figure 2). Superconductivity, as it came to be called, was soon found to be widespread amongst the metallic elements, although the transition temperature T_c varies from a small fraction of a degree above absolute zero to 9.2 K for niobium. However, some groups of elements never become superconducting: magnetic metals like iron and nickel; the alkali metals sodium, potassium, etc.; the noble metals copper, silver and gold. Thus, the good room temperature conductors such as copper and aluminium either fail to become superconducting or have low transition temperatures; on the other hand, the metals with a high T_c are those, such as lead and mercury, that have high resistivity at room temperature.

The reasons for this correlation became apparent many years later (see ¶ 7).

How low is the resistance of a superconductor? Kamerlingh Onnes' experiments, which measured the voltage drop along a wire carrying current, showed that it was less than about a ten-thousandth of the resistance in the normal state (metals are described as being either in the normal state when they display their usual resistive behaviour, or in the superconducting state). A more sensitive test is to induce a current in a superconducting ring, and monitor the magnitude of the current using the magnetic field it generates. In a normal metal, the electrical resistance causes the induced current to decay in a fraction of a second. On the other hand, in a superconductor, these currents show no decay over a period of a year or more, which implies that the resistivity in the superconducting state must be less than about 10^{-25} ohm m.

Thus, superconductivity is a remarkable phenomenon; the current-carrying electrons proceed totally unimpeded! Even when some impurities are added deliberately, the material usually remains a superconductor, although the transition temperature may be altered (figure 2). In its early years, the 1930's and 40's, solid state physics tended to focus on pure metals, leaving the study of alloys and intermetallic compounds (in an intermetallic compound the different atomic species have distinct sites within the crystallographic structure) to the metallurgists. so it was not appreciated until the mid-1950's that large numbers of metallic alloys and intermetallic compounds are superconducting, and some were then discovered that have substantially higher transition temperatures than the elemental superconductors (Table II). Until 1986, the record T_c was 23 K for Nb_3Ge .

Given a material of zero resistance, the natural question to ask of a superconductor is how much current can it carry?

Unfortunately, it turns out that above a certain current, the critical current, there is a reversion from the superconducting to the normal state, and in the elemental superconductors, these

critical currents are too low to be useful. Furthermore, magnetic fields also suppress superconductivity, and again for the elemental superconductors the critical field B_c is too small to have any practical application (Table II, the earth's magnetic field is about 10^{-4} Tesla, that of a conventional laboratory electromagnet is about 1 Tesla).

However, the superconducting alloys and compounds that were discovered around 1960 included materials, such as Nb-Ti and Nb_3Sn , that retained their superconductivity and substantial current-carrying capacity to very high magnetic fields. It is these materials that have been developed over the last two decades, and have found quite wide application.

† 3 THE NEW SUPERCONDUCTORS

Since 1960 or so, most solid state physicists had convinced themselves that the fundamentals of superconductivity were well understood, and that no significant improvement in transition temperature above 30 K could be expected. For this reason, interest and activity in the fundamental aspects of superconductivity declined steeply. However, a small minority were not satisfied that all had been explained, and took the example of the metallic oxide $Ba(Pb-Bi)O_3$ to heart. This compound had been shown in 1975 to be superconducting at about 13 K - by no means a world record, but unexpectedly high for a material of that composition and structure. It was by exploring this avenue that early in 1986 Bednorz and Müller came across the ternary oxide $(La-Sr)CuO_x$, which appeared to become superconducting at about 35 K. The parent binary oxide $LaCuO_x$ is not superconducting, but partial replacement of La by Sr, indicated in the chemical formula by $(La-Sr)$, yields the superconducting phase. By the end of the year, this result was confirmed independently by a number of other laboratories, and immediately the race was on to find even higher transition temperatures. In January 1987, Chu's group in Houston discovered that a mixture of

yttrium, barium and copper oxides produced material with superconducting behaviour at 92 K, and a few weeks later the superconducting phase was identified as the oxide $\text{YBa}_2\text{Cu}_3\text{O}_7$, whose structure is shown in figure 3. It is a concomitant of a high T_c that the material has also a high critical field, and that is certainly the case for both $(\text{La-Sr})\text{CuO}_x$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ (see Table II).

Naturally, in the year since Chu's discovery, literally thousands of oxide mixtures have been made and tested, but at the time of writing, there are no confirmed materials that have any higher transition temperatures. Certainly, there have been dozens of reports of higher temperature superconductivity, some of them in newspapers, and occasionally in scientific journals, but so far none of them satisfy the test of true stable superconductivity.

T 4 CRYOGENIC ASPECTS

The conventional superconductors, those known prior to 1986, all used liquid helium for cooling even if they had transition temperatures above the boiling point of hydrogen. The reason is that the performance of a superconductor, in particular the critical current density (the current per unit cross-sectional area of conductor at which the material ceases to be superconducting), deteriorates rapidly as the transition temperature T_c is approached, so the operating temperature is usually held at $0.7T_c$ or less. Liquid helium is expensive, typically not less than \$2 per litre in large quantities in industrialised countries, and, because it has to be air-freighted in fragile and costly storage vessels, ten or twenty times higher in price in small quantities in less-industrialised regions. Furthermore, some specialist training is needed if it is to be used efficiently.

Even without any further advance, a crucial barrier for the wider application of superconductivity has now been crossed, because the $YBa_2Cu_3O_7$ superconductor can be usefully cooled with liquid nitrogen. The superconductive performance is less good than that at lower temperatures, because 77 K is only about $0.8T_c$, but it can be enhanced by reducing the liquid nitrogen temperature to about 65 K ($0.7 T_c$) by pumping on it with a simple rotary pump. Liquid nitrogen is very widely available, being used in tonnage quantities, and the price can be as low as \$0.05 per litre; equally important, it can be transported in simple and robust storage containers, and can be handled with little training.

Both helium and nitrogen are inert cryogenic liquids, so that safety precautions are simple; this is in contrast to liquid hydrogen and liquid oxygen (the latter is particularly dangerous).

Although the use of a cryogenic liquid is usually the cheapest and easiest means of cooling, with the new superconductors it is possible to use instead closed-cycle refrigerators that can

provide cooling down to 10 or 20 K. These machines require only electrical power, and small ones, with a cooling power of several Watts at 20 K, cost about \$10,000.

7 5 FABRICATION OF THE NEW SUPERCONDUCTORS

Although the superconductive properties of the new materials are closely analogous to those of conventional superconductors, the means of making them are very different. Above all, $(\text{La-Sr})\text{CuO}_x$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ are ceramics, and the whole range of ceramics technology, both traditional and modern, can be applied to them. Fortunately, related compounds such as LaCuO_x and LaNiO_x have been studied extensively over the last ten years or so; they have been of interest to the oxide chemists, and have found wide application as catalysts in organic chemistry. Also, many of these oxides are oxygen fast-ion conductors, that is, the oxygen ions are sufficiently mobile to contribute quite high ionic conductivities at temperatures of 300 or 400 C.

Thus, the first of the new superconducting materials were made with a simple ceramics "mix, grind and fire" approach, which is readily accessible with only rather limited facilities. Although a couple of trials are usually enough to obtain material that is superconducting, its properties are almost invariably poor. In particular, the critical current density tends to be extremely low. To focus on $\text{YBa}_2\text{Cu}_3\text{O}_7$, a number of materials problems have now become apparent:

- (i) The reaction of the mixed oxides of Y, Ba and Cu to form the ternary oxide must be carried out below 950 C, for otherwise the ternary oxide decomposes. At this temperature, all the components are solid, and solid state reactions are notoriously slow. Therefore, the starting materials have to be mixed very thoroughly, preferably on an extremely fine (sub-micron) scale.
- (ii) There are several common contaminant phases, such as silica from the grinding process, alumina from

crucibles, and so on. There are also phases that may be formed by reaction with atmospheric moisture and/or carbon dioxide that are stable at the firing temperature. Any or all of these phases tend to migrate to grain boundaries, and form electrically-insulating layers.

- (iii) The phase that forms at the firing temperature is actually $\text{YBa}_2\text{Cu}_3\text{O}_6$, (the "green phase"), which is semiconducting rather than metallic, and certainly not superconducting. Furthermore, its structure is tetragonal instead of orthorhombic. In order to obtain superconducting material, annealing in oxygen at considerably lower temperatures is required, as illustrated in the phase diagram of figure 4. There is very strong evidence that the occupancy of the oxygen sites shown in figure 3 is crucial to the superconductivity. Both the structural phase transformation and the insertion of oxygen cause the lattice parameters to alter significantly, so that at the boundary between two grains of different crystal orientation, substantial strain develops, perhaps enough to cause microcracks. The phase transformation itself invariably introduces large numbers of twin boundaries; whether these affect superconductivity is not yet established.
- (iv) As far as obtaining a good superconductor is concerned, a dense material, free of voids and cracks, is required. On the other hand, in a dense material the insertion of oxygen is limited by the bulk diffusion rate. Although this diffusion rate is relatively high - as mentioned earlier, the materials are fast-ion conductors - the rate does diminish exponentially with temperature. Thus, in order to ensure that the oxygen stoichiometry is as close as possible to 7, it is necessary to anneal below about 400 C for long periods.

- (v) There may be a more fundamental limitation associated with grain boundaries and free surfaces: the actual structure, interatomic distances, oxygen stoichiometry, and so on, at a boundary or a surface will be slightly different from those of bulk material. Depending upon the crystallographic orientation of the boundary or surface, the structure change may be enhance or diminish superconductivity.
- (vi) There is the question of the compatibility of the superconductor to other materials, as at the junction to ordinary copper conductor, or at the interface between a thin film and its substrate. This question has both chemical and physical dimensions: Is there a chemical reaction or change in stoichiometry? Does differential thermal expansion cause the superconducting material to crack? Is there good electrical contact between the two materials? Are there electrochemical effects when current is passed from one to the other?
- (vii) Finally, there are seemingly mundane, but all-important, questions about the material: Its resistance to atmospheric corrosion, mechanical strength, brittleness, toxicity, and so on.

This list is certainly long, and at first sight a depressing one. However, it is important to appreciate that many of the problems have been encountered before by the ceramicists. In other materials, approaches have been found that overcome these problems, and now a great deal of routine systematic work is being done on $\text{YBa}_2\text{Cu}_3\text{O}_7$, trying out those techniques, and if they do not succeed, exploring new ones.

For fundamental studies of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $(\text{La-Sr})\text{CuO}_2$, single crystals are needed, mm in size or larger. Over the last few

months, several laboratories have succeeded in growing such crystals, and rapid improvements have been made in their degree of perfection, measured for example by the temperature and width of the superconducting transition.

When one looks in detail at potential applications, it becomes apparent that the new materials will be needed in a number of different forms:

- (a) Bulk polycrystalline material, with emphasis on clean grain boundaries and high density, and perhaps also with some degree of texturing (preferential alignment of crystallite orientations). The preparative routes that are being investigated here aim at achieving homogeneity on a microscopic scale by chemical or physical means, rather than by mechanical mixing and grinding. They include: Co-precipitation from aqueous or organic solution of Y, Ba and Cu salts, such as nitrates and citrates. Freeze drying of such solutions. Co-decomposition of mixed Y, Ba and Cu organometallics. Mist pyrolysis, in which mixed precursors are sprayed into a hot zone. These techniques aim also at producing the stoichiometric powder mixture in very fine (sub-micron) particles, so that the sintering stage can be accomplished at lower temperatures.

A novel technique has been reported recently by Bell Laboratories, but full details are not yet available. The stoichiometric mixture is heated and cooled extremely rapidly, and produces bulk material that has significantly higher critical current density than that of other bulk materials (figure 8).

- (b) Tapes, cables, wires and filaments for use as conductor, probably with a substantial degree of crystallite texturing, and again having clean grain boundaries and high density. Preliminary attempts have

been made to fabricate wires using methods analogous to those that have been successful with Nb-Ti and Nb₃Sn superconductors: Bulk YBa₂Cu₃O₇ material is crushed, and then packed into a silver tube; the tube is swaged down and annealed in oxygen (to which silver is permeable at high temperatures). Most attempts have produced wire that is superconducting, but with extremely low critical currents; recently, however, Hitachi have reported fabrication of a wire with J_c greater than about 10⁹ amps m⁻². An approach perhaps better suited to the new materials is to use the proprietary processes that have been developed over many years to make filaments of other ceramics; certainly this route is being attempted, but little information has been published.

- (c) Thin films for electronics and devices. Here, the many techniques that have been developed for semiconductors are being tried out: Co-evaporation of the metals and simultaneous oxidation. Sputtering in all its forms. Molecular beam epitaxy. Metal organic chemical vapour deposition. So far, it seems that one of the simplest techniques, laser ablation, works the best. Here, a high power laser pulse is used to ablate a target of the correct composition, and the ablation products are condensed on a nearby substrate. As with all thin film processes, the subsequent thermal and oxygen annealing of the thin film are crucial. Strontium titanate appears to be the most satisfactory substrate, in that there is less chemical reaction with the film than occurs with quartz or sapphire substrates; however, the cost of strontium titanate, typically \$200 per cm², is a major problem.

T 6 APPLICATIONS

T 6.1 Background

Although it is important to remain open to totally new ideas for areas in which the new superconductors may find a use, one should first of all examine those applications where conventional superconductors have been considered, and in some cases, are actually used. Thus, in relation to conventional superconductors, the new materials may extend their range of application, or give enhanced performance, or they may move superconductivity into totally new areas.

In the space of this short article, it is not possible to describe potential applications and their feasibility in more than brief outline; however, some more detailed studies are available (see the Bibliography), and as the material parameters become better defined, the economic benefits can be costed more precisely.

Most of the media publicity has been directed at the high current side of potential applications: magnets, generators and motors, transmission cables and so on. However, there is another, electronic, side to superconductivity that has developed with conventional superconductors over the last 20 years, and in which the new materials may well make an earlier contribution.

T 6.2 Power Applications

Here, the superconductive property that is being used is that of being able to carry a high current, often in a high magnetic field, without dissipation. These applications came about only with the advent of the high critical field conventional superconductors such as Nb-Ti and Nb₃Sn nearly thirty years ago. Almost all the commercially available superconductors are manufactured from these two materials, and their performance has been improved considerably over the years. Although there are compounds such as Nb₃Ge that have higher T_c's, the metallurgical

difficulties of preparing them in wire or tape form have inhibited their use.

The reader will have noticed from Table II that the very high critical fields of the alloy superconductors are more than would be expected from the elemental superconductors by simply scaling with T_c ; the reason is that something rather different is happening in these materials when a field is applied, compared with an elemental superconductor like Pb. When a magnetic field is applied to a superconductor (figure 5a), the magnetic flux is unable to penetrate the material because, as required by Faraday's Law of Electromagnetic Induction, screening currents are set up in a surface layer that exclude it. This flux exclusion is analogous to the skin effect in ordinary conductors, where alternating magnetic fields and currents are confined to the surface layer for the same reason; however, in an ordinary conductor, the finite resistance causes the eddy currents to decay with time, so that steady currents and fields do eventually penetrate uniformly. In a superconductor, the eddy currents, usually called screening currents in this context, persist indefinitely.

There is one further subtle aspect of a superconductor: if the magnetic field were to be applied *before* the material was cooled into its superconducting state (figure 5b), and the flux had penetrated fully, the eddy current argument would suggest that the flux would be stuck there when the material became superconducting. In fact, on going through the superconducting transition, the magnetic flux is *expelled*. In practice this flux expulsion, which is known as the Meissner effect, is never total, because invariably the sample contains some defects that trap, or "pin", the flux lines. However, observation of at least a partial Meissner effect is an important diagnostic test of true superconductivity.

Most elemental superconductors exclude magnetic flux from their interior until the applied field exceeds the critical field B_c ; equally, they show a more or less complete Meissner effect up to

this field. These are known as Type I superconductors. However, the technically useful Type II superconductors behave rather differently (figure 6): at the lower critical field B_{c1} , magnetic flux begins to penetrate the material to form a mixed state; it is only at a substantially higher field, the upper critical field B_{c2} , that reversion to the normal state is complete. Because exclusion of magnetic flux costs magnetostatic energy (the flux lines can be thought of as being elastic, and as figure 5 shows, flux exclusion requires the flux lines to be stretched), the mixed state reduces this cost, and thereby allows a Type II material to retain its superconductivity to much higher applied fields. It has been well-established that both $(La-Sr)CuO_x$ and $YBa_2Cu_3O_7$ are extreme Type II superconductors, where the ratio of upper to lower critical fields is huge, 10^3 or more.

There are two important consequences to the penetration of magnetic flux inside the technically useful materials:

- (1) When a current is carried, there is the usual Lorentz force between it and the magnetic flux, as shown in figure 7. This force acts on the flux lines (in a direction perpendicular to both field and current), and, unless pinned, the flux lines move. This process is known as flux creep. Moving flux, by Faraday's Law of Induction, sets up a voltage which appears along the length of the conductor, and so introduces Joule heating. Flux pinning is strongest at low temperatures, and flux moves much more easily as the temperature approaches T_c , causing J_c to drop sharply. It is this effect which is probably responsible for the poor performance of $YBa_2Cu_3O_7$ conductors at 77 K (figure 8).

A great deal of materials development effort has gone into the conventional superconductors Nb-Ti and Nb₃Sn so as to maximise the density of pinning centres for the flux, and thereby increase J_c . Useful pinning centres include fine-scale precipitates of other phases, grain boundaries, dislocation tangles, etc. The

success of this work in improving the critical current density as a function of magnetic field is indicated in figure 8. The new materials are being improved rapidly too, but there is still an enormous amount to be done before usable, reliable conductors are available. In particular, no specific flux pinning centres have yet been identified.

- (ii) For most power applications, AC operation is greatly to be preferred to DC. Consider a Type II conductor, in the case that the only magnetic field is the self-field (figure 9); every half-cycle, the direction of the current, and therefore of the associated field, reverses. The magnetic flux penetrates the material (because the self-field is well above B_{c1}), but is partially pinned, and this again leads to dissipation. These AC losses have been a major barrier to the use of conventional superconductors for AC purposes; some success has been obtained with cables composed of thousands of ultra-fine filaments of micron diameter, and a similar approach will be needed with the new materials.

Let us then look at a range of applications, progressing from those that are technically least stringent, for example low current and low applied field, to those that are most demanding:

¶ 6.2.1 *Flux transformers*

All conventional transformers work only at AC; however, there are circumstances where DC transformers are useful, transforming signal rather than power, as indicated in figure 10. Both current levels and applied magnetic fields are extremely low, milliAmps and milliTesla or less. Signal transformers of this kind wound from conventional superconducting wires have been used extensively with SQUID sensors (see ¶ 6.3.3); reliable flux

transformers made from $\text{YBa}_2\text{Cu}_3\text{O}_7$ should soon be available, and could extend the usefulness of the SQUID sensors themselves.

¶ 6.2.2 *Magnetic Shielding*

It is sometimes important to contain the stray magnetic field of large-scale magnetic machinery; for example, in hospitals the stray fields of MRI scanners (see ¶ 5.2.5) can be a problem. The usual solution is to surround the magnetic source with sheets of soft iron, but the sheer weight of the iron is a difficulty. The idea of using thick films of the new superconductor, perhaps plasma sprayed, as a magnetic shield, is an attractive one particularly if the magnetic source already has some cryogenic cooling associated with it. The shielding is then provided by the (persistent) screening currents in the superconductor described earlier. The converse problem, of preventing stray fields entering, is also of laboratory and medical interest (see ¶ 6.3.3); helium-cooled superconducting lead shields have quite often been used in laboratory work, and are extremely effective. For these shielding applications, the applied fields are always rather low; the current densities obviously depend upon the magnitude of the field to be screened and the thickness of superconducting film. Thick films, perhaps on the order of 1 mm, might be needed.

¶ 6.2.3 *Superconducting interconnects*

In high speed digital devices, as used in very fast computers, the propagation delay along the conductors between chips is beginning to become important. As gallium arsenide devices, which are several times faster than silicon, come into use (largely for military applications, where the substantial additional cost is not an inhibitory factor), this delay becomes more significant. In principle, some gain can be achieved with superconducting interconnects, and the prospect of cooling the entire board to liquid nitrogen temperatures is quite an attractive one, as many semiconductor devices perform better at those temperatures. As

far as the superconductor is concerned, the applied fields are negligibly small, but the current densities as used at present with copper interconnects are rather high, up to 10^9 Amps m^{-2} . The problems here are likely to those associated with microcircuit processing and compatibility between materials, rather than the superconductor itself. It has to be borne in mind also that, if a cryogenic approach is envisaged, the use of ordinary copper conductor at 77 K gives a substantial gain anyway (figure 1).

¶ 6.2.4 *High Power Cables*

Detailed studies were made in the 1960's and 70's of the economics of underground superconducting cables, and prototype cables were constructed. The cost advantage that has to be considered is that over underground copper cables, possibly cooled with liquid nitrogen to reduce their resistivity (figure 1). With conventional superconductors, some cost advantages were visible for cables of very high power, thousands of MVA, as might be used in the most densely industrialised regions. For superconductors to be of interest, current densities of about 10^9 Amps m^{-2} are needed, and the magnetic fields are very modest, being just the self-field. Perhaps because of uncertainties about reliability, particularly under fault conditions, no superconducting cable has ever been put into service. Given that the cost advantage is likely to be no more than marginal, that the range of application is limited, and that reliability is a prime factor in electrical distribution systems, the widespread incorporation of the new superconductors into electrical transmission would seem to be a long way off.

¶ 6.2.5 *Generators and Motors*

A large number of motor and generator configurations, both AC and DC, have been considered for incorporation of (conventional) superconducting windings, almost always in a manner to diminish

the AC currents and fields in the superconductor itself. A large (2 MW) low-speed DC motor was constructed in the 1960's, and various prototype generators have been, and are being built. The elimination of resistive losses contributes only a small economic gain; the indirect advantages of the use of the superconductor, such as the greater compactness of the machine, and consequent savings in construction and infrastructure costs, appear to be the more important. A great deal more needs to be known about the new materials before the prospects for their use in these machines can be assessed reliably.

¶ 6.2.6 *Magnets*

It is convenient to divide consideration of magnets into low and high precision, where the precision refers to how tightly the field must be controlled. For low fields (< 1 Tesla) the competition is with iron-cored electromagnets, for higher fields and large volumes, it is with water-cooled solenoids. The Joule heating in a solenoid of interior volume $V \text{ m}^3$ (internal cross-section times length) wound from copper conductor and generating a field B Tesla is of order $10^6 B^2 V$ Watts; not only must this electrical power be paid for, but it must be removed efficiently from all parts of the winding so as to prevent runaway overheating.

Low-precision magnets Magnetic separation is a widely dispersed industrial technique, used to clean magnetic impurities from other minerals (e.g., rare-earth contaminants from china clays, pyrites from coal), and more sophisticated extensions have been considered, for example to separation of red cells (which are weakly magnetic because of the iron they contain) from blood. Prototype machines using conventional superconductors have been built, and it would seem likely that this is an area where the new materials could make an early impact, once good wire or tape conductor becomes available. The advantages of simplified cooling

(¶ 4) would make it much easier to site magnetic separators close to production sites.

High-precision magnets It is in this area that the advent of Nb-Ti and Nb₃Sn superconductors has made its mark. In research laboratories, steady fields above 1 Tesla are now almost always obtained using helium-cooled superconducting solenoids, which are available for fields up to 15 Tesla, and an internal bore of 100 mm or more. At these high fields, an iron core makes almost no contribution to the field, and is never used. Note that a 15 Tesla copper solenoid of 100 mm bore would consume electrical power of order 1 MW, and so would require also a major investment in the cooling circuit (pumps, filters, deionisers, etc.). Furthermore, in a solenoid the winding can be tailored to provide a very exacting specification on the field profile, for example uniformity to 1 part per million or better over small regions, which is needed for the nuclear magnetic resonance (NMR) magnets used in chemical and biochemical research. Frequently, these laboratory superconducting magnets are used in persistent mode (figure 11) by short-circuiting the winding with a superconducting switch; this mode of operation not only saves on cooling (because it eliminates the Joule heating in the current leads, and indeed enables these leads, which conduct substantial amounts of heat into the cryogenic fluid, to be physically withdrawn), but it provides a field of great stability, far greater than is attainable with a current supply.

The greatest commercial impact of these superconducting magnets has been in the medical field, where solenoids of very large volume, up to 1 m bore, and 1 to 2 Tesla field are used in whole-body nuclear magnetic resonance scanners, now known as Magnetic Resonance Imaging (MRI) scanners; well over a thousand scanners have been built world-wide. The other large-scale application has been to magnets for particle accelerators, where provision for some superconducting magnets has been included in machines that are now being built.

In most of these applications, where the magnets are being used in a sophisticated and complex environment, the advantages of liquid nitrogen cooling over that with liquid helium are marginal, so that $\text{YBa}_2\text{Cu}_3\text{O}_7$ will not easily replace Nb-Ti and Nb₃Sn. The higher critical field of the new materials suggests that they could be useful above the 15 Tesla available with conventional superconducting magnets. However, at these high fields the Lorentz force between the field and the current-carrying conductor becomes very large, so that the mechanical strength of the superconductor becomes the limiting factor. So far, the mechanical behaviour of the new superconductors is poor, and limits severely their possible application.

This discussion is intended to be illustrative of the problems that arise with applying superconductors, and of the likely impact of the new materials, rather than to be exhaustive. Other applications that are being assessed include: large-scale energy storage systems, levitation magnets for trains, power transformers, fault current limiters in electrical distribution systems, and magnets for compact X-ray synchrotrons. The reader is referred to the relevant papers listed in the Bibliography for further information.

One of the most remarkable features of superconductivity is that, as Josephson predicted in 1962 (work for which he was later awarded a Nobel Prize), a supercurrent can flow through the insulator of a superconductor-superconductor Giaever junction (figure 12a), although the magnitude of the critical current is very small, typically μAmps . Similar behaviour is observed if the two pieces of superconductor are connected through a narrow bridge, a micron or less in width, of superconductor. One important application uses the possibility of feeding a Josephson junction with a constant current, and switching it from the zero voltage state to the dissipative state. With conventional superconductors, this switching can be very fast and involve low power dissipation. On this basis, during the 1970's IBM developed a superconducting computer, although it was abandoned a few years ago because of the difficulty of ensuring reliability of vast numbers of junctions. Crude Josephson junctions have been made with the new materials, but because of fabrication difficulties and other more fundamental reasons, it seems unlikely that they will be used in logic devices for a long time to come.

When a Josephson junction is irradiated with electromagnetic radiation of frequency ν , the voltage-current characteristic develops structure (figure 12b) at voltage intervals δV given precisely by the Josephson relationship $h \nu = n 2 e \delta V$, where h is Planck's constant and n is an integer; numerically, the relationship corresponds to 484 MHz irradiation giving structure at 1 μVolt intervals. Because frequencies are easy to measure with high precision, this AC Josephson effect is now utilised in many national standards laboratories to provide a voltage standard. Given some development of junction fabrication with $\text{YBa}_2\text{Cu}_3\text{O}_7$, we can anticipate that such voltage standards will become rather more widely available and portable; however, there seems to be little need for them ever to become commonplace.

¶ 6.3.3 *Superconducting Quantum Interference Devices - SQUIDS*

One further feature of superconductivity that reflects its quantum nature is that a ring of superconductor threaded by magnetic flux forces that flux to be quantised (magnetic flux is field times area, or more strictly, the integral of the field over the area) in units of $h/2e$, which is equivalent to 2.07×10^{-15} Weber. The earth's magnetic field is about 10^{-4} Tesla, so that the flux quantum corresponds to the earth's field through a loop of area 2×10^{-11} m², or say 5 μ m in diameter.

Superconducting devices, SQUIDS, have been developed over the last 20 years, mostly using niobium as the superconductor, that allow this quantization to be used in measurement (figure 13). In principle, SQUIDS could be used to monitor the ambient magnetic field, but in practice they are constructed inside a magnetic shield, and the signal is fed into a small coil that alters the magnetic flux seen by the superconducting ring. SQUIDS can be used to monitor minute changes in magnetic field, electrical current, voltages, etc. For fifteen or more years, SQUIDS have been available commercially, and now cost, complete with the associated electronics \$5,000 to \$10,000.

Areas in which SQUID sensors have found application include: Ultrasensitive laboratory measurements of electrical and magnetic properties. Geomagnetic surveying for minerals, arch. ological searches, and (by the military) submarine detection. One rapidly developing field is biomagnetism, where the magnetic fields associated with muscular and nervous activity are extremely small, but large enough to be monitored using SQUIDS (figure 14). This technique complements the monitoring of physiological electric fields, as in an electrocardiogram (ECG) or in an electroencephalogram (EEG), by providing a magnetocardiogram (MCG) or a magnetoencephalogram (MEG), and may be particularly useful for certain kinds of neurological disorder, such as epilepsy.

SQUID devices utilising the new superconductors and operating at liquid nitrogen temperatures have already been demonstrated, and several groups are attempting to produce reliable SQUIDs using thin film techniques. Here again, the outstanding problems are materials ones. Because of the higher operating temperature, $\text{YBa}_2\text{Cu}_3\text{O}_7$ SQUIDs have a noise level significantly greater than that of SQUIDs constructed from conventional superconductors, but they are of course still extremely sensitive. The main advantages of liquid nitrogen temperature operation are those of portability, so one can foresee that a rapid expansion in the use of SQUIDs for magnetic surveying. In sophisticated medical applications, such as magnetoencephalography, sensitivity really is at a premium (figure 14) and the additional cost of liquid helium is a less important factor, so that ceramic SQUIDs may not be useful here. However, hybrid systems with a $\text{YBa}_2\text{Cu}_3\text{O}_7$ flux transformer (see ¶ 6.2.1) having one end at 77 K, and the other end coupled into a niobium SQUID at 4 K may have advantages: the relaxed cooling constraints at 77 K mean a much smaller thickness of thermal shielding, and by allowing a closer approach to the magnetic source, help to locate its position more precisely.

In almost all situations where SQUIDs are used, their extreme sensitivity to magnetic fields requires that they be carefully screened from ambient field fluctuations (which arise from power lines, electrical machinery, passing vehicles, etc., and typically have magnitude 10^{-7} Tesla). Magnetic screening with superconductors, as described in ¶ 6.2.2, is often used, and the new materials could play a role here.

¶ 7 SUPERCONDUCTORS, PAST, PRESENT AND FUTURE

Are we about to see room temperature superconductors? Obviously, if we were to do so, the economic implications would be enormous. However, a T_c of 300 K would be insufficient, because to obtain reasonable performance, the operating temperature should be no more than about $0.7 T_c$ (see ¶ 4); thus for room temperature

applications, a T_c above about 400 K would be required. We discuss here what is known about the mechanism of superconductors and what limits the transition temperature T_c .

It took more than forty years from the discovery of superconductivity to understand it at a microscopic level. It became clear gradually that the superconducting state is a distinct phase in the true thermodynamic sense (as solids, liquids and gases are distinct phases), and that the conduction electrons that carry the electrical current in a normal metal condense into a more ordered state in the superconductor. The ability of the conduction electrons to move through the crystal lattice without dissipation is a reflection of their ordered state.

The effect of temperature is always to cause disorder, and when the thermal fluctuations are large enough, there is a phase transition from the more ordered state, e.g. a solid, to a less ordered one, e.g. a liquid. The stronger the bonding in the ordered state, the higher the temperature of the transition. Thus strongly bonded solids, such as diamond, melt at much higher temperatures than weakly bonded materials, such as ice. In the case of a conventional superconductor, the "glue" that keeps the conduction electrons together in the superconducting state is an interaction between those electrons and the vibrations of the atoms in the crystal. This is the electron-phonon interaction of the Bardeen-Cooper-Schrieffer (generally abbreviated to BCS) theory of 1957, and is the same interaction that is responsible for the resistivity of a metal at ambient temperatures; hence the correlation (see ¶ 2) between high resistivity at room temperature and a high superconducting transition temperature. One of the vital pieces of direct evidence that pointed to the involvement of atomic vibrations in conventional superconductivity was the isotope effect: In general, different isotopes do have almost identical chemical and physical properties; however, it was discovered 40 years ago that the superconducting transition temperatures *do* depend on isotopic

mass M_{ion} . For a given element, separated isotopes have T_c 's that scale as $\sqrt{M_{ion}}$.

The electronic structure of normal metals is now understood in great detail, as is the nature of the lattice vibrations, and also the basis of the electron-phonon interaction. Thus, in principle, and to a large degree in practice, the superconducting T_c can be calculated for an element or a compound with a fair degree of accuracy. Conversely, the question can be posed, and answered, of what is the maximum attainable T_c with the BCS electron-phonon mechanism; the answer seems to be not much above 30 K. Thus the discovery by Bednorz and Müller of superconductivity at 35 K in $(La-Sr)CuO_4$ raised the question immediately of whether the same mechanism was at work as in conventional superconductors; the transition temperature of 92 K in $YBa_2Cu_3O_7$ gave even greater stimulus to the search for other mechanisms. However, the structure of these oxides (figure 3) suggests that the conduction electrons are concentrated around the Cu-O bonds, so that there might be an exceptionally large electron-phonon coupling involving the vibrations of the O atoms (at any given temperature, the lighter the atom the larger the amplitude of vibration; in both $(La-Sr)CuO_4$ and $YBa_2Cu_3O_7$, the O atoms are four times lighter than the next heaviest atoms). Thus, a more direct test of the relevance of the electron-phonon mechanism was provided by a search for the isotope effect in the new materials. It turns out that when ^{18}O is substituted for ^{16}O in $(La-Sr)CuO_4$, T_c is lowered, but three or four times less than would be predicted by the BCS theory. In $YBa_2Cu_3O_7$, the effect is proportionately even smaller. The present situation therefore is that most physicists believe that some mechanism other than the BCS interaction has to have the prime responsibility for superconductivity in the new materials, perhaps one involving electron-electron interactions of the kind that in many metal oxides are responsible for producing magnetic ordering. Certainly, the chemistry of the new materials is important, and a

number of suggestions have been made as to why it is that copper oxides are the crucial component.

The search for materials with yet higher T_c 's has been going on for a year or so; some of it totally empirical, and at the lowest level consisting of no more than preparing hundreds of mixtures of metal oxides. Other work is better focussed, looking perhaps for oxides where the oxygen environment of the copper has some particular configuration, or following some other line of reasoning.

What about the reports of higher transition temperatures? They are too numerous and too well documented to be simply dismissed. However, all the reports share several features: The transition that is observed refers almost always to a sudden drop in resistance, but because the measuring currents are small (otherwise the phenomena disappear), the resistivity could still be quite large. No laboratory has reported observation of a true Meissner effect (see ¶ 6.2), which is the acid test of superconductivity, at any temperature above about 95 K. The effects tend to be transient, lasting only for a few hours or days, and difficult to reproduce even within a batch of samples. In general, the samples that show these effects are of rather poor quality, perhaps deviating from the intended composition or containing contaminant phases. Thus, there is no evidence so far of true, bulk, superconductivity at any higher temperature than about 95 K. Perhaps what has been observed is associated with grain boundaries or with other phases, with a transition in that material from a resistive state to one of much lower resistivity, but which is not necessarily superconducting.

Because we do not yet have any microscopic theory of superconductivity in the new materials that is totally convincing, there are no clear signposts of the avenues that should be explored. We can be almost sure that in 1986 Bednorz and Müller did indeed discover an example of a new mechanism of superconductivity; within a matter of weeks only, and without any substantial clues to the mechanism involved, T_c had been

raised to 92 K. It would indeed be unkind of Nature, but not impossible, if this were to be the highest transition temperature that will ever be.

Of course, we cannot preclude the possibility that yet another new class of superconductors will be discovered with even higher T_c 's; but unless that happens, almost all the scientific effort will be devoted toward understanding the materials we now have, and to the slow, unglamorous, process of learning how to make them into useful conductors and devices.

18 CONCLUSIONS

The new oxide superconductors $YBa_2Cu_3O_7$ and $(La-Sr)CuO_4$ do represent a major leap forward for the science of superconductivity. It is one that is not well understood microscopically, and that lack of understanding perhaps inhibits the development of superconductors with transition temperatures significantly above 90 K.

The scope for applications of the newly discovered materials is constrained by the difficulties of making them in suitable form. Certainly, the earliest applications will be to relatively simple devices that do not need to carry large currents. Whether the oxide superconductors will ever be used to replace conventional conductors or superconductors in electrical machines, magnets and so on, is a question that awaits the solution of major problems in materials preparation.

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More detailed discussions are provided in a number of graduate-level texts, including:

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A highly readable and concise survey of superconductivity in relation to the new materials is:

P. Campbell *A superconductivity primer*
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The British journal *Nature* and the US journal *Science* have both followed developments closely, and because they are published weekly, they provide up-to-date and informed news in their editorial pages. They publish also some reports of research conferences, and a number of technical papers of more general interest.

More than a thousand scientific papers have already been published on the new superconductors, in journals such as *Physical Review Letters*, *Physical Review B*, *Japanese Journal of Physics*, *Zeitschrift für Physik*, *Journal de Physique*, *Journal of Physics C & F*, *Solid State Communications*.

Recent conference proceedings that contain large numbers of relevant papers include:

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As far as applications are concerned, a number of reports have been written in recent months, primarily directed at power engineering aspects. Naturally, as the available materials improve, or difficulties emerge, their conclusions will need to be reconsidered.

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TABLE I
COMMON CRYOGENIC GASES

Gas	Boiling point (at 1 atmosphere)	
	C	K
Helium	-269	4.2
Hydrogen	-253	20
Nitrogen	-196	77
Oxygen	-183	90

TABLE II
TYPICAL SUPERCONDUCTORS

	T_c	B_c
	K	Tesla
Metallic elements		
W	0.012	1×10^{-4}
Zn	0.88	5.3×10^{-3}
Al	1.18	1.0×10^{-2}
Sn	3.72	3.1×10^{-2}
Hg	4.15	4.1×10^{-2}
Pb	7.2	8.0×10^{-2}
Nb	9.2	2.0×10^{-1}
Alloys and intermetallic compounds		
Nb-Ti	9	14
Nb ₃ Sn	18	24
Nb ₃ Ge	23	38
Metal oxides		
Ba(Pb-Bi)O ₃	13	6
(La-Sr)CuO ₄	35	50?
YBa ₂ Cu ₃ O ₇	92	100?

The listed critical field is the maximum field, for $T \ll T_c$, at which superconductivity is sustained. In Type II superconductors, it is the upper critical field B_{c2} .

FIGURE CAPTIONS

Figure 1. The electrical resistivity of copper below room temperature (300 K). Note that at liquid nitrogen temperatures (77 K), the resistivity has fallen by a factor of about 8. At the lowest temperatures, the residual resistivity ρ_{resid} is controlled by the level of impurities; in commercial high-purity copper it is less than the room temperature value by a factor of typically 100. Other pure metals such as aluminium, zinc, silver, etc. behave similarly.

Figure 2. The superconducting transition in lead. Notice that the difference between a relatively pure sample (a) and an impure one (b) is in the magnitude of ρ_{resid} ; the impurities do not contribute any resistivity in the superconducting state, although they may affect the transition temperature.

Figure 3. The crystal structure of the oxide superconductor $YBa_2Cu_3O_7$. The material loses oxygen preferentially from the arrowed sites when heated above about 400 C. Material that has less than about 6.5 atoms of oxygen per formula unit never becomes superconducting.

Figure 4. The oxygen stoichiometry x of $YBa_2Cu_3O_x$, as a function of temperature; the data presented are for 1 atmosphere oxygen pressure. Notice that at typical sintering temperatures of 800 C or more, the material is in its tetragonal form, and is highly deficient in oxygen.

Figure 5. (a) A superconductor (shaded) excludes flux when a magnetic field is applied, as would a perfect conductor, but also (b) a material that is cooled in a magnetic field and then becomes superconducting, expels flux, which a perfect conductor would not do. This flux expulsion from a superconductor is known as the Meissner effect, and is a key test of true superconductivity.

Figure 6. Type II superconductors show a more complicated behaviour in a magnetic field. At low fields, they exclude flux, as do the Type I superconductors of figure 5. However, above the lower critical field B_{c1} , flux starts to penetrate; this mixed state persists to the upper critical field B_{c2} , where superconductivity is destroyed. In the commercially useful conventional superconductors, such as Nb-Ti and Nb₃Sn, B_{c2} is about 100 times greater than B_{c1} .

Figure 7. Current J flowing through a Type II superconductor in a magnetic field B . There is a Lorentz force F on the flux lines, and if they move, energy is dissipated.

Figure 8. Critical current densities J_c in YBa₂Cu₃O₇ in different forms. At 4 K, J_c is extremely high in single crystals and thin films, but at 77 K J_c in bulk material is much smaller, and drops rapidly with applied field. The best materials reported so far are those from Bell and Hitachi. For comparison, the performance of the conventional superconductors Nb-Ti and Nb₃Sn at 4 K is shown, and also that of ordinary copper conductor at room temperature.

Figure 9. Magnetic flux inside a Type II superconductor carrying an AC current. Flux motion again leads to dissipation.

Figure 10. Schematic superconducting flux transformer. Changes in field in the primary induce a persistent current which alters the field in the secondary. The primary and secondary can be well separated, and their areas and number of turns optimised to suit the specific application.

Figure 11. Superconducting magnets are often equipped with superconducting switches. To energise the magnet, the short-circuit is heated above its superconducting transition temperature, so that current from the power supply passes through the magnet winding. When the required current has been reached, which may be 100 Amps or more, the short circuit is allowed to cool and become superconducting. The current then circulates through an entirely superconducting circuit, and the power supply

can be disconnected; furthermore, the copper leads (which conduct a lot of heat into the cryogen) can be physically removed, so as to cut cryogenic losses.

Figure 12. (a) The current-voltage characteristic of a junction between two pieces of superconductor, separated by a thin layer of insulating oxide. At zero voltage, a small super-current can flow. (b) When the junction is irradiated with microwaves, steps appear at regular and very precisely known voltage intervals δV ; this phenomenon is now used as the basis of national voltage standards.

Figure 13. Principle of a SQUID. The niobium ring with its junction responds in a periodic fashion to the magnetic flux coupled to it by the signal coil. The flux period is only 2.07×10^{-15} Webers, making the device extremely sensitive. The magnetic shield protects the SQUID from extraneous magnetic disturbances.

Figure 14. The magnitudes of physiological magnetic fields. Notice that they are much smaller than typical ambient fluctuations, and cannot be seen by even the most sensitive non-superconducting device, which is a flux-gate magnetometer.

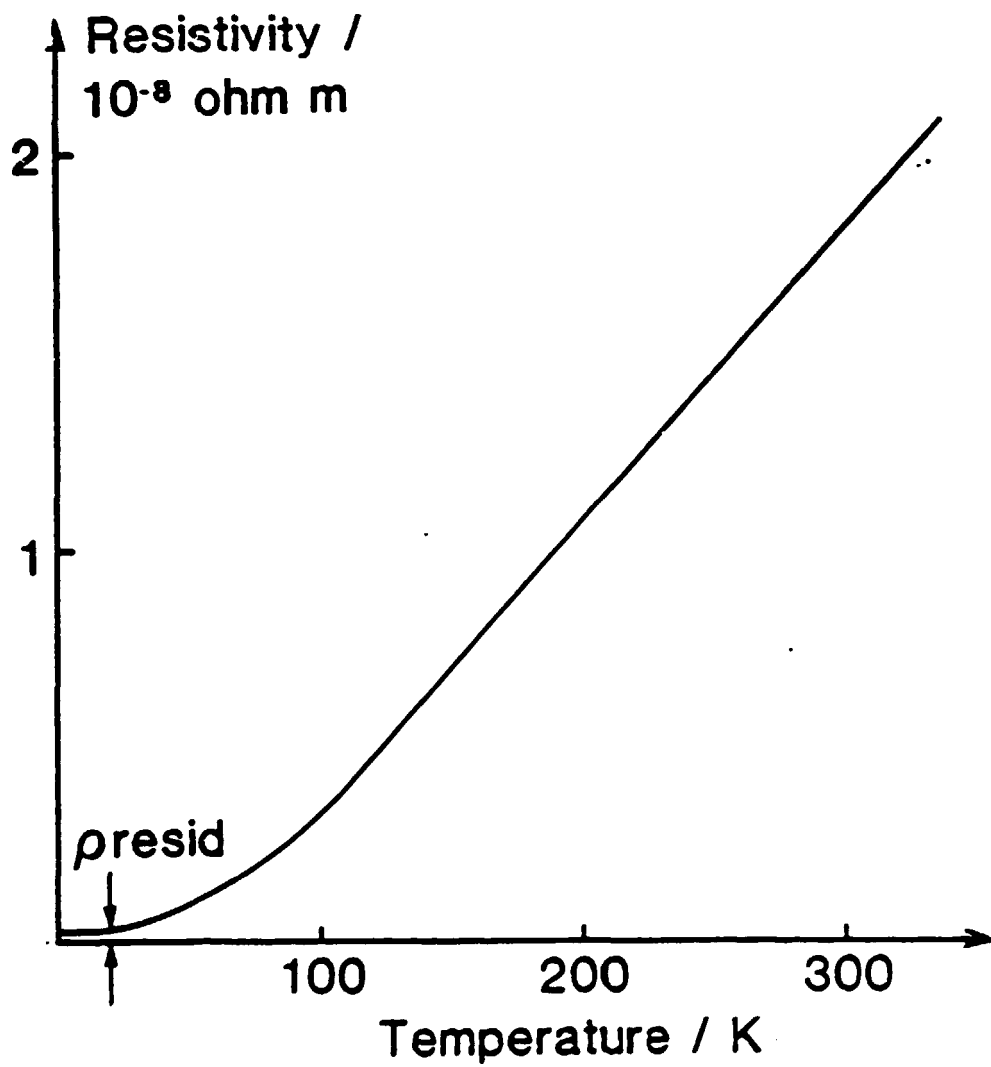


Figure 1

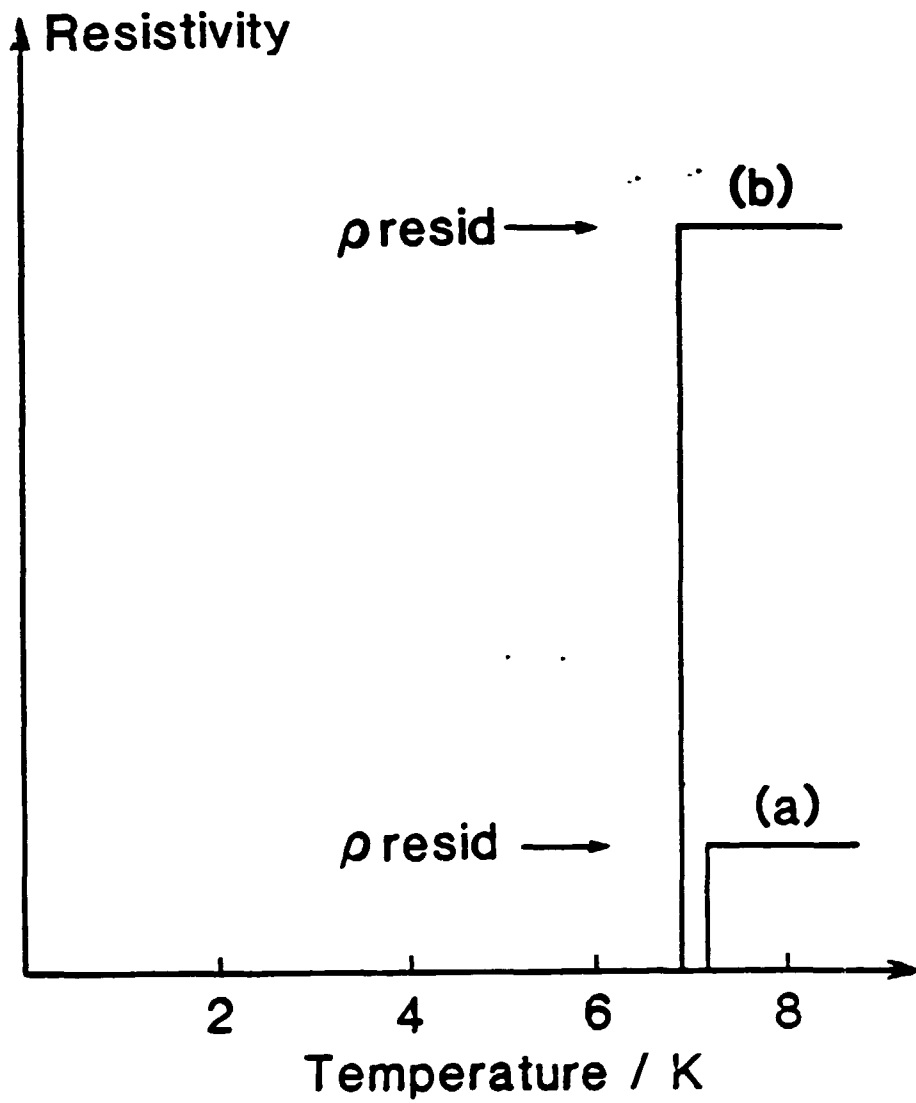


Figure 2

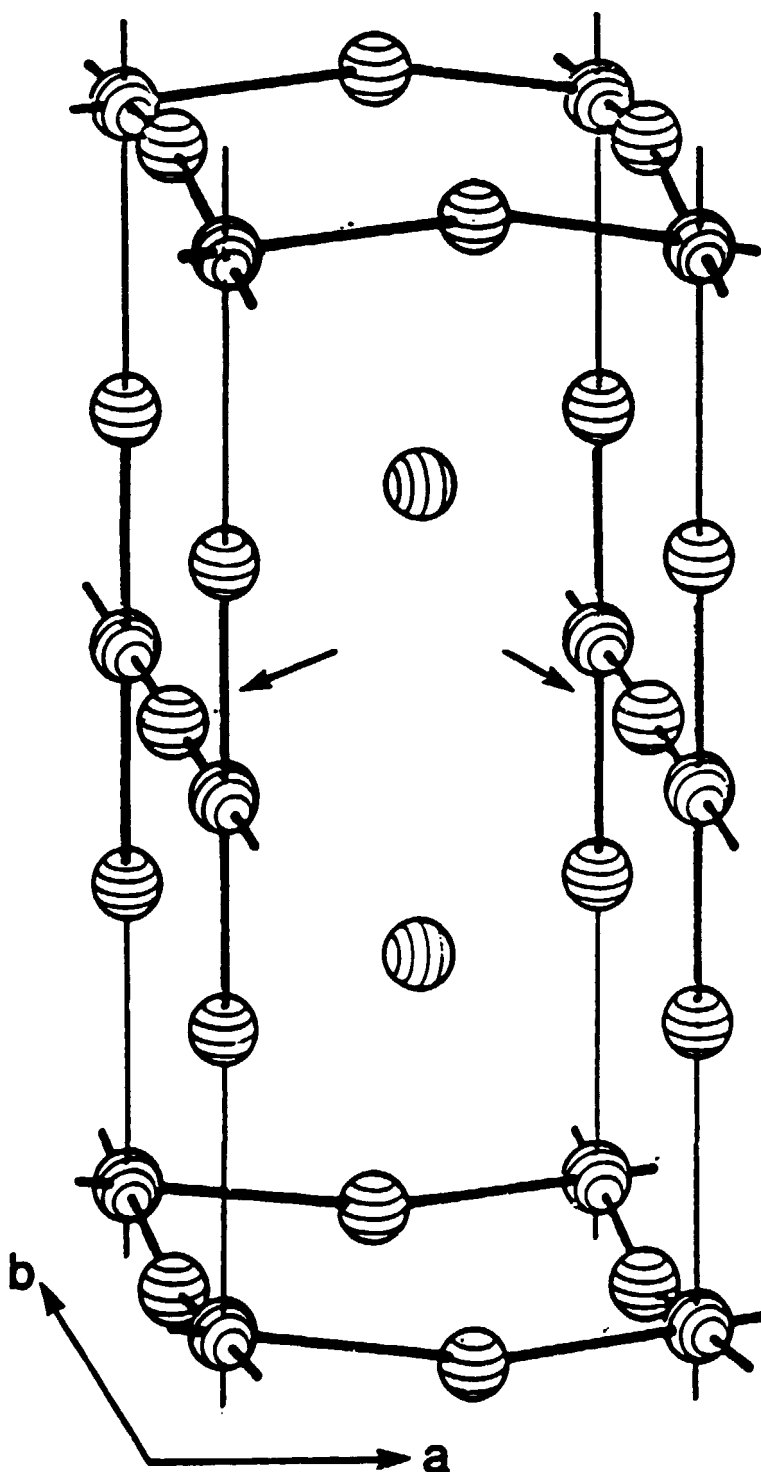


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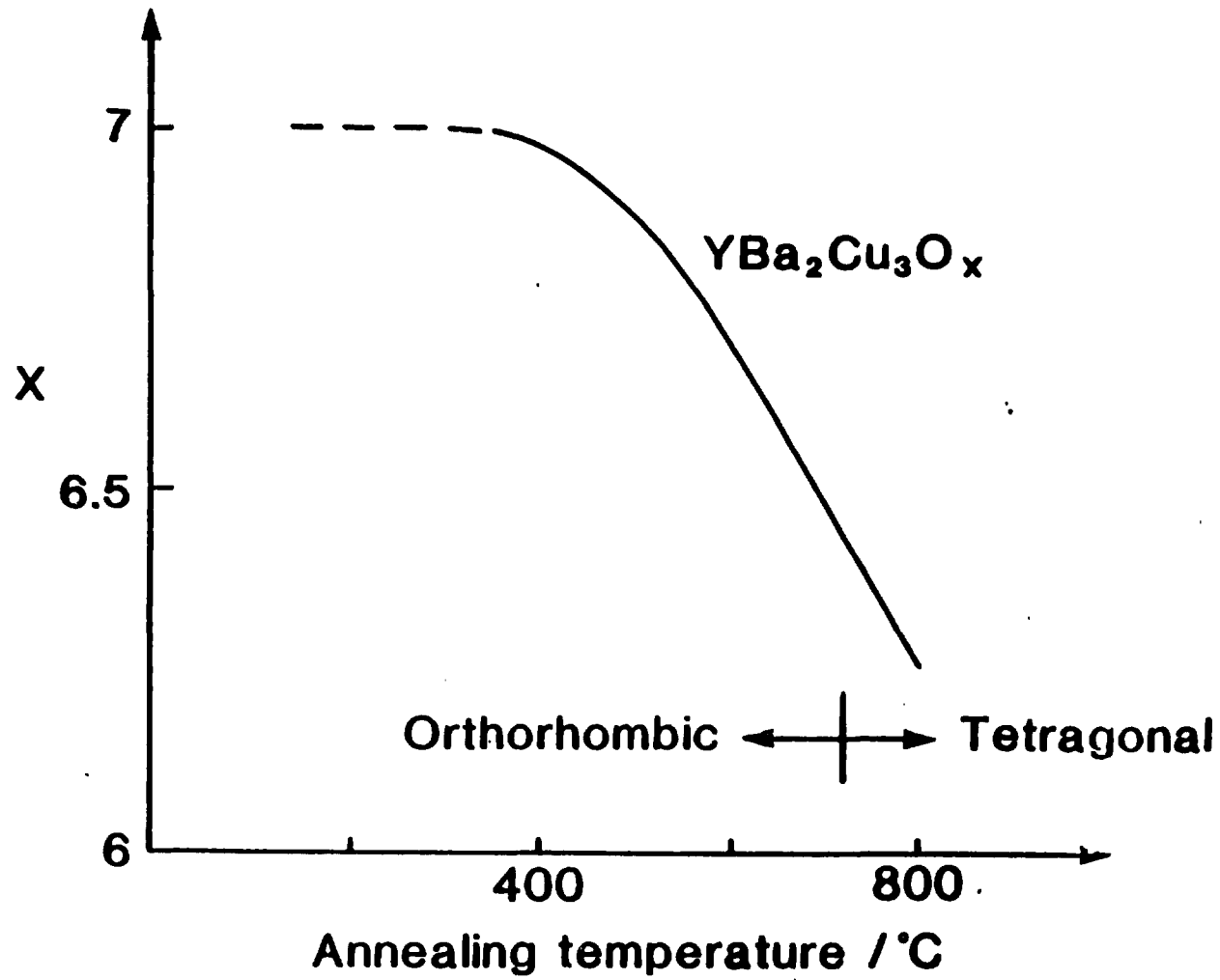


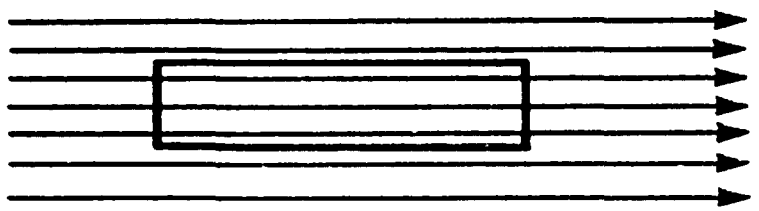
Figure 4

(b)

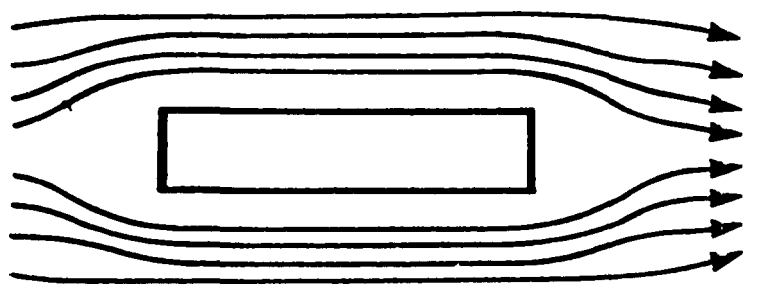
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$T > T_c$
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$T < T_c$
 $B > 0$



T_c
 μ

(a)

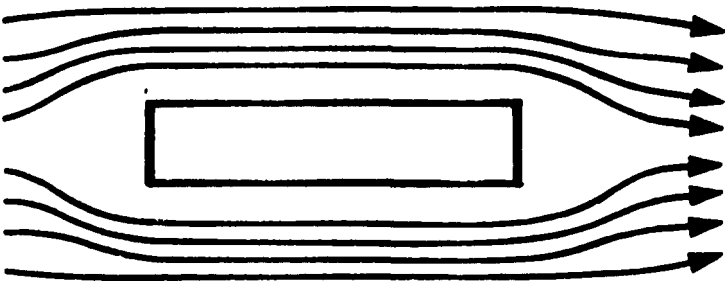
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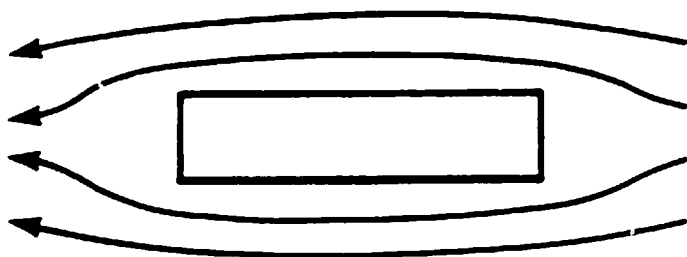


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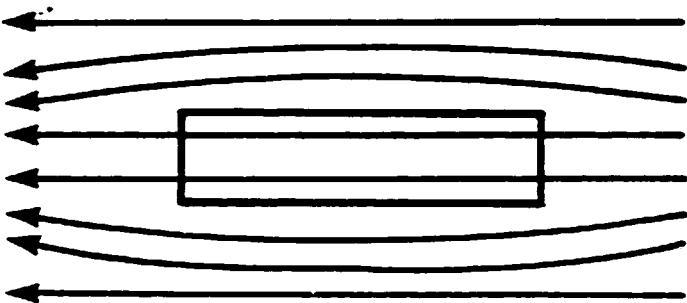




$B=0$



$B < B_{c1}$



$B_{c1} < B < B_{c2}$



$B > B_{c2}$

1.1.6

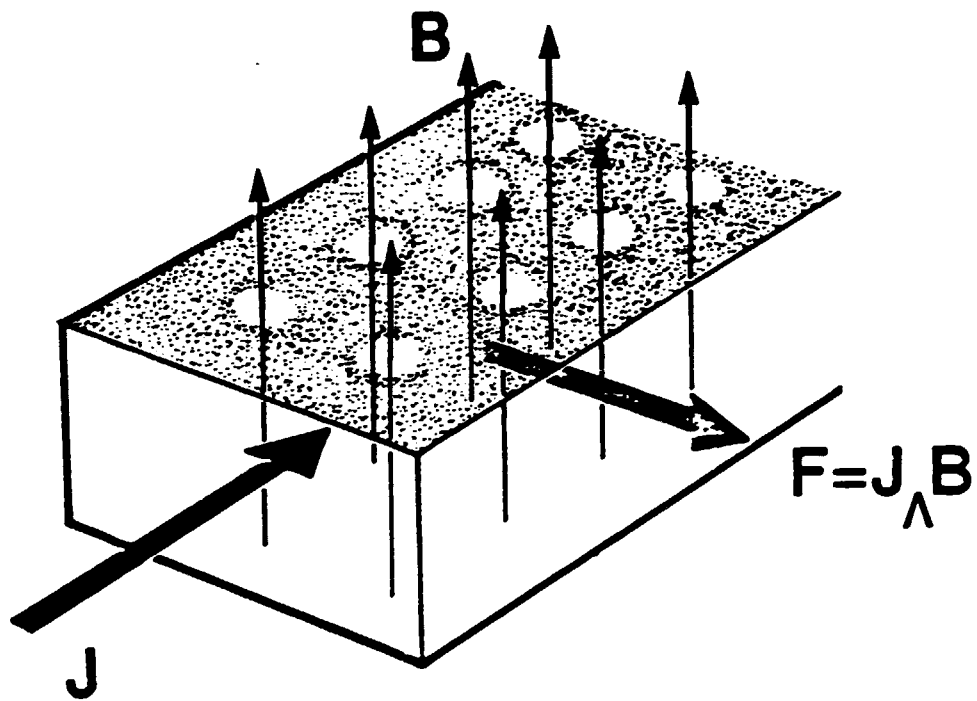


Figure 7

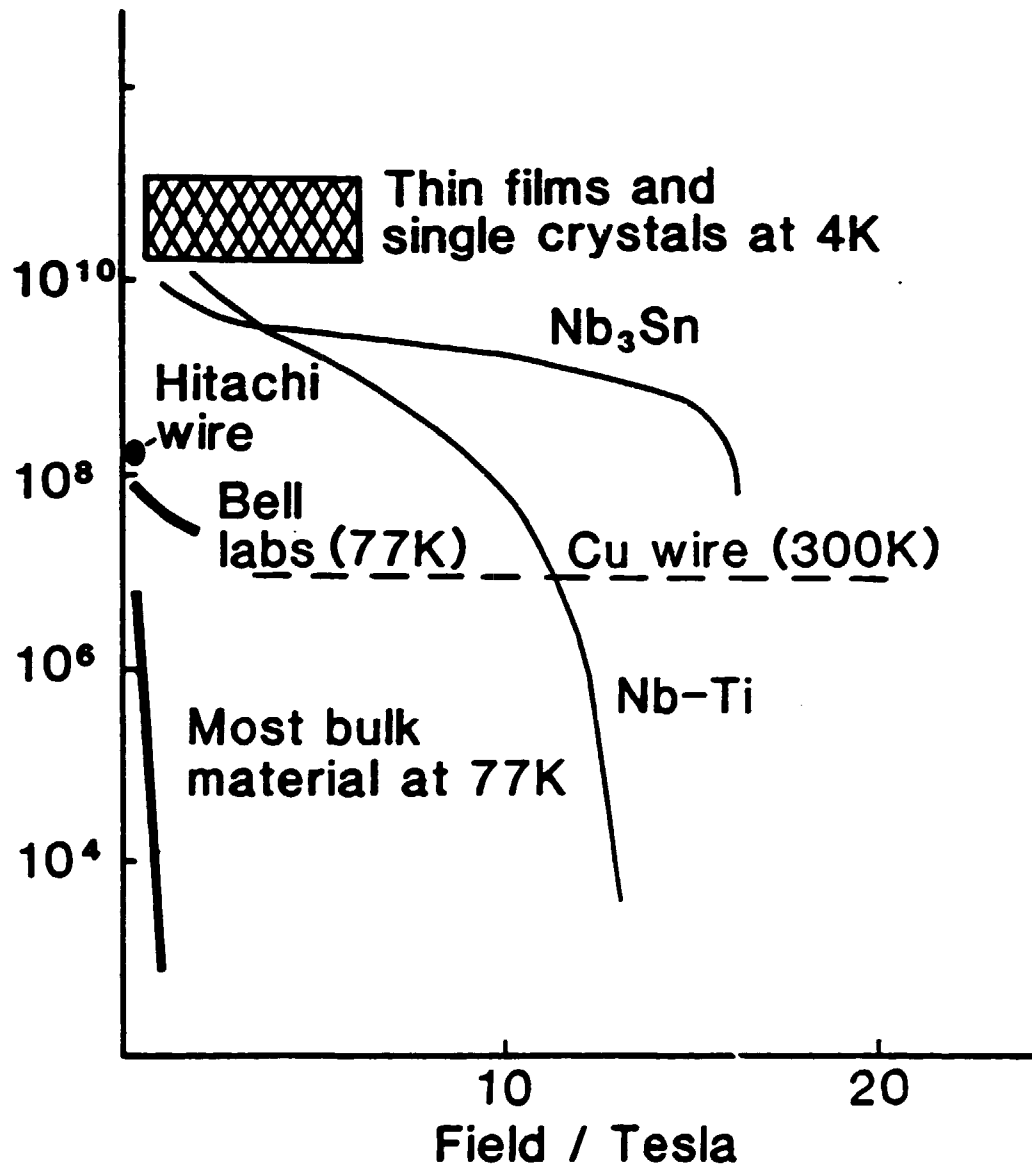
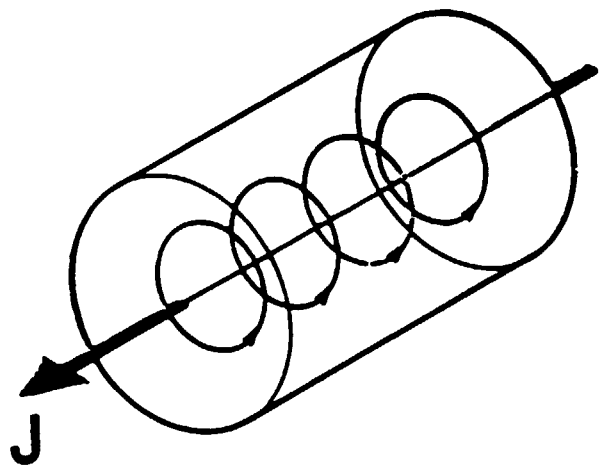
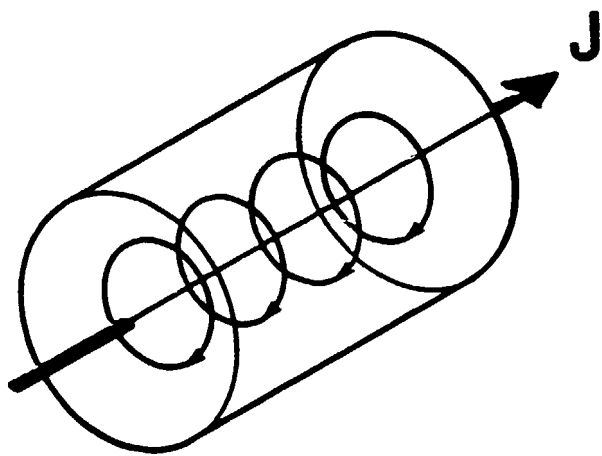


Figure 8



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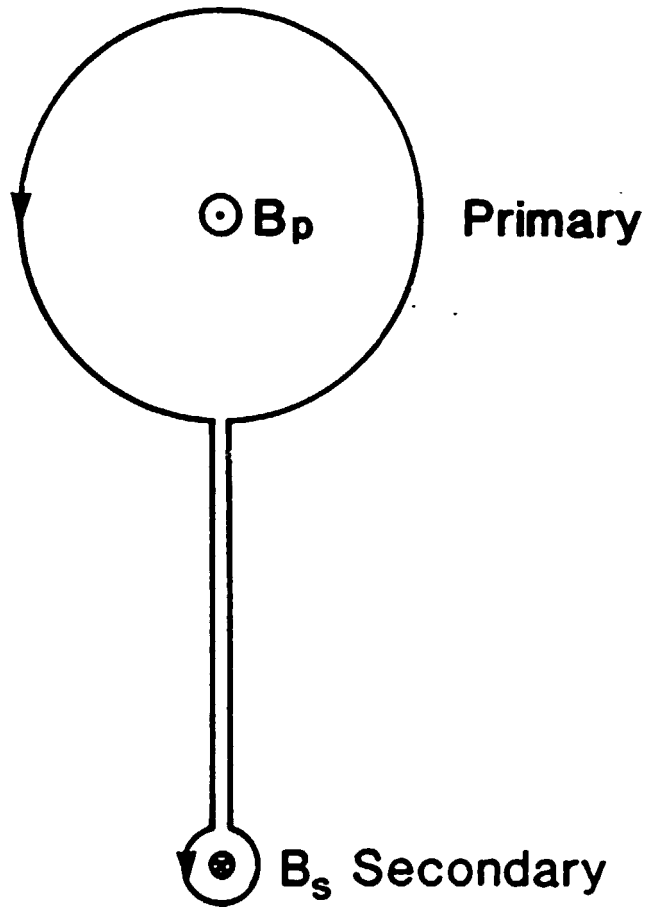


Figure 10

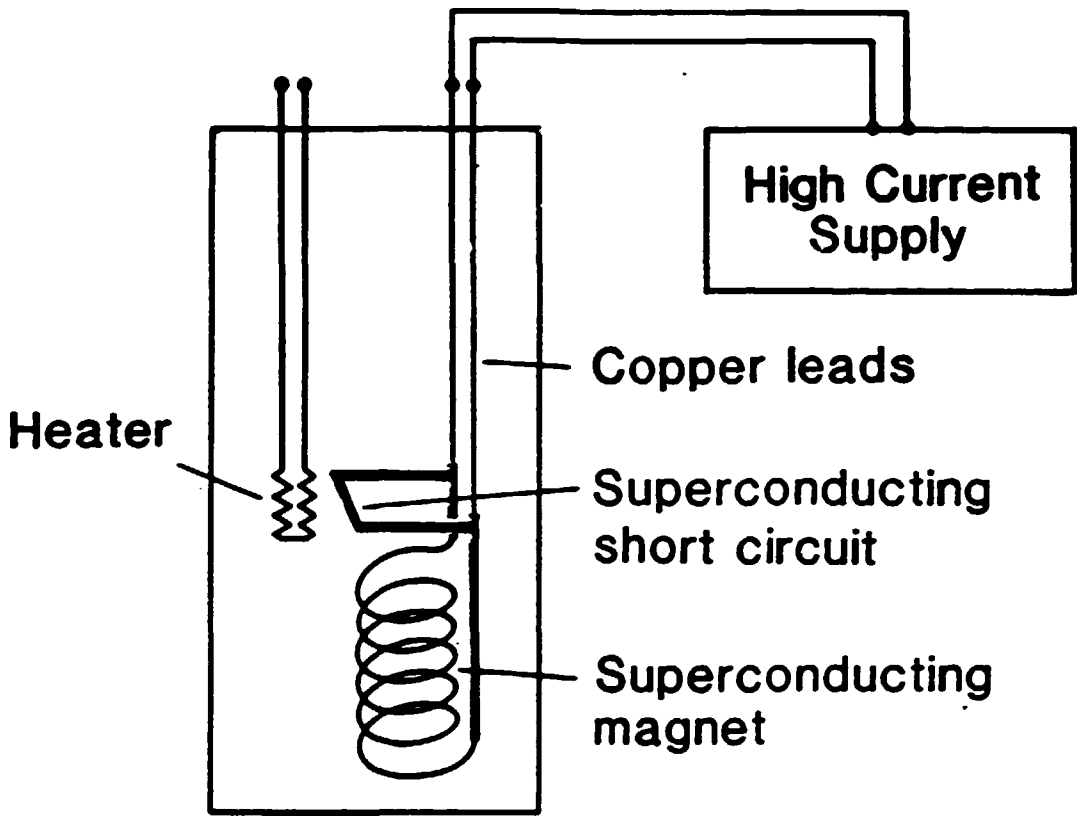


Figure 11

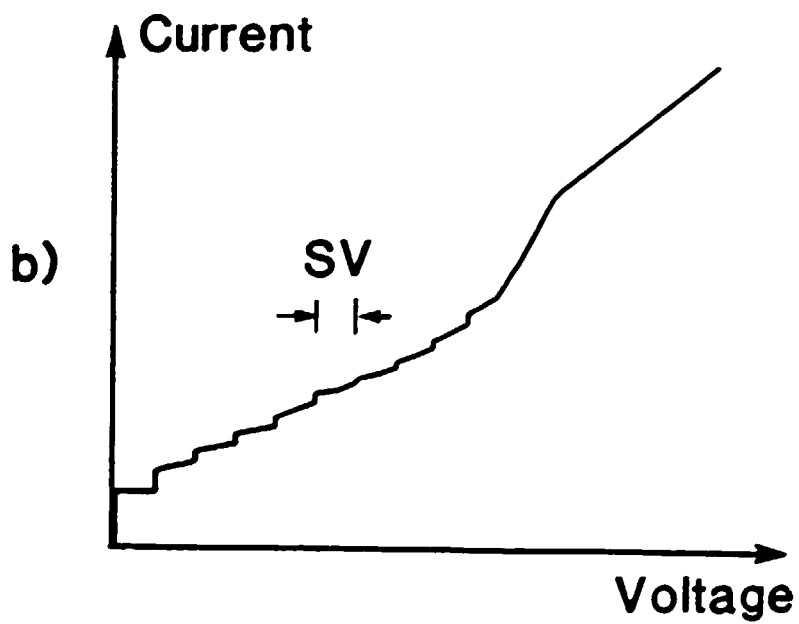
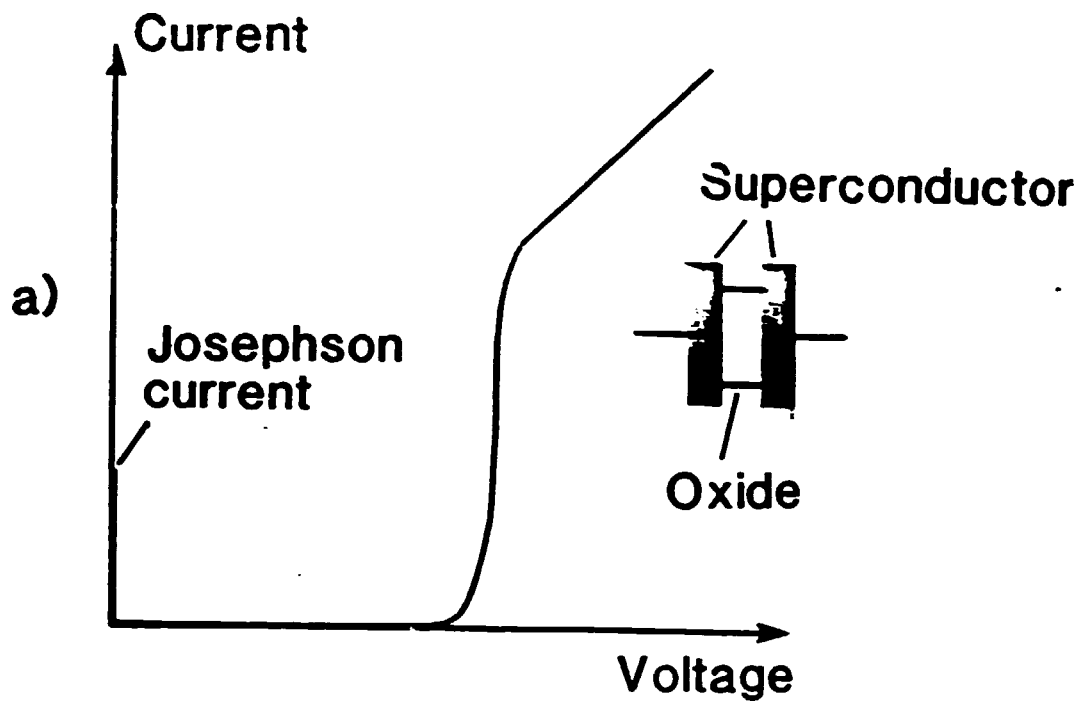


Figure 2

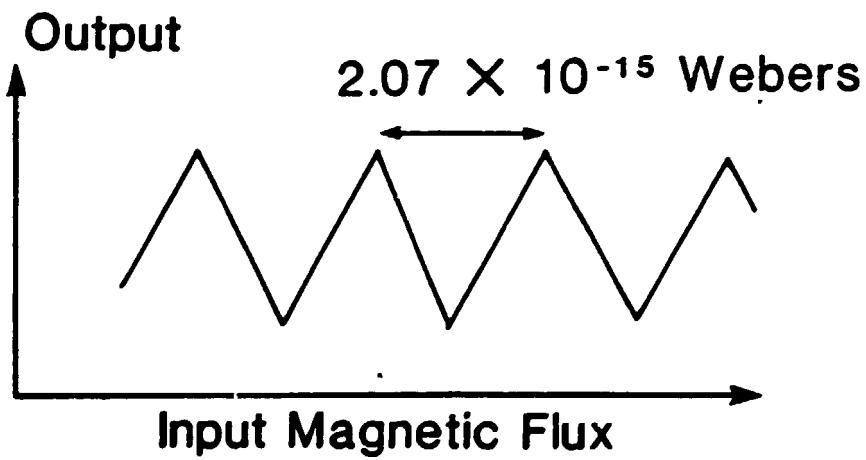
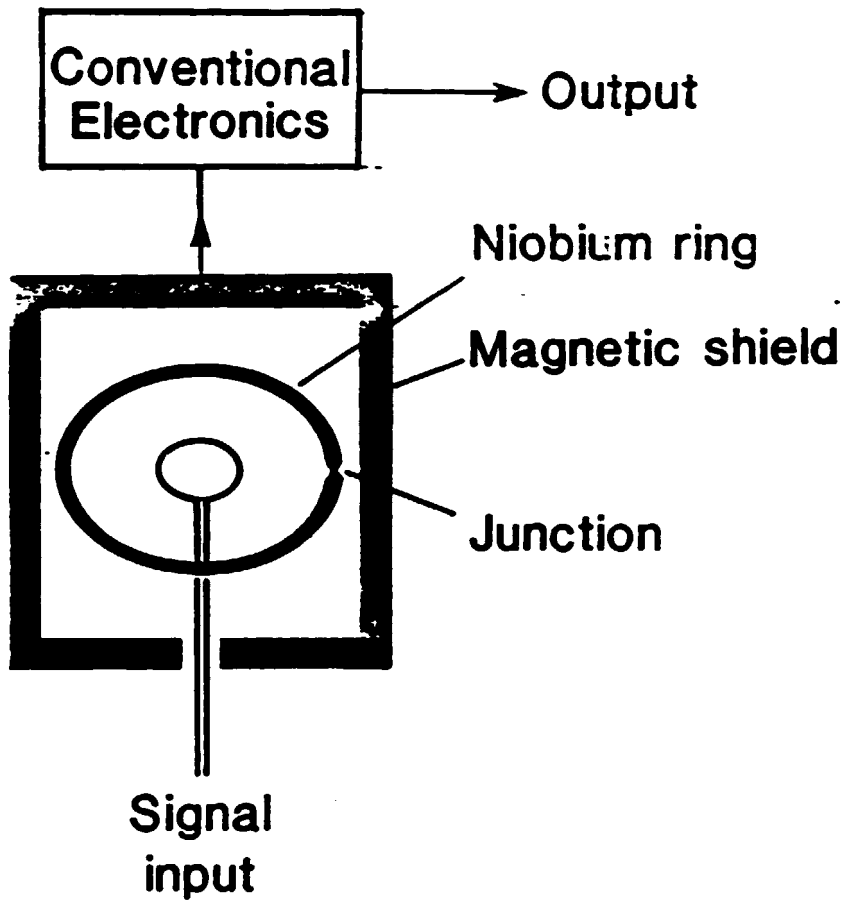


Figure 13.

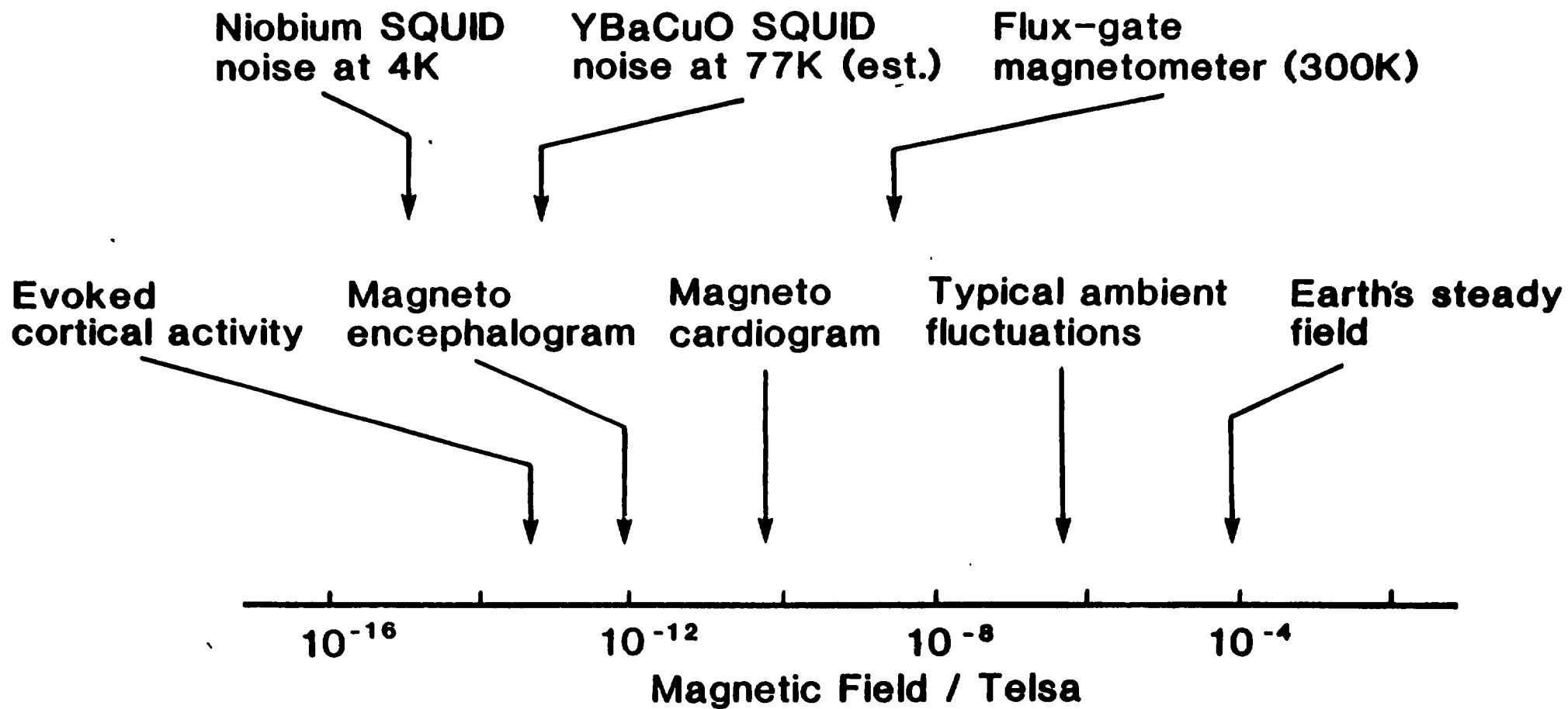


Figure 11