

High-Temperature Superconductivity: History and Outlook

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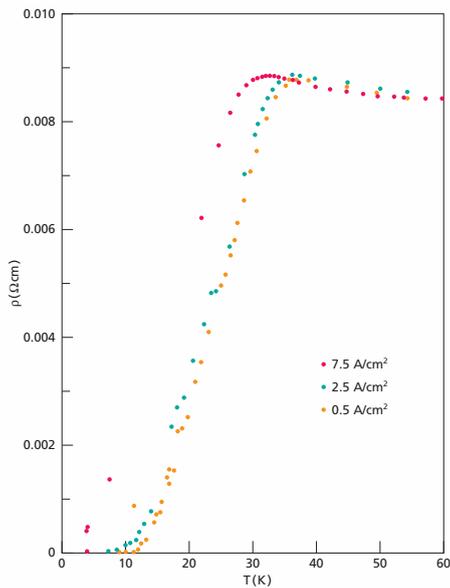


Fig. 1 Low-temperature Resistivity of a Ba-doped LaCuO_3 Sample with $x(\text{Ba})=0.75$, Recorded for Different Current Densities

HISTORY OF HIGH-TEMPERATURE SUPERCONDUCTIVITY

After superconductivity was discovered by Onnes in 1911, many superconductors were discovered and the critical temperature rose year by year. More than 2000 superconducting materials had been discovered by 1975, and the critical temperature had reached 22.3 K with the discovery of Nb_3Ge in 1973. After that, however, no higher critical temperature was obtained for more than 10 years.

When the BCS theory in 1957 provided an elegant explanation for superconducting phenomena, many scientists believed that higher critical temperatures could not be reached without finding new superconducting phenomena. Already in 1954 Fröhlich¹⁾ had proposed a model of high-temperature super-

conductivity in charge density wave systems, and in 1964 Little²⁾ proposed a so-called excitonic superconductivity model. No such superconductors, however, have actually been found.

Sleight³⁾ reported in 1975 that superconductivity was seen in $\text{BaPb}_{(1-x)}\text{Bi}_x\text{O}_3$ and that the critical temperature of this material, which can be as high as 13 K, changes with the Bi/Pb ratio. This was just the beginning of research on the oxide superconductors. Tanaka and others⁴⁾ immediately studied this material and found that the carrier concentration in it is more than an order of magnitude smaller than that in ordinary metals. At that time there was a little bit of hope that the superconductivity seen in this material is non-BCS superconductivity, but today it is still thought to be BCS superconductivity.

In the early 1980s investigators all over the world began looking for new types of superconductivity. In Switzerland a new superconductor, PbMo_6S_8 was found by Chevrel. It had high upper magnetic critical field, but its critical temperature was still only about 16 K. In Japan a government project called "New Superconducting Material" started in 1984, and in the United States a new conference on the "Material and Mechanism of Superconductivity" was held in 1985.

Bednorz and Müller⁵⁾ found early in 1986 that in Ba-doped LaCuO_3 the temperature dependence of the conductivity in the transition region from the normal state to the superconducting state changes with the current density (Fig. 1) and they pointed out this might indicate the possibility of high-temperature superconductivity. Tanaka, Kitazawa, Uchida, and Takagi⁶⁾ at the University of Tokyo immediately started to explore this possibility and at the end of 1986 reported that measurements of resistivity and diamagnetism confirmed that the critical temperature for superconductivity in Ba-doped La_2CuO_4 was as high as 30 K (Fig. 2). Furthermore, in early 1987 Tanaka⁷⁾ pointed

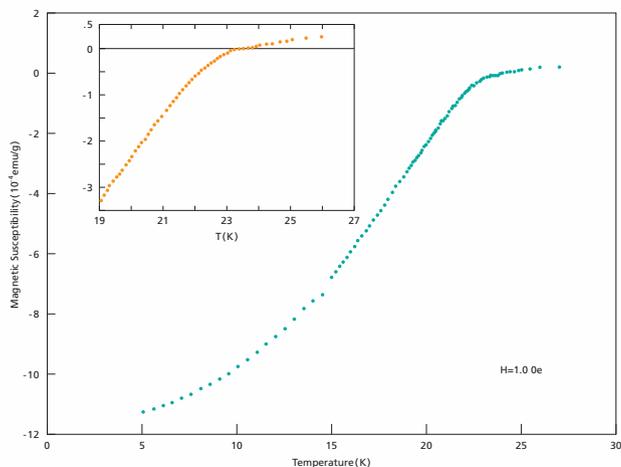


Fig. 2 Temperature Dependence of the Magnetic Susceptibility in Ba-doped La_2CuO_4



Fig. 3 OCMG-processed Gd-Ba-Cu-O Bulk (Single-domain 48 mm ϕ sample)
 Mixing ratio Gd123:Gd211=10:5
 Trapped magnetic field 2.2T at 77K



Silver alloy sheath
 85 strands; width: 3.96 mm; thickness: 0.255 mm; silver ratio design: 1.60;
 $I_c = 96A(77K, 0 T)$; $J_c = 25 \text{ kA/cm}^2$; $J_e = 9.5 \text{ kA/cm}^2$

Fig. 4 Characteristics of High-Jc Bi2223 Conductor

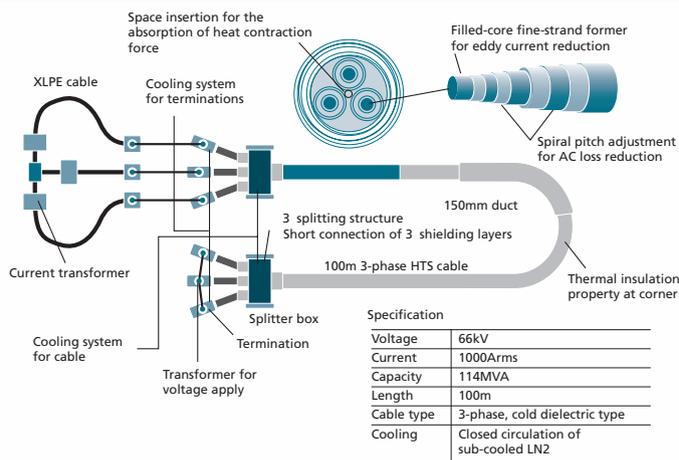


Fig. 5 Superconducting Transmission Cable System & Design Concept



Fig. 6 Cryogen-Free R&D Magnet

out the possibility of two-dimensional superconductivity due to the layer structure of this material. At almost the same time, Anderson⁸⁾ proposed the mechanism of the high-temperature superconductivity based on the two-dimensional resonating valence band model. At that time, many scientists began to think that the superconductivity of Ba-doped La_2CuO_4 cannot be explained by the BCS theory.

In February of 1987 Chu and others⁹⁾ found a new superconducting material, $\text{YBa}_2\text{Cu}_3\text{O}_7$, with a critical temperature above 90 K. Many scientists all over the world then began to search for new superconducting materials with higher critical temperatures. On March 15 of 1987 the American Physical Society held a special symposium on high-temperature superconductivity. Several thousand scientists gathered in the main hall of the Hilton Hotel in New York City, where the enthusiastic atmosphere of the symposium continued until the dawn of the next day. One physicist called this meeting a Woodstock in physics.

Tremendous advances were made in theoretical and experimental research, and new materials were found in quick succession. As a result the critical temperature reached 112 K in a Bi-compound, 126 K in a Tl-compound and 135 K in a Hg-compound. The physical properties of these compounds were also investigated very intensively, and it was confirmed that in all cuprate superconductors the superconductivity occurred in very thin layers including CuO_2 planes. Many kinds of peculiar properties were observed, but except the d-wave symmetry of the superconductivity, most of them are not explained with consistency. The most peculiar property may be the appearance of the stripe structure observed recently in neutron diffraction experiments. In this structure, the electric charges exist in stripes that are separated by the array of magnetically ordered stripes.

The physical properties in the normal state of the high temperature superconductors are so complicated that any theory can not yet explain them in a consistent way. Deeper understanding on "the strongly correlated system" may be necessary in order to solve the origin of the high temperature superconductivity.

OUTLOOK FOR THE FUTURE OF HIGH-TEMPERATURE SUPERCONDUCTIVITY

[1] Material developments

There have in the past ten years been

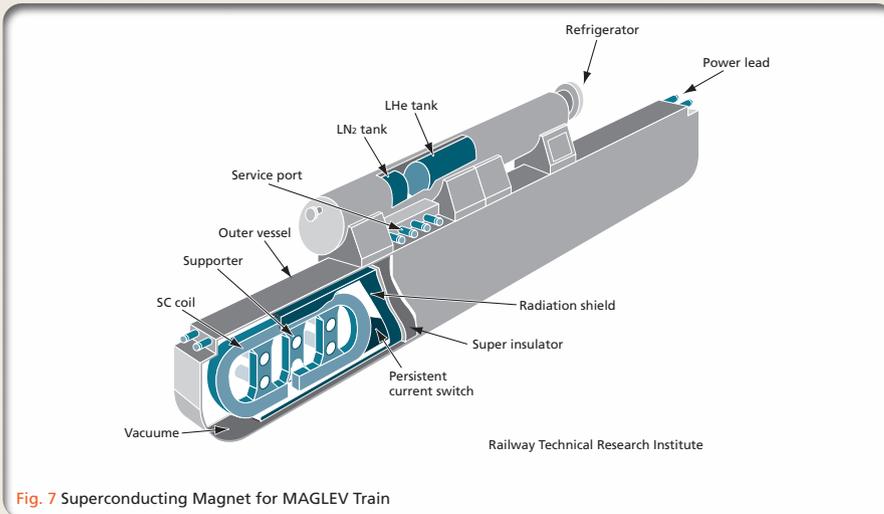


Fig. 7 Superconducting Magnet for MAGLEV Train

posed, but even today there is no consensus among theoretical physicists. There are so many various kinds of interactions in such complicated systems—electron-phonon interactions, spin-spin interactions, charge density waves, spin density waves, and so on—that it may be considered we are just beginning to understand the physics of these complex systems. Explaining this phenomenon clearly will take a long time.

[3] Applications

Since room temperature superconductivity has not been found yet, the applications of high-temperature superconductivity¹²⁾ are restricted to temperatures around that of liquid

many attempts to obtain high-temperature superconductivity in materials other than cuprates. Superconductivity was observed in alkali-ion doped C_{60} at 33 K¹⁰⁾, and Akimitsu very recently found superconductivity in MgB_2 at of 39 K¹¹⁾. But the superconductivity in both these materials is explained by the BCS theory, so it can be said at present that all the non-BCS superconductors belong to cuprate family. We therefore need to find new non-BCS superconductors outside the cuprate family if we raise the critical temperature beyond room temperature. Room temperature superconductivity is still a dream of many scientists, but there is no guideline to reach it at present. A little bit of hope, however, may be found when we consider organic compounds. The methods for analyzing very complicated biological materials, like the human genome, are developing very fast and it may soon be possible to analyze the interactions between complicated genomes and proteins. This would enable us to simulate new organic materials on high-speed supercomputers and evaluate the interaction between electrons and molecules in new materials. This is a way to realize excitonic superconductivity suggested by Little in 1964. This means the progress of future computing science will open a new way for science and technology of new superconducting materials.

[2] Theoretical Developments

After the discovery of the high-temperature superconductivity in cuprates, many kinds of theoretical models of the mechanism of the high-temperature superconductivity were pro-

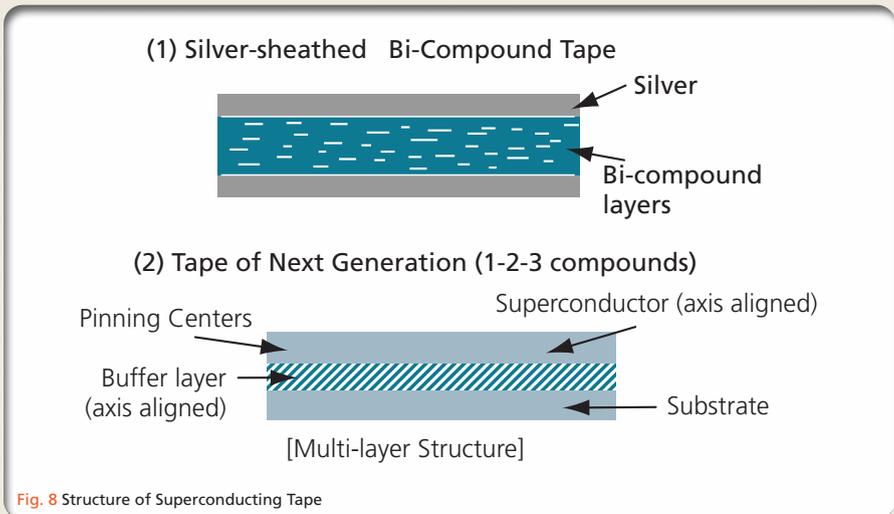


Fig. 8 Structure of Superconducting Tape

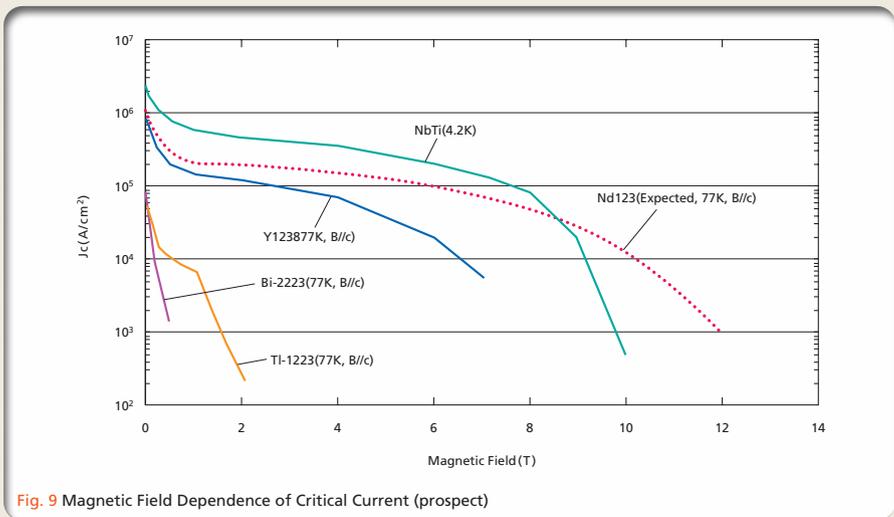


Fig. 9 Magnetic Field Dependence of Critical Current (prospect)

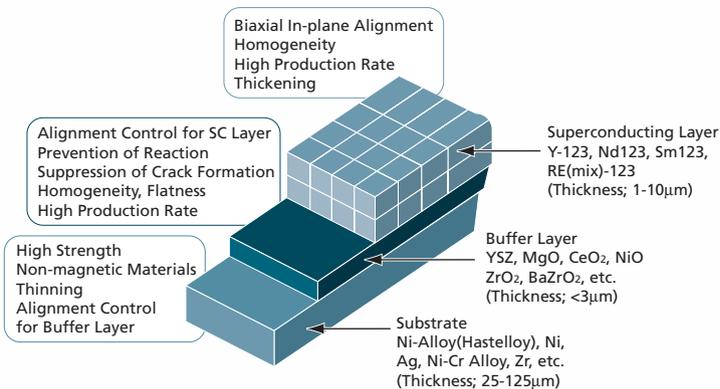


Fig. 10 Structure of Coated Conductor

(b) Superconducting Tapes

The first generation of superconducting tape using high-temperature superconductors is the so-called Silver-Sheathed Bi-Compound Tape. The Bi-compound usually used is Bi₂Sr₂Ca₂Co₃O₁₀, and the cross section of the tape is shown in Fig. 4. At 77 K the critical current of this tape is more than 110 A, and the length of commercial tape is more than 1000 m. Trials of the actual applications of this tape in various fields have already begun. A high-current transmission cable is very important when large amounts of electric power are sent to the central part of a big city. Because digging new underground tunnels is very expensive, it is necessary to use the old tunnel and new superconducting cables that can carry large amounts of power even though they have a small cross section. These trials are being made in Detroit in the United States and in Tokyo, Japan. In Fig. 5 is shown the scheme of the superconducting transmission cable which is under construction in Tokyo Electric Power Company.

Another application is in the superconducting magnet for the pulling system used to make large-diameter crystals of silicon. To prevent oxygen from the crucible of fused quartz from entering the molten silicon, a strong magnetic field must be applied. The photograph in Fig. 6 shows a magnet developed for this system by Toshiba and Sumitomo Electric Co. The newest application trial is the development of a race-track-shaped magnet for the magnetically levitated transportation system (MAGLEV) train in Japan. As shown in Fig. 7, this magnet is about 1 m long and 50 cm in wide, and at 20 K the strength of the mag-

nitrogen. As the refrigeration systems are well developed recently, those applications at liquid nitrogen temperature will greatly contribute to the society.

The fundamental technologies for applications are classified into those of (a) superconducting bulk, (b) superconducting tapes and (c) superconducting devices.

(a) Superconducting Bulk

Materials for superconducting bulks are REBa₂Cu₃O₇, where RE is Nd, Sm, Gd, or Y. The bulk is made by using the quenched melt growth (QMG) method in the case of YBa₂Cu₃O₇, and in other cases is made by using the oxygen controlled melt growth (OCMG) method under a low partial pressure of oxygen. The diameter of the circular plate of bulk reaches more than 10 cm and crystal c-axis is perpendicular to the plate. In the bulk, the pinning force of magnetic flux in the superconducting state is very strong and at 77 K the critical current density is more than 10⁴ A/cm². The applications of the bulk are of two kinds. (1) As the pinning force of the magnetic flux is so strong, the outside magnetic field cannot penetrate the bulk in the superconducting state. This results in a strong levitation force when the bulk is close to an ordinary permanent magnet, and at 77 K this force usually reaches 15 kg/cm². This phenomenon can be exploited to make friction-free flywheel-type electricity storage systems that can store, say, 10 kWh and be used as emergency power supplies. (2) When the bulk is in the normal state, a magnetic field applied from outside is uni-

formly distributed throughout the bulk. But after the bulk is cooled to below the critical temperature, the magnetic field is quantized and quantized flux is pinned by strong pinning centers. Then when the external field is removed, the quantized flux is left inside and behaves like a permanent magnet. The strength of the trapped magnetic field in GdBa₂Cu₃O₇ bulk reaches more than 2 T at 77 K and more than 3.5 T at 30 K (Fig. 3). This is several times the strength of the magnetic field of an ordinary permanent magnet.

One very fruitful application of this bulk would be in a water-cleaning system using the magnetic separation effect. This system would be more than 100 times as efficient as the magnetic-separation cleaning systems available today.

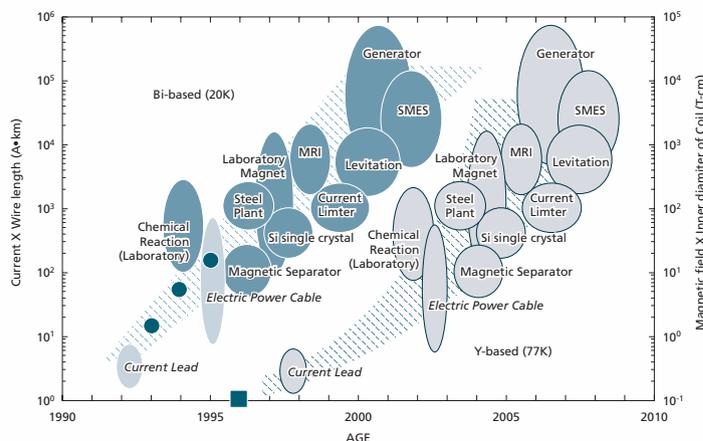


Fig. 11 Expectations of the Development of Superconducting Tape

netic field at the center of the magnet is 5 T. It is hoped that this magnet can replace the magnet made of Nb-Ti wire and operated at 4.2 K, since no quenching phenomena in it is expected and this is very robust against electromagnetic disturbance from outside.

Possible applications of superconducting magnets of this type are appearing all the time: in the continuous casting systems in steel mills, in high-power motors for ship propulsion systems, and in the superconducting magnetic energy storage (SMES) system.

The development of the next generation of superconducting tape is underway in Japan, the U.S., and Europe. This tape, shown in cross section in Fig. 8, has three layers (metal substrate, oxide buffer layer, and superconducting layer) and is called a coated conductor. The superconducting layer is made of $REBa_2Cu_3O_7$, and the critical current density (J_c) and its magnetic field dependence expected from the results of testing the materials are shown in Fig. 9. The question of what kind of combination of three kinds of layers is the most preferable is quite serious at present as is shown in Fig. 10. If the critical current is to be large, the c-axis of superconducting layer must be perpendicular to the surface of substrate. Therefore the alignment of crystal grains in the a-b plane becomes important, as the critical current decreases rapidly when the grain boundary angles are more than 10 degrees.

As mentioned above, in the developments of the coated conductors there are still difficult problems left unsolved, but this superconducting tape is expected to reach the market at around the year of 2005 (Fig. 11).

(c) Superconducting Electronic Devices

The most prominent phenomenon in superconductivity is Josephson tunneling, and most applications of the superconductivity in electronics are based on this phenomenon. The most well known application is the superconducting quantum interference device (SQUID). Its extremely high sensitivity to magnetic fields is exploited in many fields: medical electronics, mass production (e.g., as non-contact defect detectors), and so on.

Another important application is the single quantum flux (SFQ) device. As shown in Fig. 12, the principle operation of the SFQ device is rather simple. The presence and absence of a single magnetic flux quantum in the SQUID ring respectively correspond to information signals

one and zero, and logical circuits can be made by combining SFQ devices. The most important features of this device are that its operation time is only a few picoseconds and its power dissipation is only of the order of 1 nanowatt. As a result, the circuits comprising these devices have very high operating frequencies, of the order of 100 GHz, and consume very little power, of the order of 1 mW. This operation speed is almost 100 times faster than that of ordinary semiconductor circuits and the power consumption is about 1/100 that of the semiconductor circuits. Of course there are many kinds of difficulties in the development of the circuits, as the operating principle of this type of circuit is completely different from that of semiconductor circuits and the design

method is not well established yet.

With regard to the production process, on the other hand, the SFQ circuits have some advantages over semiconductor circuits (Table 1). The most important thing is that SFQ circuits with a 1-micrometer line width are good enough that operating frequencies greater than 100 GHz can be obtained. This means that we can use 10-year-old lithography equipment in the semiconductor industry and that we will be able to produce better characteristic circuits in the future.

A SFQ circuit consisting of several thousand Nb junctions has already been tried and proven to work at very high frequencies at 4.2 K. High-Tc junctions have been made using YBCO, and very recently high-quality Joseph-

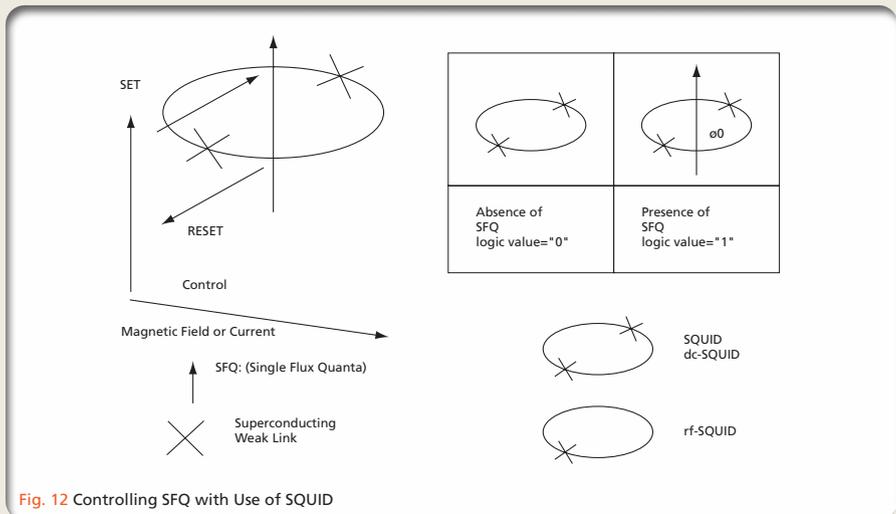


Fig. 12 Controlling SFQ with Use of SQUID

Table 1 Comparison between Semiconductor and Superconductor circuits

	Semiconductor	Superconductor
1. Line Width	< 0.1 μ m	0.8 μ m
2. Lithography	after 2005	completed
3. Structure	Three Dimensional	Two Dimensional
4. Number of Marks	> 20	\approx 10
5. Wiring	Multi-layered ; high resistance heating	Multi-layered ; no resistance no heating
6. Wafer	8 inches ; surface roughness several nm's	3 inches ; surface roughness several nm's
7. Design	Efficient Tool ; Margin. large	Small Tool ; Margin. small
8. Frequency	5 GHz (2005)	50~100 GHz
9. Output	\approx 1V	\approx 0.1mV

Which is easier to make, semiconductor devices or superconductor devices?

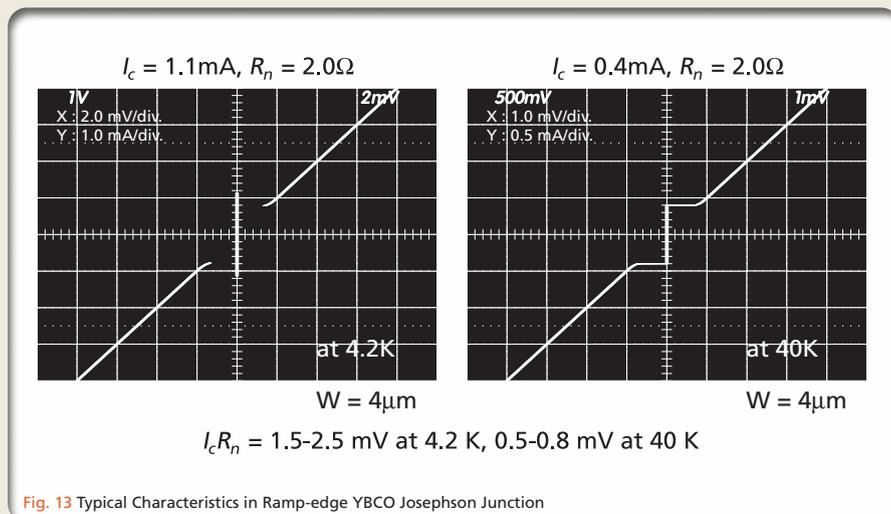


Fig. 13 Typical Characteristics in Ramp-edge YBCO Josephson Junction

son junctions have been made by using an ion-bombarded barrier. These types of junctions are called ramp-edged junctions, and the typical characteristics of this type of junction are shown in Fig. 13. This figure indicates that circuits consisting of this type of junction can work at 40 K.

In order to integrate the junctions, the distribution 1σ of the critical current through junctions is critically important and until now 8%

of distribution in 100 junctions and 10% in 1000 junctions have already been obtained. The relation between possible circuits and the distribution 1σ of junctions is shown in Fig. 14. This figure shows that a high-speed (40 GHz) sampler has already been made and that some circuits of small-scale integration can be made in the very near future. If very inexpensive superconducting chips with excellent characteristics appear on the market, the features of elec-

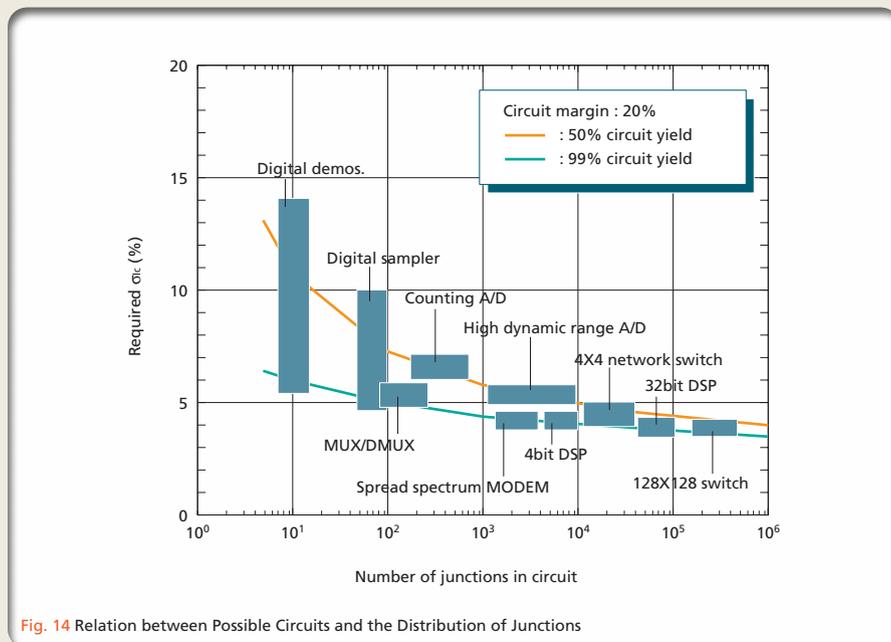


Fig. 14 Relation between Possible Circuits and the Distribution of Junctions

tronics will greatly be changed.

High-quality superconducting microwave filters operating in the gigahertz region are used in the base stations of wireless communication systems, and some of them have already been commercialized. Wireless communication is becoming increasingly important in the information society, and therefore it must play an important role in connection with the development of future software communication systems.

SUMMARY

Fifteen years have already passed since high-temperature superconductivity was discovered in 1986. Many new materials have been found and the critical temperature of superconducting materials has increased to 135 K. To obtain superconductivity at room temperature, however, we must find materials other than those in the cuprate family. It is very difficult to say when that can be done and who can do it. The theoretical basis of high-temperature superconductivity is still uncertain and it must remain in the forefront of solid state physics.

On the other hand, we can see the future of the superconducting technologies more clearly than ever and can expect the superconductivity industry to take off around the year 2005. It must play an important role in the new industrial revolution now underway.

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