Review

Towards higher-\(T_c\) superconductors

By Jun AKIMITSU*1,*2,†

(Communicated by Sumio IJIMA, M.J.A.)

Abstract: New superconductors discovered in the Akimitsu laboratory are reviewed here. These materials can be categorized into two groups:

1) Cu-oxide superconductors.
   1-1 Cu-oxide system having CuO₂ planes.
   1-2 Ladder lattice superconductor.

2) Exploration of new metal-based superconductors.
   2-1 MgB₂ and its application.
   2-2 \(Y_2C_3\).
   2-3 Carrier-doped wide-gap semiconductors.
   2-4 New superconductor with a cage-type structure: \(R_5T_6Sn_{18}\) (\(R = Sc, Y, Lu; T = Rh, Ir\)).

Finally, all of the new superconductors discovered in our laboratory are summarized. The outlook for the high-\(T_c\) superconductors and our present work are also described.

Keywords: high-\(T_c\) superconductors, Cu-oxide system, ladder superconductor, MgB₂, doped semiconductors, Ir oxide

1. Superconductivity and its applications

Superconductivity was discovered in mercury (Hg) by Kamerlingh Onnes of Leiden University in 1911 (\(T_c = 4.2\) K). That was three years after the great achievement of helium (He) liquefaction.

The three major characteristics of superconductivity are first pointed out, and then each of them is explained briefly. They are:

1) Zero electrical resistance (a current will persist indefinitely) (\(E = 0\)),
2) The Meissner effect (\(B = 0\)),
3) The Josephson effect.

(1) Zero electrical resistance. It is well known that many free electrons exist in metals, and that an electric current is a flow of those electrons. In general, electrons are scattered by the oscillations of atoms (phonons), or by impurities in metals. This can be described by Ohm’s law. Since all metal contains impurities, and atoms oscillate, electrons are always being scattered. Thus, it seems to be impossible to ever experience zero electrical resistance. However, zero electrical resistance actually exists under superconductivity. It can thus be concluded that if an electric current is initiated in a circular superconductor, it would continue to flow indefinitely. This is a totally mysterious phenomenon and it is a puzzle that motivates many physicists to understand. Its final solution was offered by three physicists, (Bardeen, Cooper and Shrieffer), which is now known as the BCS theory.

There may be many applications of the phenomenon of zero electrical resistance, such as superconducting magnets, superconducting power transmission, and electricity storage. For example, there is a grand plan to set up global networks of electric power plants using wind-power generation, or solar batteries in deserts or waste land, and to send electricity generated in these plants to remote urban areas through superconducting cables. Another example is linear-motor cars that run by ‘floating their bodies’, using the repulsive power of magnetic fields generated by superconducting magnets.

(2) The Meissner effect. In addition to zero
electrical resistance, superconductivity has another unique characteristic. Superconductors have no internal magnetic flux or no lines of magnetic force within their substance ($B = 0$). This phenomenon is called the Meissner effect, named after its discoverer, which may have many applications, such as magnetic shielding, magnetic levitation, magnetic bearings, and so on.

(3) The Josephson effect. The third major characteristic of superconductivity is the Josephson effect. This is a phenomenon where superconducting electrons flow through between two superconductors separated by a thin barrier, without any voltage being applied. It is a quite unique phenomenon, causing superconducting electrons to flow without a voltage to drive them (DC Josephson effect) or AC current to flow when a DC voltage is applied (AC Josephson effect). In 1962, Josephson, at that time a graduate student at Cambridge University, predicted this phenomenon, specific to superconductivity, that would be a macroscopic effect of quantum mechanics. The most significant application is in a superconducting quantum interference device (SQUID). This may be used in magnetic-field sensors or super high-speed computing machines in the future. Thus, superconductivity is not only wide and deep as fundamental aspect of physics, but also extremely important concerning applications, and it is expected to be a key to such issues as solving ‘Energy problem’. It is no exaggeration to say The 21st century is a century of superconductivity.

2. History of superconductivity exploration—before the discovery of copper oxide superconductors

As mentioned above, superconductivity is a very interesting study area, and has many possible applications. The most serious difficulty, however, is that the superconducting state is only achieved below a certain temperature, the critical temperature ($T_c$), which is usually very low. Nb$_3$Ge was a substance with the highest critical temperature obtained by 1980, at 22 K. B.T. Matthias wrote that a room-temperature superconductor is only pure science fiction. However, many scientists have continuously attempted to find superconductors with a higher $T_c$, and I was one of those people.

The next problem concerns what guiding principles are required to produce a higher $T_c$? The only clue is an equation for the superconducting transition temperature ($T_c$) can be expressed as follows:

$$T_c \cong \Theta_D \exp \left(-\frac{1}{\lambda}\right),$$

where $\Theta_D$ is the Debye temperature, $N(0)$ is the state density on the Fermi surface in the normal conducting state, and $\lambda$ is the size of the electron-phonon interaction.

The parameters that may be easily controlled are the Debye temperature, $\Theta$, and $N(0)$. Matthias focused on substances having a high $N(0)$ (the Matthias Rule). Upon systemic exploration of substances by this method, however, a breakthrough concerning the upper limit of $T_c$ could not be obtained. Therefore, we focused on substances with a large electron-phonon interaction, $V$. However, when the electron-phonon interaction is increased steadily, electrons are combined in real space, form pairs in real space and stop moving, which becoming insulators. These are called charge density wave (CDW) type insulators. Based on this idea, we discovered that Nb$_{1-x}$Ta$_x$Se$_3$ became a superconductor when $T_c \cong 4$ K, by substituting the Ta at the Nb site to the CDW material, NbSe$_3$ to form Nb$_{1-x}$Ta$_x$Se$_3$ and reducing $V$ (Fig. 2).

![Fig. 1. Phase diagram of the electron-phonon coupling constant $V$ vs. superconducting critical temperature $T_c$. (N. Tsuda, K. Nasu, J. Fujimori and K. Siratori: Electronic Conduction in Oxide (in Japanese) p. 120.)](image-url)
3. Discovery of copper oxide superconductors

3-1. New Cu-oxide system having CuO$_2$ planes. Meanwhile, Bednorz and Müller discovered copper oxide superconductors (1986). The substance they found was an oxide, called La–Ba–Cu–O. It is said that they first noticed that crystals were distorted because Cu$^{2+}$ was a Jahn-Teller ion, and they supposed that a high $T_c$ might be obtained by changing the static distortion to a dynamic charge fluctuation. This is very similar to our idea. After that discovery, many groups figured out that this substance was two-dimensional, and that $T_c$ was quickly increased to 160 K just a few years later.

This “revolution within the history of science” eliminated the widely accepted major prejudice that superconductivity is only possible in non magnetic materials. Leaving to other books the dramatic historical details of how a small bud germinated by Bednorz and Müller blossomed into a mainstream concept, here we describe what I did during this period. It is well known that after Bednorz and Müller discovered superconductivity in a copper oxide, a group led by Paul Chu found YBa$_2$Cu$_3$O$_y$ (YBCO). Around that time, I started studying the Cu-oxide system in earnest. My idea of how to create a new superconductor centered on the radius of ions. As shown in Table 1, I noticed that all ionic radii of elements in superconductors obtained until then were in the vicinity of 1 Å. Are there any other elements with ionic radii in that vicinity? I found that only four such ions exist: Bi$^{3+}$, Tl$^{3+}$, Hg$^{2+}$, and Cd$^{2+}$, as listed in Table 1. Surprisingly, these elements (except for Cd), were components of Bi-based, Tl-based, and Hg-based superconductors with a higher $T_c$.

![Diagram](image_url)

**Fig. 2.** (a) Normalized resistance as a function of the temperature for Nb$_{1-x}$Ta$_x$Se$_3$ with several Ta concentrations. (b) Ta concentration dependence of $T_c$. Substituting Ta to CDW material NbSe$_3$, forming Nb$_{1-x}$Ta$_x$Se$_3$ to be superconductive.© K. Kawabata.

Table 1. Ionic radius around 1 Å. Upper part (Ca $^{2+} \sim$ Y$^{3+}$) shows the elements, being composed of La-Sr(Ba)-Cu-O and Y-Ba-Cu-O systems. Lower part (Bi$^{3+} \sim$ Cd$^{2+}$) is the expected elements. Later, these elements Bi$^{3+}$, Tl$^{3+}$ and Hg$^{2+}$ are composed of the high-$T_c$ superconductors, called Bi-, Tl- and Hg-systems.

| Cation | Ionic radius [Å] (6-coordination) |
|--------|----------------------------------|
| Ca$^{2+}$ | 1.02 |
| Sr$^{2+}$ | 1.18 |
| Ba$^{2+}$ | 1.38 |
| Y$^{3+}$ | 0.91 |
| La$^{3+}$ | 1.08 |
| Bi$^{3+}$ | 1.04 |
| Tl$^{3+}$ | 1.08 |
| Hg$^{2+}$ | 1.04 |
| Cd$^{2+}$ | 0.97 |

We now describe here some successful and unsuccessful stories. At that time, we started with the combination of Bi–Sr–Cu–O suggested by Table 1, and immediately obtained a superconductor with $T_c = 6$ K. Figure 3 shows its crystal structure and electrical resistance. In a search of superconductors with a higher $T_c$, we replaced Nd$^{3+}$, etc. with different valences at the site of Sr$^{2+}$ for carrier doping. We then found signs of superconductors with $T_c = 50$ K, and were excitedly working on its single-phase formation. Meanwhile we heard about the discovery of Bi–Sr–Ca–Cu–O with $T_c = 77$ K and $T_c = 105$ K by Maeda et al. I was disappointed by this discovery, because when one of my students tried to replace Sr$^{2+}$ with Ca$^{2+}$, I did not agree with his idea, because Sr$^{2+}$ and Ca$^{2+}$ are both divalent elements, and they would only dissolve, leading to
nothing interesting chemically. However, it became clear that, in fact, when Sr and Ca are mixed, they enter into completely different sites due to their different ionic radii, resulting in different crystal structures (Fig. 4).

Here is another example of our successful and unsuccessful cases. There is a substance, Nd₂CuO₄, called a fluorite type structure, whose structure was known at that time. Unlike La₂CuO₄, it does not have oxygen above and below the copper in its crystal structure. We figured out that this substance became metallic when Ce⁴⁺ was replaced with Nd³⁺.

Then, one of my students suggested, “let’s mix Sr²⁺ in addition to Ce⁴⁺.” But I objected to this idea, saying that the number of carriers might be canceled if Sr²⁺ was mixed with Ce⁴⁺. But I remembered my previous mistake, and agreed to try this idea, in fact, a superconductor with a totally new structure emerged.²)³) Figure 5 shows its crystal structure (called “T* structure”) and electrical resistivity.

Shortly after that, however, Tokura et al. discovered a new type of superconductor,¹⁰) an electron-doped type, by reducing the oxygen in (Nd₁₋ₓCeₓ)₂CuO₄. This is called the T’ structure. Figure 6 shows the “214”-type crystal structure with a different coordination having a CuO₂ plane.

Meanwhile, some essential characteristics of copper oxide superconductors had become clear.

1. The first is the existence of a CuO₂ plane consisting of Cu and O. This “parent compound” is both antiferromagnetic and insulating at the same time. This is called a Mott insulator.

2. The second characteristic is that a superconductor emerges after holes or electrons are introduced into this Mott insulator, and electricity starts flowing. Block layers adhere to the CuO₂ plane and adjust the electric charges. Figure 7 is a schematic diagram of these block layers.¹¹) Superconductors with different Tc are generated by replacing these block layers.
The next logical step is to assemble new superconductors using these block layers. This idea is specifically to create new superconductors by finding new block layers, and combining them with existing block layers. For example, there is a substance with the crystal structure $\text{Sr}_2\text{CuO}_2(\text{CO}_3)^{12}$ This is a new copper oxide that includes a carbonate group, but this is not a superconductor itself. What should be done to dope this with a carrier? One of my doctor-course students, Masatomo Uehara (currently Yokohama National University), came up with an interesting method. It was to replace $\text{CO}_3^{-2}$ with $\text{BO}_3^{-3}$, and thus effectively inject a carrier, and generating a new superconductor, $\text{Sr}_2\text{CuO}_2(\text{CO}_3)_{1-x}-(\text{BO}_3)_x$. Figure 8 shows a phase diagram with the boron content $x$ vs. temperature in $\text{Sr}_2\text{CuO}_2-(\text{CO}_3)_{1-x}(\text{BO}_3)_x$. This superconductor is a new copper oxide that includes a carbonate group. Is it possible to create a new type superconductor by combining this crystal structures and those of existing superconductors? It was not as easy as it sounds, but we finally were able to synthesize a

![Fig. 7. Concept of the block layer. CuO$_2$ layers are inserted between block layers.](image)

![Fig. 8. Phase diagram of $\text{Sr}_2\text{CuO}_2(\text{CO}_3)_{1-x}(\text{BO}_3)_x$. Carriers can be controlled by (BO$_3$) content.](image)

![Fig. 9. Three types of superconductor composed of different block layers including the carbonate layers. (a) $\text{Sr}_2\text{CuO}_2(\text{CO}_3)_{1-x}(\text{BO}_3)_x$ ($T_c = 55\,\text{K}$) (b) $\text{Sr}_2\text{CaCuO}_2(\text{CO}_3)_{1-x}(\text{BO}_3)_x$ ($T_c = 105\,\text{K}$) (c) $\text{Sr}_2\text{Ca}_2\text{CuO}_4(\text{CO}_3)_{1-x}(\text{BO}_3)_x$ ($T_c = 115\,\text{K}$).](image)
new superconductor under high pressure. Figure 9 shows an example of such a superconductor. We were successful in synthesizing 3 new superconductors with \( T_c = 55 \) K, 105 K and \( T_c = 115 \) K.\(^{14,15}\)

### 3-2. Discovery of ladder lattice superconductors

A common characteristic of these superconductors is having a CuO\(_2\) plane, which does not essentially introduce any new physics. Is it possible to discover yet more superconductors that belong to new categories? To search for such a situations, we focused on a ladder lattice, which has the structure shown in Fig. 10. The Takano Group of the Institute for Chemical Research at Kyoto University discovered SrCuO\(_2\) with a two-leg ladder lattice, and Sr\(_2\)CuO\(_3\) with a three-leg ladder lattice. It was experimentally demonstrated that two-leg ladder lattice substances had spin gaps and three-leg ladder lattice substances had no spin gaps.\(^{16}\) Since then, T.M. Rice,\(^{17}\) E. Dagotto\(^{18}\) and others have pointed out the theoretical possibility of superconductivity in ladder lattice substances. They noted that superconductivity was expressed in the even-numbered ladder lattices and that spin gaps survived.

Are there really such convenient ladder lattice substances? It is amazing how well things work out in nature! Such a substance does exist in reality: Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\). It is called a ‘telephone-number’ compound due to its peculiar sequence of numbers: 14–24–41. As shown in Fig. 11, this substance’s crystal structure is layered with one-dimensional chain layers on a CuO\(_2\) plane and two-leg ladder layers on a Cu\(_2\)O\(_3\) plane. As is evident in its valence of Cu\(^{2.25+}\), many holes already exist in this substance. These holes are mainly localized in one-dimensional chain layers, and their electrical conductivity is similar to that of semiconductors. What should be done to move these holes in the chain layers to ladder layers? The easiest method is to shorten the distance between layers. To achieve this, the Sr site may simply be filled instead with Ca. In fact, when Sr is replaced by Ca in Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}\)O\(_{41}\), its electrical resistivity decreases. In actual experiments, Ca may replace Sr only up to \( x = 8.4 \). Under a high oxygen pressure, however, Ca successfully replaced Sr up to \( x = 13.6 \). Unfortunately, however, superconductivity did not emerge. As a last resort, we measured its electrical resistivity under pressure in cooperation with Dr. Mori’s group in the Institute for Solid State Physics (ISSP) at the University of Tokyo, and in fact we found superconductivity of \( T_c = 12 \) K at 3 GPa (Fig. 12).\(^{19}\) It was also confirmed by using the single crystal.\(^{20}\)

### 4. Exploration of metal-based new superconductors

#### 4-1. MgB\(_2\) and its applications

During these explorations, we felt that we hit a dead-end with oxide superconductors, and decided to start exploring metal-based ones. Our guiding principle at that time was again the BCS theory. As shown in Eq. [1], \( T_c \) is proportional to the Debye temperature (\( \Theta \)). In general, the lighter are the elements, the higher becomes the Debye temperature. It is expected that superconductivity with lighter elements would have a higher \( T_c \). Thus, we focused on boron (B). I provided Jun Nagamatsu, an undergraduate student at that time, a research topic: to explore compounds of Mg with each of Ti and B. We included Ti because we thought that magnetic ions would play an essential role in some way, and B because it is a light element. Shortly after we began this study, Nagamatsu found a decrease in the magnetization, which was a precursory phenomenon of superconductivity. But
we had a hard time to make it a single phase. Finally, Nagamatsu was able to figure out that Ti was not necessary in this superconductivity, and the essential point was to create a substance with a very simple structure, called MgB2. Figure 13 shows the electrical resistivity, and magnetic susceptibility, as a function of temperature. Figure 14 shows the crystal structure of MgB2. There were two points that surprised us upon the discovery of this substance. First, MgB2 was a reagent available on the market. It was surprising that a substance commercially available as a reagent is actually a superconductor with a high $T_c$. This was picked up in the “News and Views” section of Nature with the title “Genie in a bottle” (pp. 23–24). The second interesting news was that MgB2’s crystal structure was called the AlB2 structure, which consists of a honeycomb structure of B and a triangular grid of Mg, the layers of which created a characteristic 2-D lattice. In fact, this type of AlB2 structure exists in large numbers (Table 2), and most of these substances were synthesized by B.T. Matthias. Strangely, however, Matthias did not synthesize MgB2. He would have regretted this oversight greatly if he were alive today. MgB2 itself, obtains a high $T_c$ through the electron-phonon interaction coupled with the strong lattice vibration of B, and it is believed that this is a typical (textbook) superconductivity, described by electron-phonon interaction. What is interesting about MgB2 is that the band on the B plane (called $\sigma$ band) and the band connecting the Boron and Mg ions (called the $\pi$ band) both contribute to the superconductivity, which is called two-band superconductivity. Figure 15 shows this band structure and the Fermi surface.

Thus, MgB2 is a typical BCS-type superconductor, mostly explained by the electron-phonon interaction, but its most interesting point is its applications. The critical temperature ($T_c$) is not the only parameter to be considered in applications. In general, superconductivity breaks down in a strong enough magnetic field, termed the critical magnetic field ($H_c$). Superconductivity also breaks if a large amount of electric current is applied, termed the critical current ($J_c$). In short, superconductivity exists in a region defined by a critical temperature, critical magnetic field and critical current. For the widest range of practical applications, superconductors with high $T_c$, $H_c$, $J_c$ are needed. Unlike $T_c$, $H_c$ and $J_c$ may be increased by various means. For

---

**Table 2. List of the MB$_2$-series materials synthesized by B.T. Matthias, except for the MgB$_2$**

| MB$_2$ | Tc (K) | Reference |
|--------|--------|-----------|
| ScB$_2$ | 86 | (J. C. Castaing et al. J. Phys. Chem. Solids (1972) Vol. 33, 533) |
| TiB$_2$ | 143 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| ZrB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| NbB$_2$ | 0.41 | (J. C. Castaing et al. J. Phys. Chem. Solids (1972) Vol. 33, 533) |
| HfB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| TaB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| MoB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| Wb$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| ReB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| TcB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| RuB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| OsB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| MoB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| Wb$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| ReB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| TcB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| RuB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| OsB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| MoB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| Wb$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| ReB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| TcB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| RuB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| OsB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| MoB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| Wb$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| ReB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| TcB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| RuB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| OsB$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
| MoB$_2$ | 0.42 | (L. Andersson et al. Solid State Communications Vol. 47, 1986) |
| Wb$_2$ | 0.42 | (L. Leyarde et al. J. Less-Common Metals 67, 1979) |
example, $J_c$ and $H_c$ is drastically increased by mixing in small amounts of impurities.

To be used in superconducting magnets and transmission cables, MgB$_2$ must be turned into wires. In that regard, MgB$_2$’s advantages include:

1. It may be used at a relatively high temperature (approximately 20 K), which is impossible for conventional metal-based superconducting materials.

2. Since bonding between crystal grains is strong, which makes it possible to transfer a large amount of superconducting current from one crystal grain to an adjacent one, it is not necessary to align the direction of crystal grains (as in copper oxide high-temperature superconductors). Therefore, it is relatively easy to create wires.

3. From the perspective of resources, both Mg and B are abundant raw materials that can be obtained at relatively low prices in a stable supply. Values of $H_c$ and $J_c$ for MgB$_2$ may be enhanced with the processing procedures mentioned above. Thus, many studies have been conducted globally to create wires since the discovery of MgB$_2$ superconductivity, and wires longer than several km have been produced experimentally.
Some of the methods for the creation of MgB$_2$ wires have been proposed based on past knowhow. Figure 16 shows two fabrication methods: (1) \textit{In situ} powder-in-tube (PIT) method and (2) Internal Mg diffusion (IMD) method. Recently, the most common method has been Powder-in-Tube (PIT), where a starting powder is stuffed into metal tubes, and processed before and/or after placement in the tube. There are basically two PIT methods. One is an \textit{ex-situ} method, where pre-processed MgB$_2$ powder is stuffed into metal tubes, such as stainless steel. The other is an \textit{in-situ} method, where a mixed powder of Mg and B is stuffed in a tube to fabricate tapes, which are then heat-treated. In the \textit{ex-situ} method, the greatest advantage is that a worthwhile $J_c$ may be obtained, even without the heat-treatment process. A further heat treatment (annealing) improves the binding between crystal grains, leading to a higher $J_c$. In the \textit{in-situ} method, the reactivates of Mg and B are enhanced with a heat treatment, and at the same time, unlike in the \textit{ex-situ} method, there is our advantage that the crystal grains are rarely oriented.

Another effective method to increase the MgB$_2$ core density is an internal Mg diffusion (IMD) process. The IMD method is believed to provide a higher $J_c$ due to our improved connectivity of MgB$_2$. The starting materials used are also important. Recently, there have been many reports that the characteristics of $J_c$ are improved when a trace amount of minute impurities is added to a mixed powder of Mg and B. Currently, the most effective method is to add minute SiC particles that are in the nanometer range. Figure 17 shows the temperature dependence of $B_{c2}$ in MgB$_2$ tapes with no additives, and those with SiC added. In wires with SiC added, $B_{c2}$ for 4.2 K was as high as 30 T. This value is equal to or greater than the value of $B_{c2}$ in Nb$_3$Sn wires. The $B_{c2}$ in 20 K wires ranges up to 11 T. This shows that currently used utility wires may be replaced with MgB$_2$.

Naturally, for use in magnet wires, the magnetic field dependence of $J_c$ is an important factor. Figure 18 shows the present status of MgB$_2$ wires prepared by both the PIT and IMD methods. As shown in Fig. 18, for the practical level at 20 K and
2T, $J_c$ in PIT wire keeps $J_c \sim 10^5 \text{A/cm}^2$. Unfortunately, $J_c$ reduces to $1.2 \times 10^4 \text{A/cm}^2$ at 20K and 5T. However, there has recently been rapid progress in this area. By using the IMD method, it reached to almost $9 \times 10^4 \text{A/cm}^2$ at 20K and 5T. The future is promising.

4-2. $Y_2C_3$. Since discovering the MgB$_2$ superconductor, we have conducted broad explorations of superconductors that include light elements, such as boron (B) and carbon (C). As a result, we found that $Y_2C_3$ is a superconductor ($T_c = 18$ K) synthesized under high pressure. Figure 19 shows the temperature dependence of the resistivity and susceptibility at ambient pressure. $T_c$ is controllable by a synthesis condition$^{25-27}$ Afterwards, we found that this substance had already been reported by Krupka et al.$^{28}$ as having a maximum $T_c$ of 11.5 K. Figure 20 shows its crystal structure to be the Pu$_2C_3$-type, with a body-centered cubic structure (b.c.c.). Its Y atoms line up along the $<111>$ direction, and its carbon atoms form dimers, with an extremely short C-C bond length. It is expected that its C-C stretching phonon mode is very high. Therefore, the relatively high $T_c$ of $Y_2C_3$ is thought to be the result of electron-phonon coupling between high-frequency phonons and the C-C antibonding state in the vicinity of the Fermi level. A characteristic of both $Y_2C_3$ and La$_2C_3$, which has the same structure as $Y_2C_3$, is that they are superconductors with two gaps. This was first suggested by NMR measurement of spin-lattice relaxation.$^{29}$ It was then clarified further in a µSR measurement.$^{30}$ Figure 21 shows the temperature...
dependence of the muon spin relaxation rates of La$_2$C$_3$ and Y$_2$C$_3$. Solid and dashed lines are fitted with the s-wave’s phenomenological double-gap model.\textsuperscript{30} It was theoretically suggested that in the crystal structure of Y$_2$C$_3$, a strong spin-orbit interaction might lead to a mixed state of symmetric isotropic and anisotropic superconducting properties due to the lack of a space inversion symmetry. It was reported later that $B_{c2}$ is very high, at approximately 30 Tesla, which may be related to the above state.

4-3. Superconductivity of carrier-doped semiconductors.

(1) Superconductivities of boron-doped diamond and Si. Diamonds, famously known as jewels, do not allow the flow of electricity, as is evident from their sparking. Surprisingly, however, it was discovered that diamonds become superconductive if carrier-doped ($T_c = 3$ K).\textsuperscript{31} By making films even thinner, its $T_c$ was raised to 12 K.\textsuperscript{32} The superconducting transition $T_c = 0.35$ K was also reported when B was doped into silicon (Si), with a similar crystal structure.\textsuperscript{33} Both substances are typical wide-gap semiconductors with the well-known diamond structure. If highly concentrated hole carriers are doped to those wide-gap semiconductors, superconductivity will be created. Since then, many theoretical studies have been actively conducted, indicating the possibility of the emergence of superconductivity at considerably higher temperatures, depending on the doped B atoms’ order or alignment.\textsuperscript{34}

We tried to create superconductivity by B replacement (hole doping) in SiC, with characteristics similar to those of diamonds and Si, and discovered that its bulk was a superconductor with $T_c = 1.4$ K.\textsuperscript{35}

We also tried to use aluminum (Al) as a hole dopant in the same manner, and verified a superconducting transition at a similar $T_c$ ($\approx 1.4$ K).\textsuperscript{36} In the following sections, the basic physical properties that have been discovered so far are explained.

(2) Crystal structure of SiC. SiC has a crystal structure in which C and Si are basically placed at even intervals in a diamond-type structure. However, when one looks precisely, many different structures emerge (polytype: crystal polymorphism), depending on the type of lamination layer formed. Although 200 or more polytypes have been verified currently, 3C-, 4H-, 6H-, and 15R-SiC (Ramsdell notation system) are the most important in applications, and have a high probability. In this notation system, the first number refers to the number of Si-C unit layers included in the layer direction (c, axis direction) during one cycle; C, H and R are the initial letters of crystal systems (C: cubic, H: hexagonal, R: rhombo-
The zincblende structure that often emerges in other semiconductors is expressed as 3C, and the wurtzite structure is 2H. All band structures are of the indirect transition type, the same as that of Si. Among these polytypes, we focused on 3C-SiC and 6H-SiC (Fig. 22), and attempted hole doping in each of them.

(3) Superconductivity of B-doped SiC. Figure 23 shows the temperature dependence of the electrical resistivity in SiC samples (3C-SiC:B, 6H-SiC:B), where B was doped into 3C-SiC and 6H-SiC. In both, though the $T_c$ values are low (approximately 1.4 K), a sharp superconducting transition can be observed. Also, in these transitions, substantial Meissner diamagnetism has been observed in measurements of the DC magnetic susceptibility (Fig. 23), and specific-heat jumps have been observed, confirming bulk superconductivity. It is considered that differences in $T_c$ and the residual resistance between these substances show their disparity in reactivity, since 3C-SiC is in its low-temperature stabilized phase and 6H-SiC is in its high-temperature stabilized phase.

Figure 24 shows a magnetic field vs. temperature phase diagram of the superconducting state, as determined by measuring the electrical resistivity with changing temperature under a constant magnetic field ($T$-scan), and also with a changing magnetic field under a constant temperature ($H$-scan). As shown in Fig. 24, $T_c$ during the cooling process starting from $T > T_c$ and the $T_c$ observed during the warming process do not match. This
strongly suggests that B-doped SiC is a Type I superconductor. In general, simple elements, such as tin (Sn) and lead (Pb), become Type I superconductor, and Type I superconductivity in a chemical compound is very rare. The above-mentioned B-doped diamonds and B-doped Si are reported to be Type II superconductors.

(4) Superconductivity of Al-doped SiC. Figure 25 shows the temperature vs. electrical resistivity and magnetic susceptibility in SiC samples (3C-SiC:Al), where 3C-SiC was doped with Al. $T_c$ was approximately 1.5 K, almost equal to that of the above B-doped SiC, for which superconductivity can be verified. Also, in this transition, substantial Meissner diamagnetism has also been observed in measurements of the DC magnetic susceptibility, and a specific-heat jump has also been observed, confirming bulk superconductivity.

Figure 26 shows a magnetic field and temperature phase diagram of the superconducting state, as determined by measuring the electrical resistivity with changing the temperature under a constant magnetic field, and also with changing magnetic field under a constant temperature. Unlike the above B-doped SiC, under a finite magnetic field, that observed during the cooling process matched the $T_c$ observed during the warming process, suggesting that this is a Type II superconductor, the same as B-doped diamond and B-doped Si.

(5) Discussion and outlook. The superconductivity of B-doped SiC involves almost the same carrier density as the superconductivity in B-doped diamond and B-doped Si, and its crystal structure is almost the same as that of diamond. It is very interesting to understand why only B-doped SiC is a Type I superconductor. Our experimental results may contribute to a qualitative understanding of this question by using the impurity level formed in semiconductors.

Table 3 summarizes the normal-state properties, including the impurity levels ($E_A$), and also the superconducting parameters of B-doped diamond (C:B), B-doped Si (Si:B), B-doped SiC (SiC:B), and Al-doped SiC (SiC:Al).

Although B-doped Si has been reported as forming Type II superconductors, recent studies
suggest that they may be Type I superconductors, as revealed by samples with improved quality. B-doped Si’s Type I superconductivity may have been hidden due to the crystals’ irregularities and/or disorder, resulting in their being reported as Type II superconductivity despite the fact that it is essentially Type I superconductivity. What is observed from these parameters is that the disorder of the impurity or its level has a large impact if the acceptor level is deep, and leads to Type II superconductivity. SiC:Al may be positioned on the border of Type I and Type II superconductivities in hole-doped superconductors. Also, since the state density in the vicinity of SiC’s Fermi level is mainly due to the Si structure, it is inferred that the Si may be more important than the C for superconductivity. Based on structural analysis results, it is considered that Al may show Type II superconductivity due to the stronger impact of any disorder of Al, since it is supposed that B is then transposed to the C site and Al is transposed to the Si site.

### 4-4. New superconductor with a cage-type structure—R<sub>5</sub>T<sub>6</sub>Sn<sub>18</sub> (R = Sc, Y, Lu; T = Rh, Ir).

In this section, a new superconductor with a cage-type structure that we have worked on is briefly explained. R<sub>5</sub>T<sub>6</sub>Sn<sub>18</sub> (R = Sc, Y, Lu; T = Rh, Ir) was first discovered by Remelika et al. We, however, discovered a totally new experimental fact by systematically synthesizing single-crystal samples of it. R<sub>5</sub>T<sub>6</sub>Sn<sub>18</sub> has a cage-type structure consisting of R<sub>5</sub>T<sub>6</sub>Sn<sub>18</sub> (Fig. 27). This is a group in which the superconducting state changes as the R element included in the cage changes. The superconducting transition temperatures are T<sub>c</sub> = 5, 3, or 4 K, for R = Sc, Y, or Lu, respectively. Sc, with the smallest ionic radius, has the highest T<sub>c</sub> (Fig. 28). The most noteworthy characteristic of this group is that the superconducting gaps change substantially depending on the rare-earth ion, R. The magnetic field dependencies of the quasiparticle state densities
resulting from specific-heat measurements in Lu$_5$Ir$_6$Sn$_{18}$ and Lu$_5$Rh$_6$Sn$_{18}$ at various temperatures are $\gamma \sim H^{0.50}$ and $\gamma \sim H^{1.1}$, respectively, representing isotropic superconducting gaps. While these isotropic superconducting gaps may be explained by the BCS theory, the magnetic-field dependencies of $\gamma$ in Y$_5$Ir$_6$Sn$_{18}$ and Y$_5$Rh$_6$Sn$_{18}$ are $\gamma \sim H^{0.58}$ and $\gamma \sim H^{0.56}$, respectively, representing anisotropic superconducting gaps (Fig. 29).

Table 4 summarizes the normal and superconducting parameters. Unfortunately, the physical reason why such a major physical property changes so substantially when rare-earth elements are changed is not yet clear.

![Fig. 29. Quasiparticle state density ($\gamma$) vs. magnetic field.](image)

Table 4. Superconducting parameters obtained from experiments in R$_5$T$_6$Sn$_{18}$ (R: Sc, Y, Lu, T: Rh, Ir). It is noted that anisotropic superconductors only appear for R = Y.

| Space group | Sc$_5$Rh$_6$Sn$_{18}$ | Sc$_5$Ir$_6$Sn$_{18}$ | Y$_5$Rh$_6$Sn$_{18}$ | Y$_5$Ir$_6$Sn$_{18}$ | Lu$_5$Rh$_6$Sn$_{18}$ | Lu$_5$Ir$_6$Sn$_{18}$ |
|-------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Gap asymmetry | $I_a/\ ac$ | $I_a/\ ac$ | $I_a/\ ac$ | $I_o/\ ac$ | $I_a/\ ac$ | $I_a/\ ac$ |
| $a$ (nm) | 1.3601 | 1.3595 | 1.3792 | 1.3735 | 1.3671 | 1.3602 |
| $c$ (nm) | 2.7198 | 2.7180 | 2.7498 | — | 2.7330 | 2.7315 |
| $T_c$ (K) | 5.0 | 1.0 | 3.0 | 2.1 | 4.0 | 3.0 |
| $\mu_0H_c(0)$ (mT) | 99.1(1) | 12.2(1) | 50.1(4) | 30.4(1) | 75.0(2) | 47.6(1) |
| $\mu_0H_{c2}(0)$ (mT) | 5.64(1) | — | 2.49(2) | 1.46(1) | 4.38(1) | 1.87(2) |
| $\lambda(0)$ (nm) | 34.2(1) | — | 51.4(2) | 67.2(1) | 38.8(1) | 59.2(2) |
| $\xi(0)$ (nm) | 6.74(1) | — | 8.84(4) | 15.9(1) | 7.68(2) | 13.0(1) |
| $\kappa(0)$ | 51.7(1) | — | 59.1(4) | 62.1(1) | 50.5(1) | 66.8(1) |
| $\gamma$ (mJ/(mol-K$^2$)) | 51.0(4) | 27.3(4) | 37.8(4) | 32.1(2) | 49.1(4) | 31.9(1) |
| $\Theta_D$ (K) | 276(2) | 246(2) | 185(1) | 212(2) | 158(1) | 193 |
| $\Delta(0)$ (meV) | 0.990(3) | 0.140(1) | — | — | 0.719(2) | 0.544(3) |
| $\Delta_c/\gamma T_c$ | 2.55(36) | 1.39 | 1.96 | 1.68 | 2.02 | 1.83 |
| $2\Delta(0)/k_BT_c$ | 4.26(3) | 3.26(6) | — | — | 4.12(2) | 4.07(5) |
5. Summary and outlook

5-1. Summary—Discovery of new superconductors. In the previous sections, the main topics concerning the new superconductors discovered in our laboratory are described, which can be categorized into two groups:

1. Cu-oxide superconductors.
   1-1 Cu-oxide system having CuO$_2$ planes.
   1-2 Ladder lattice superconductor.

2. Exploration of metal based new superconductors.
   2-1 MgB$_2$ and its application.
   2-2 Y$_2$C$_3$.
   2-3 Carrier-doped wide-gap semiconductors.
   2-4 New superconductor with a cage-type structure: R$_5$T$_6$Sn$_{18}$ (R = Sc, Y, Lu; T = Rh, Ir).

These superconductors are representative materials that we discovered.

Finally, we summarize here all of the superconductors discovered in our laboratory (Table 5).

From the Table 5, we chose typical examples of superconductivities as well as crystal structures in Cr$_2$Re$_3$B$_6$ $^{61}$ NaAlSi$_6$ $^{62}$ and Li$_x$IrSi$_2$ (Fig. 30).

5-2. Outlook for the higher-$T_c$ superconductors. In a previous section, we described what we have done. Next is our future prospects concerning what we should attack. We present here several candidates to achieve higher-$T_c$ ($T_c \geq 100$ K) superconductors.

(1) Hydride system. The first one is the hydride system. Hydride system has long been expected to be a candidate of room-temperature superconductor. Unfortunately, however, only a moderate $T_c \sim 17$ K was observed in the Pd hydrate experimentally. Recently, much attention has been paid to superconductivity at 203 K at ultra-high pressure in SH$_3$. $^{63}$ Subsequently, superconductivity above 260 K (near room temperature!) has been discovered in LaH$_{10}$. $^{64,65}$ Disappointedly, it has only been achieved under ultra-high pressure at around 200 GPa, which is not a practical pressure. The next step is to discover a new hydride system, and to realize a high-$T_c$ superconductor under ambient pressure.

(2) Superconductivity in 4d, 5d system. The second big problem is that “Is there any other existing transition metal (except for Cu, Fe) oxide/chalcogenide superconductor? In particular, a high-$T_c$ superconductor of the 4d, 5d system is unexplored?” This will be discussed in the next section.

(3) High-$T_c$ superconductor originated from charge fluctuation or valence skipping system. It is well known that the origin of a high-$T_c$ superconductor in Cu-oxide is due to magnetic fluctuation instead of some electron-phonon interaction. In this sense, the

Fig. 30. Typical examples of superconductivities and crystal structures chosen from Table 5. (a) Cr$_2$Re$_3$B$_6$ $^{61}$ (b) NaAlSi$_6$ $^{62}$ and (c) Li$_x$IrSi$_2$. 

J. AKIMITSU [Vol. 95,
charge fluctuation is another candidate to produce high-$T_c$ superconductivity, for example $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($T_c \approx 30 \text{ K}$) is believed to be a charge fluctuation-mediated superconductor.

However, why can we not get a higher-$T_c$ ($T_c \geq 100 \text{ K}$) superconductor mediated by charge fluctuation? This is a third big problem.

### 5-3. Our present work

In this section, we briefly describe what we are presently working on.

Recently, much attention has been paid to superconductivity in the Iridate system. If superconductivity is realized in this system with the strong spin-orbit coupling (S.O.C), it will open the new dimension in condensed-matter physics. In partic-

#### Table 5. New superconductors discovered in the Akimitsu laboratory

| Year | Superconductor | $T_c$ (K) | Reference |
|------|----------------|-----------|-----------|
| 1987 | Bi-Sr-Cu-O     | 6         | 5, 6      |
| 1988 | Nd-Fe-Sr-Cu-O  | 28        | 8, 9      |
| 1989 | (Eu,Ce)-(Ba,Ln)-Cu-O (Ln = Nd, Sm, Eu) | 43 | 40 |
| 1992 | (Y,Ca)-Sr-Cu(CO$_2$)-O | 63 | 41 |
| 1992 | (Bi,Pb)-Sr-Cu-(CO$_2$)-O | 41, 54 | 42 |
| 1993 | Sr-Ca-Cu-(CO$_2$)-(BO$_3$)-O | 33, 55, 105, 115 | 14, 15 |
| 1993 | Ti-(Ba,Sr)-Cu-(CO$_3$)-O | 70 | 43 |
| 1993 | Hg-Ba-Sr-Cu-(CO$_3$)-O | 66 | 44 |
| 1994 | Ba-Ca-Cu-(CO$_2$)-(BO$_3$)-O | 120 | 45 |
| 1994 | (Ca,Na)-Ca-Cu-O-Cl | 49 | 46 |
| 1995 | (Ca,A)-Cu-O-Br (A = Na, K) | 19 | 47 |
| 1996 | Ba-Ca-Cu-O-F | 38, 106, 108 | |
| 1996 | Sr-Ca-Cu-O(14-24-41) | 12 | 19 |
| 1998 | Cu-Sr-(Y,Ce)-Cu-O | 43 | 48 |
| 1999 | Ru-Sr-Y-Cu-O | 40 | 49 |

| Year | Superconductor | $T_c$ (K) | Reference |
|------|----------------|-----------|-----------|
| 1984 | (Nb,Ta)Se$_3$ | 4 | 1 |
| 2001 | MgB$_2$ | 39 | 21 |
| 2003 | Re-B | 5 | 50 |
| 2004 | Y$_2$C$_3$ | 18 | 25 |
| 2006 | (W,Mo)-Re-(B,C) | 7, 8 | 51 |
| 2007 | NaAlSi | 7 | 62 |
| 2007 | SiC:B | 1.4 | 35 |
| 2008 | SiC:Al | 1.5 | 36 |
| 2008 | AlN$_x$ | 2.8 | |
| 2009 | W$_x$Si$_3$ | 2.8 | 52 |
| 2010 | YSn$_2$ | 7 | 53 |
| 2010 | Y$_3$Pt$_5$Ge$_6$ | 2.6 | 54 |
| 2011 | W$_x$SiB$_2$ | 5.8 | 55 |
| 2012 | (Ta,W)$_3$SiB$_2$ | 6.5 | 56 |
| 2012 | KAIX (X = Si, Ge) | 3.5, 4 | |
| 2012 | AE(TM,Si)$_2$ (AE = Ca, Sr, Ba; TM = Ni, Pd, Pt, Cu, Ag, Au) | 0.9–3.5 | 57 |
| 2013 | KSn$_2$ | 3.2 | 58 |
| 2013 | A$_4$(Al,Ge)$_{16}$ | 4, 4.4 | 59 |
| 2013 | Lu$_2$SnC | 5 | 60 |
| 2014 | Cr$_2$Re$_2$B | 6 | 61 |
ular, Sr$_2$IrO$_4$/Ba$_2$IrO$_4$ has been predicted to be a high-temperature superconductor upon electron doping, since it highly resembles the cuprate in the crystal structure and magnetic coupling constant. Particularly, the remarkable resemblance between Sr$_2$IrO$_4$/Ba$_2$IrO$_4$ and La$_2$CuO$_4$ makes a good candidate to expect unconventional HTSC in Sr$_2$IrO$_4$/Ba$_2$IrO$_4$ (Fig. 31). Indeed:

1) A low-temperature STM study on the K-doping (effectively electron doping) in the clean surface of Sr$_2$IrO$_4$ demonstrates the clear spin gap state.

2) Moreover, Y.K. Kim et al. observed the low-temperature nodal Fermi surface and high-temperature Fermi arcs.

Fig. 31. (a) Crystal structure of La$_2$CuO$_4$ and Sr$_2$IrO$_4$. (b) Schematic diagram of the 5d energy levels split by the crystal field ($\Delta$), spin–orbit coupling (SOC), and on-site Coulomb repulsion (U) leading to the formation of unoccupied (upper) and occupied (lower) Hubbard bands at around the Fermi level from the $J_{\text{eff}} = 1/2$ band and the fully occupied $J_{\text{eff}} = 3/2$ band.

Fig. 32. (a)–(c) Second derivative of ARPES intensity plots as a function of the binding energy and wave vector on Sr$_{2-x}$La$_x$IrO$_4$ ($x = 0$, 0.04 and 0.08) measured along the $k$ direction. (d) Schematic graph of the doping-induced change in the electronic structure of Sr$_{2-x}$La$_x$IrO$_4$ derived from our ARPES study.

Fig. 33. Magnetic phase diagram of Sr$_{2-x}$La$_x$IrO$_4$ determined from magnetic susceptibility and µSR measurements.
These experimental results suggest clear evidence of a d-wave pairing correlation. However, direct evidence of superconductivity, such as zero resistivity ($\rho = 0$) and the Meissner effect ($B = 0$), can not be observed in the bulk system. We have tried to observe evidence of superconductivity in a carrier-doped bulk material. Recently, we published our evidence of superconductivity in the bulk system. We have tried to observe such a d-wave pairing correlation. However, direct evidence of superconductivity can be realized with increasing the carrier concentration (Fig. 32).

Our conclusions are summarized as follows at the present stage:

1. We can successfully enhance the solubility limit until $x = 0.13$ by using a mechanical alloying method.
2. The $\mu$SR measurement indicates that there is non-oscillatory signal that indicates the absence of a long-range order below $T_N$ (Fig. 33).
3. At around $x = 0.1$, the Griffith phase (short-range AF clusters) appears to grow upon cooling in the paramagnetic phase.
4. Magnetic susceptibility becomes dramatically suppressed with more fluorine substitution at on apical oxygen site.

In conclusion, however, we can not get a bulk superconductivity, probably due to insufficient carriers in the IrO$_2$ planes.

Acknowledgements

I deeply acknowledge my colleagues, Drs. H. Sawa, M. Uehara, T. Muranaka, Y. Zenitani, S. Akutagawa, K. Kawashima, K. Horigane, Z.A. Ren, S. Kuroiwa, N. Kase and all our members in my laboratory for our collaborations. In particular, I deeply acknowledge Dr. Kumakura for the discussion of applications of MgB$_2$. Finally, we thank to K. Horigane, M. Akimitsu, E. Sakamoto and H. Tanaka for assisting me to prepare the manuscript.

References

1) Noma, S., Saito, T., Ekino, T., Akimitsu, J. and Sueno, S. (1993) Superconducting phase in Nb$_{1-x}$Ta$_x$Se$_3$ ($0.135 < x < 0.16$). Phys. Rev. B 48, 9620–9627.
2) Kawabata, K. (1985) Impurity effects on superconductivity and charge density waves in NbSe$_3$. J. Phys. Soc. Jpn. 54, 762–770.
3) Bednorz, J.G. and Müller, K.A. (1986) Possible high-$T_c$ superconductivity in the Ba-La-Cu-O system. Z. Phys. B 64, 189–193.
4) Wu, M.K., Ashburn, J.R., Torng, C.J., Hor, P.H., Meng, R.L., Gao, L. et al. (1987) Superconductivity at 93K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure. Phys. Rev. Lett. 58, 908–910.
5) Akimitsu, J., Yamazaki, A., Sawa, H. and Fujik, H. (1987) Superconductivity in the Bi-Sr-Cu-O system. Jpn. J. Appl. Phys. 26, L2080–L2081.
6) Akimitsu, J. (1988) Superconducting and physical properties of Bi-Sr-Cu-O system. Jpn. J. Appl. Phys. Ser. 1 Supercond. Mater. 19–23.
7) Maeda, H., Tanaka, Y., Fukutomi, M. and Asano, T. (1988) A new high-$T_c$ oxide superconductor without a rare earth element. J. Appl. Phys. 27, L209–L210.
8) Akimitsu, J., Suzuki, S., Watanabe, M. and Sawa, H. (1988) Superconductivity in the Nd-Sr-Ce-Cu-O system. Jpn. J. Appl. Phys. 27, L1859–L1860.
9) Sawa, H., Suzuki, S., Watanabe, M., Akimitsu, J., Matsubara, H., Watabe, H. et al. (1989) Unusually simple crystal structure of an Nd-Sc-Sr-Cu-O superconductor. Nature 337, 347–348.
10) Tokura, Y., Takagi, H. and Uchida, S. (1989) A superconducting copper oxide compound with electrons as the charge carriers. Nature 337, 345–347.
11) Tokura, Y. and Arima, T. (1990) New classification method for layered copper compounds and its application to design of new high $T_c$ superconductors. Jpn. J. Appl. Phys. 29, 2388–2402.
12) Miyazaki, Y., Yamane, H., Kajitani, T., Oku, T., Hiraga, K., Morii, Y. et al. (1992) Preparation and crystal structure of Sr$_2$CuO$_2$(CO$_3$)$_3$. Physica C 191, 434–440.
13) Uehara, M., Nakata, H. and Akimitsu, J. (1993) Superconductivity in the new compound Sr$_2$CuO$_2$(CO$_3$)$_3$. Physica C 216, 453–457.
14) Nakata, H., Uehara, M., Akimitsu, J. and Matsui, Y. (1994) A new family of superconductors containing carbonate group. Bull. Electrotech. Lab. 58, 468–472.
15) Uehara, M., Uoshima, M., Ishiyama, S., Nakata, H., Akimitsu, J., Matsui, Y. et al. (1994) A new homologous series of oxy carbonate superconductors Sr$_2$(Ca,Sr)$_{n-1}$Cu$_n$(CO$_3$)$_{3n-1}$(BO$_3$)$_n$O$_{(2n+1)}$ ($n = 1$, 2 and 3). Physica C 229, 310–314.
16) Azuma, M., Hiroi, Z., Takano, M., Ishida, K. and Kitaoka, Y. (1994) Observation of a spin gap in SrCu$_2$O$_3$ comprising spin-1/2 quasi-1D two-leg ladders. Phys. Rev. Lett. 73, 3463–3466.
17) Rice, T.M., Gopal, S. and Sigrist, M. (1993) Superconductivity, spin gaps and luttinger liquids in a class of cuprates. Europhys. Lett. 23, 445–449.
18) Dagotto, E., Riera, J. and Scalapino, D. (1992) Superconductivity in ladders and coupled planes. Phys. Rev. B 45, 5744–5747.
19) Uehara, M., Nagata, T., Akimitsu, J., Takahashi, H., Mori, N. and Kinoshita, K. (1996) Superconduct-
tivity in the ladder material Sr$_{12}$Ca$_{14}$Cu$_{25}$O$_{41.84}$. J. Phys. Soc. Jpn. **65**, 2764–2767.
20) Nagata, T., Uehara, M., Goto, J., Akimitsu, J., Motoyama, N., Eisaki, H. *et al.* (1998) Pressure-induced dimensional crossover and superconductivity in the hole-doped two-leg ladder compound Sr$_{14-x}$Ca$_x$Cu$_2$O$_{41}$. Phys. Rev. Lett. **81**, 1090–1093.
21) Nagamatsu, J., Nakagawa, N., Muranaka, T., Zenitani, Y. and Akimitsu, J. (2001) Superconductivity at 39 K in magnesium diboride. Nature **410**, 63–64.
22) Kortus, J., Mazin, I.I., Belashchenko, K.D., Antropov, V.P., and Boyer, L.L. (2004) Superconductivity in (Bi,Pb)-oxycarbonate system. Physica C **396**, 13–17.
23) Kuroiwa, S., Saura, Y., Akimitsu, J., Uehara, M., Goto, J., Akimitsu, J. *et al.* (2007) Superconductivity at 39 K in magnesium diboride. Nature **444**, 465–468.
24) Akutagawa, S., Ohashi, T., Kitano, H., Maeda, A. *et al.* (2007) Microwave electrical resistivity of moderately high $T_c$ superconductor, $Y_2$C$_3$. Physica C **460–462**, 649–650.
25) Amano, G., Akutagawa, S., Muranaka, T., Zenitani, Y. and Akimitsu, J. (2004) Superconductivity at 18 K in yttrium sesquicarbide system, $Y_3C_2$. J. Phys. Soc. Jpn. **73**, 530–532.
26) Akutagawa, S. and Akimitsu, J. (2007) Superconductivity of $Y_3C_2$ by specific heat measurement. J. Phys. Soc. Jpn. **76**, 024713.
27) Akutagawa, S., Ohashi, T., Kitano, H., Maeda, A. and Akimitsu, J. (2007) Microwave electrical resistivity of moderately high $T_c$ superconductor, $Y_2$C$_3$. Physica C **460–462**, 649–650.
28) Kuroiwa, S., Saura, Y., Akimitsu, J., Hiraishi, M., Miyazaki, M., Satoh, K.H. *et al.* (2008) Multigap superconductivity in sesquicaricides $La_2C_3$ and $Y_2$C$_3$. Phys. Rev. Lett. **100**, 097002.
29) Kuroiwa, S., Saura, Y., Akimitsu, J., Hiraishi, M., Miyazaki, M., Satoh, K.H. *et al.* (2008) Multigap superconductivity in sesquicaricides $La_2C_3$ and $Y_2$C$_3$. Phys. Rev. Lett. **100**, 097002.
30) Kuroiwa, S., Saura, Y., Akimitsu, J., Hiraishi, M., Miyazaki, M., Satoh, K.H. *et al.* (2008) Multigap superconductivity in sesquicaricides $La_2C_3$ and $Y_2$C$_3$. Phys. Rev. Lett. **100**, 097002.
31) Ekinov, E.A., Sidorov, V.A., Bauer, E.D., Mel'nik, N.N., Curro, N.J., Thompson, J.D. *et al.* (2004) Superconductivity in diamond. Nature **428**, 542–545.
32) Takano, Y., Nagao, M., Sakaguchi, I., Tachiki, M. and Hatanaka, T. (2004) Superconductivity in diamond thin films well above liquid helium temperature. Appl. Phys. Lett. **85**, 2851–2853.
33) Buser, E., Marcelet, C., Achert, P., Kacmanick, J., Levy, F., Huey, A. *et al.* (2006) Superconductivity in doped cubic silicon. Nature **444**, 465–468.
34) Fukuyama, H. (2006) High-temperature superconductivity by transforming bonds into bands. J. Supercond. Novel Mag. **19**, 201–202.
35) Ren, Z.A., Kato, J., Muranaka, T., Akimitsu, J., Kriener, M. and Maeno, Y. (2007) Superconductivity in boron-doped SiC. J. Phys. Soc. Jpn. **76**, 103710.
36) Muranaka, T., Kikuchi, Y., Yoshizawa, T., Shirakawa, N. and Akimitsu, J. (2008) Superconductivity in carrier-doped silicon carbide. Sci. Technol. Adv. Mater. **9**, 044204.
37) Reimeika, J.P., Espinosa, G.P., Cooper, A.S., Barz, H., Rowell, J.M., McWhan, D.B. *et al.* (1980) A new family of ternary intermetallic superconducting/magnetic stannides. Solid State Commun. **34**, 923–926.
38) Kase, N., Kittaoka, S., Sakakibara, T. and Akimitsu, J. (2012) Superconducting gap structure of the cage compound $Se_2RhSn_18$. J. Phys. Soc. Jpn. **81**, SB016.
39) Volovik, G.E. (1993) Superconductivity with lines of GAP nodes: Density of states in the vortex. JETP Lett. **58**, 469–473.
40) Sawa, H., Obara, K., Akimitsu, J., Matsu, Y. and Horiiuchi, S. (1989) A new family of superconducting copper oxides: (Ln$_{1-x}$Ce$_x$)$_2$(Ba$_{1-y}$La$_y$)$_2$CuO$_{6-2x}$. (Ln: Nd, Sm, Eu). J. Phys. Soc. Jpn. **58**, 2252–2255.
41) Akimitsu, J., Uehara, M., Ogawa, M., Nakata, H., Tomimoto, K., Miyazaki, Y. *et al.* (1992) Superconductivity in the new compound (Y$_{1-x}$,Ca)$_{1.95}$Sr$_{2.0}$CuO$_{4}$ (CO)$_{0.6}$O$_{y}$. Physica C **201**, 320–324.
42) Uehara, M., Nakata, H., Akimitsu, J., Den, T., Kobayashi, T. and Matsu, Y. (1993) Superconductivities in the (Bi,Pb)-oxycarbonate system. Physica C **213**, 51–56.
43) Matsui, Y., Ogawa, M., Uehara, M., Nakata, H. and Akimitsu, J. (1993) Incommensurate and commensurate superstructures in the oxycarbonate superconductor $TlSr_2$Ba$_2$Cu$_2$(CO$_3$)$_x$ ($x \approx 2$). Physica C **217**, 287–293.
44) Uehara, M., Sahoda, S., Nakata, H., Akimitsu, J. and Matsu, Y. (1994) New Hg-based oxycarbonate superconductor $HgBa_2Sr_2Cu_2$O$_{6+\delta}$ (CO$_3$)$_x$. Physica C **222**, 27–32.
45) Akimitsu, J., Uoshima, M., Ishiyama, S., Sato, M., Nakata, H., Uehara, M. *et al.* (1995) New oxycarbonate superconductors $Sr_3(Ca, Sr)$_{1-y}$Ca_{1+y}$ (CO$_3$)$_x$ ($n = 1, 2, 3$) and $Ba_2Ca_{n-1}Cu_3$(CO$_3$)$_3$ ($n = 3$). In Superconductivity and Superconducting Materials Technologies (ed. Vincenzini, P.). Advances in Science and Technology, Vol. 8, Techna, Faenza, pp. 35–40.
46) Zenitani, Y., Inari, K., Sahoda, S., Uehara, M., Akimitsu, J., Kubota, N. *et al.* (1995) Superconductivity in (Ca$_{1.4}$Ba$_{0.6}$)$_{1.4}$Cu$_{2}$O$_{6}$. Adv. Synth. Met. **24**, 167–170.
47) Zenitani, Y., Sahoda, S., Akimitsu, J., Kubota, N. and Ayabe, M. (1996) New superconductor with apical bromine (Ca$_{1.4}$Ba$_{0.6}$)$_{1.4}$Cu$_{2}$O$_{6}$. Adv. Synth. Met. **24**, 167–170.
48) Tamura, M., Sato, M., Den, T. and Akimitsu, J. (1998) A new superconductor with 1222 structure
49) Takagiwa, H., Akimitsu, J., Furukawa, H. and Yoshizawa, H. (2001) Coexistence of superconductivity and (anti-)ferromagnetism in RuSr2YCu2O8. J. Phys. Soc. Jpn. 70, 333–336.

50) Kawano, A., Mizuta, Y., Takagiwa, H., Muranaka, T. and Akimitsu, J. (2003) The superconductivity in Re-B system. J. Phys. Soc. Jpn. 72, 1724–1728.

51) Kawashima, K., Kawano, A., Muranaka, T. and Akimitsu, J. (2006) Superconductivity in M7Re13X4 (M = W, Mo, X = B, C) compounds. Physica B 378–380, 1118–1119.

52) Kawashima, K., Muranaka, T., Kousaka, Y., Akutagawa, S. and Akimitsu, J. (2009) Superconductivity in the ternary germanide Y3Pt4Ge6. J. Phys. Soc. Jpn. 78, 1118–1119.

53) Kawashima, K., Maruyama, M., Fukuma, M. and Akimitsu, J. (2010) Superconducting state in YSn3 with the MgZn2-type structure. J. Korean Phys. Soc. 57, 1118–1119.

54) Kase, N., Muranaka, T. and Akimitsu, J. (2008) Superconductivity in the ternary germanide Y3Pt4Ge6. J. Phys. Soc. Jpn. 77, 054714.

55) Fukuma, M., Kawashima, K., Maruyama, M. and Akimitsu, J. (2011) Superconductivity in W5SiB2 with the T2 phase structure. J. Phys. Soc. Jpn. 80, 024702.

56) Fukuma, M., Kawashima, K. and Akimitsu, J. (2012) Superconducting state in (W,Ta)5SiB2. Phys. Procedia 27, 48–51.

57) Kawashima, K., Inoue, K., Ishikawa, T., Fukuma, M., Yoshikawa, M. and Akimitsu, J. (2012) Superconductivity in Ba(TM,Si)2 (TM = Pd, Pt, Cu, Ag and Au) with AlB2-type structure. J. Phys. Soc. Jpn. 81, 4717.

58) Miyazaki, S., Kawashima, K., Ipponjima, T., Fukuma, M., Hyakumura, D. and Akimitsu, J. (2013) Superconductivity in KSn2 with the MgZn2-type structure. J. Korean Phys. Soc. 63, 475–476.

59) Ipponjima, T., Kawashima, K., Miyazaki, S., Hyakumura, D., Yoshikawa, M. and Akimitsu, J. (2013) New germanide superconductors with the type-I clathrate type structure. Physica C 494, 74–76.

60) Kuchida, S., Muranaka, T., Kawashima, K., Inoue, K., Yoshikawa, M. and Akimitsu, J. (2013) Superconductivity in Lu2SnC. Physica C 494, 77–79.

61) Niimura, H., Kawashima, K., Inoue, K., Yoshikawa, M. and Akimitsu, J. (2014) Superconductivity in the ternary boride Cr2ReB with the β-Mn-type structure. J. Phys. Soc. Jpn. 83, 044702.

62) Kuroiwa, S., Kawashima, H., Kinoshita, H., Okabe, H. and Akimitsu, J. (2007) Superconductivity in ternary silicide NaAlSi with layered diamond-like structure. Physica C 466, 11–15.

63) Drozdov, A.P., Eremets, M.I., Troyan, I.A., Ksenofontov, V. and Shylin, S.I. (2015) Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system. Nature 525, 73–76.

64) Drozdov, A.P., Kong, P.P., Minkov, V.S., Besedin, S.P., Kuzovnikov, M.A., Mozaffari, S. et al. (2019) Superconductivity at 250 K in lanthanum hydride under high pressure. Nature 569, 528–531.

65) Somayazulu, M., Ahart, M., Mishra, A.K., Geballe, Z.M., Baldini, M., Meng, Y. et al. (2019) Evidence for superconductivity above 260 K in lanthanum superhydride at megabar pressure. Phys. Rev. Lett. 122, 027001.

66) Watanabe, H., Shirakawa, T. and Yunoki, S. (2013) Monte Carlo study of an unconventional superconducting phase in iridium oxide Jd = 1/2 Mott insulators induced by carrier doping. Phys. Rev. Lett. 110, 027002.

67) Yan, Y.J., Ren, M.Q., Xu, H.C., Xie, B.P., Tao, R., Choi, H.Y. et al. (2015) Electron-doped Sr2IrO4: An analogue of hole-doped cuprate superconductors demonstrated by scanning tunneling microscopy. Phys. Rev. X 5, 041018.

68) Kim, Y.K., Sung, N.H., Deuling, J.D. and Kim, B.J. (2016) Observation of a d-wave gap in electron-doped Sr2IrO4. Nat. Phys. 12, 37–41.

69) Terashima, K., Sunagawa, M., Fujiwara, H., Fukura, T., Fujii, M., Okada, K. et al. (2017) Evolution of the remnant Fermi-surface state in the lightly doped correlated spin-orbit insulator Sr2−xLaxIrO4. Phys. Rev. B 96, 041106.

70) Horigane, K., Fujii, M., Okabe, H., Kobayashi, K., Horigane, K., Ishii, H. et al. (2018) Magnetic phase diagram of Sr2−xLaxIrO4 synthesized by mechanical alloying. Phys. Rev. B 97, 064425.

71) Terashima, K., Paris, E., Salas-Colera, E., Simonelli, L., Joseph, B., Wakita, T. et al. (2018) Determination of the local structure of Sr2−xMxIrO4 (M = K, La) as a function of doping and temperature. Phys. Chem. Chem. Phys. 20, 23783–23788.

(Received Feb. 5, 2019; accepted Apr. 23, 2019)
Profile

Jun Akimitsu was born in Hiroshima Prefecture in 1939. He graduated from the University of Tokyo and also received a Ph.D. from there. He became Research Associate at Institute for the Solid State Physics (ISSP), the University of Tokyo (1970–1976). He moved to Aoyama Gakuin University as Associate Professor (1976–1982), and later became Professor (1982–2015). He became the Dean of the Center for Advanced Technology, Aoyama Gakuin University (1998–2015). Meanwhile, he was a visiting professor at MIT (U.S.), and Monash University (Australia) and Guest Scientist at Brookhaven National Laboratory. After retirement from Aoyama Gakuin University, he moved to Research Institute for Interdisciplinary Science, Okayama University, in 2015. He is presently Professor (Special Appointment) of Okayama University.

He has received the following Awards; 1) 1997, Superconducting Science and Technology Award (first: For the discovery of Superconductivity in a ladder compound); 2) 1998, Nishina Memorial Award; 3) 2001, Medal with Purple Ribbon; 4) 2002, The Asahi Prize; 5) 2002, Masumoto Hakaru Award; 6) 2002, Superconducting Science and Technology Award (second: For the discovery of MgB_{2}); 7) 2002, Magnetic Society of Japan Award; 8) 2003, Bernd T. Matthias Prize; 9) 2007, Nishikawa Award; 10) 2008, James C. McGroddy Prize for New Materials; 11) 2012, Special Prize from the Japanese Society for Neutron Society; 12) 2014, The order of the Sacred Treasure; 13) 2019, Superconductivity Science and Technology Award (third: For distinguished contribution to the Discovery of New Superconductors).