

RESEARCH ON HIGH- T_c SUPERCONDUCTIVITY IN JAPAN

Ongoing support for superconductivity research may have given Japanese physicists an advantage over their colleagues elsewhere in the race for high-temperature superconductors.

Shoji Tanaka

"Will a new age of superconductor technology dawn in the near future and make the current semiconductor technology obsolete?" I wondered in the early 1970s. My research until then had been mostly in semiconductors. Like many a semiconductor physicist, I felt that it was becoming difficult to carry on this research at a university laboratory. Most advances in semiconductor research were being made by that time at laboratories supported by the big industrial corporations. These considerations motivated me to move away from semiconductors, and to think of a new direction for my research.

Many theoretical proposals for raising the critical temperature for superconductivity appeared in the 1960s.¹ At the turn of the decade, the so-called A15 compounds held great promise for achieving superconductivity at high temperatures. For example, the late Bernd Matthias, Theodore Geballe (now at Stanford University) and their collaborators² discovered in 1967 that the T_c for $Nb_3Al_{0.8}Ge_{0.2}$ could be raised to over 20 K. Furthermore, Geballe³ observed some anomalies near 30 K in the resistivity of $NbSe_2$. This work raised the possibility that superconductivity in transition metal dichalcogenides might exist at temperatures even higher than those in A15 materials.

Electronic properties of transition metal dichalcogenides vary considerably with composition. Some materials in this series are insulators, some semiconductors and

some metals. Geballe's work showed that some might even be superconducting. I decided to study those materials. For these studies, I grew single crystals by the vapor transport method. Shortly after I started this research, J. A. Wilson⁴ (then at Cavendish Laboratory, Cambridge) found charge density waves in metallic materials such as TaS_2 , $TaSe_2$ and $NbSe_2$. This observation was very exciting. It opened the possibility of obtaining superconductivity by a new mechanism. This was the mechanism H. Fröhlich had suggested in the early 1950s, before John Bardeen, Leon Cooper and Robert Schrieffer (at the University of Illinois at that time) proposed their now famous theory of superconductivity. Philip Anderson (then at AT&T Bell Labs) argued, however, that impurities would pin the charge density wave and Fröhlich superconductivity would not be obtained.

Kentaro Onabe in my laboratory in 1976 studied the anisotropic superconductivity in $NbSe_2$ and NbS_2 , and later Shin-ichi Uchida observed strong nonlinear conductivity, mainly in $TaSe_2$. Other physical properties in these materials were also investigated extensively; for instance, Toshiro Tani observed thermoelectric power and Koichiro Saiki measured the optical properties. All of this work was done in reference to the CDWs.

In 1976 N. P. Ong and Pierre Moneau (both at the University of California, Berkeley, at the time) first observed strong non-ohmic conductivity in $NbSe_3$ at low temperatures. This material has a quasi-one-dimensional structure. The sudden depinning of the CDW by the applied electric field is the reason for the non-ohmic

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conductivity. Many laboratories in Japan picked up this new line of research on NbSe_3 . Takashi Sambongi of Hokkaido University, Seiichi Kagoshima of the University of Tokyo and many other physicists and chemists investigated these one-dimensional materials. I also expanded the scope of my work on chalcogenides, measuring the dynamical character of CDW motion, mainly from the noise measurements.

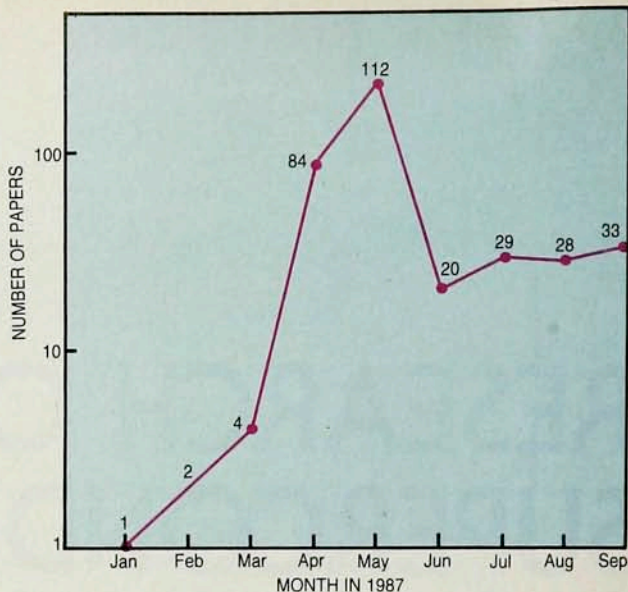
Semiconductor-metal interface

A movement to obtain superconductivity at high temperatures appeared in Japan around 1980. This movement was excited by papers of Vitaly Ginzburg and John Bardeen. Ogushi of Kagoshima University reported anomalous temperature dependence of resistivity in a thin film of niobium on silicon in 1983. He observed a sudden drop of resistivity at 180 K, but nobody has been able to reproduce it yet. In 1986, he further reported that a thin film of germanium on silicon showed an anomalous resistivity change at around 40 K. But it later became clear that the temperature measurement was not exact in Ogushi's experiment, and a professor at Tohoku University observed a critical temperature of 22 K in his sample of Ge-Si. A professor at Nihon University also reported an anomalous temperature dependence in a Si-Nb system, but nobody has confirmed it yet. Hideo Ihara of the Electrotechnical Laboratory tried to find high- T_c superconductivity in semiconductor-metal interfaces, but no remarkable effect was observed.

Superconductivity in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$

In 1975, Arthur Sleight (Du Pont Research) discovered superconductivity in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. In the course of my earlier work on semiconductors, I had studied a few oxides. Metal oxides generally have electrical conductivities much lower than those of normal metals. Therefore the discovery of superconductivity in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ surprised me. At that time I had a graduate student, Truong Dinh Thanh, who was from Vietnam and was extremely dedicated to research. Thanh was looking for a suitable topic for thesis research, and I asked him to prepare samples of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and study their transport properties.

Thanh started by trying to make good ceramic samples of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. Nobody in my laboratory then had any experience with ceramics. Thanh had to struggle hard, but he succeeded in making high-quality samples. He measured the conductivity and the Hall coefficient in many samples and examined in detail how the transport properties varied with the bismuth content x . He found that the carrier concentration in this material is lower than in ordinary metals by more than one order of



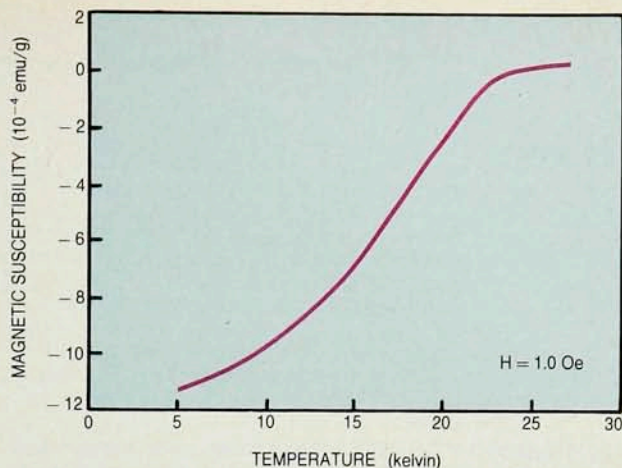
Number of papers on the new oxide superconductors published in *Japanese Journal of Applied Physics Letters* in 1987. The April and May issues of the journal ran special sections on the new superconductors.

magnitude. For x about 0.30, $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ undergoes a metal-semiconductor transition. The temperature dependence of the resistivity is quite peculiar: The resistivity varies with a power of the temperature over a wide temperature range.⁵ I was very impressed by these results. I believed that superconductivity in a material with a low carrier concentration must have special origin, and that such a material might open the door to high- T_c superconductivity.

In 1978, Koichi Kitazawa returned to Japan from the ceramics laboratory at MIT, joining Kazuo Fueki's laboratory at the department of applied chemistry of the University of Tokyo. I discussed with Kitazawa the problems we then faced in growing single crystals of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. Recognizing that Kitazawa had the expertise to push forward our research on $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, I lured him to my laboratory, first as a lecturer and later as an associate professor. Kitazawa, like me, felt that some new mechanism of superconductivity might exist in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. Kitazawa started the specific heat measurement with Takao Itoh and the single crystal growth with Hiderori Takagi. Itoh and Takagi were young graduate students at the time.

Thanh's paper⁵ got many scientists in Japan interested in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, especially, Nobukazu Niizeki, the Director of the Ibaraki Electrical Communication Laboratory of Nippon Telephone and Telegraph. Niizeki, an expert in crystal growth of dielectrics, asked Toshiaki Murakami to study this material. Niizeki's interest in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ also became the basis of a research collaboration between my group and NTT.

In 1980 Setsuko Tajima came back from Karlsruhe, West Germany, and joined my group. I suggested that she measure the plasma reflection, which was expected to appear in the near infrared. Uchida came back from Grenoble in 1983, and started the optical experiment. In 1983 I bought from SHE in the US a magnetometer for high-precision magnetic susceptibility measurements. Michio Naito started to measure the magnetic susceptibility of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ soon thereafter. The summary of



Magnetic susceptibility of a mixed-phase sample of La-Ba-Cu-O observed on 13 November, 1986. Onset of diamagnetism at about 30 K confirmed the possibility of superconductivity in the oxide material reported by Bednorz and Müller.

most of the results from these measurements was first reported at the International Conference on Mechanisms and Materials of Superconductivity, held in Ames, Iowa, in 1985, and at the International Meeting on Ferroelectricity held in Kobe in 1985.

The NTT group, on the other hand, concentrated their efforts on making high-quality thin films and single crystals of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. One of the most significant outcomes of their work was the observation of multiply connected Josephson junctions in thin films. They also developed a very-high-speed infrared detector using thin films of this material.

$\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ was also studied in other countries, in USA at AT&T Bell Laboratories and at the University of Houston and in USSR.

A special research project of Japan's Ministry of Education, entitled New Superconducting Materials, started in 1984. Sadao Nakajima is the leader of this project. (See the box on page 57.) The initiative for this project came from theorists. Superconductivity in the so-called Chevrel-phase materials and in some organic compounds was discovered a few years before the project started. These discoveries led theorists to hope that further research by experimenters might eventually find new superconducting materials in which some novel mechanism, rather than the usual phonon-mediated pairing, operates. The experimenters, however, were not optimistic that such an approach would provide a convenient shortcut to higher critical temperatures, because they knew how difficult it is to synthesize new materials.

I was invited to join the special project as leader of the group on inorganic compound superconductors. As part of the activities sponsored by the project, I continued my research on $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. In the first two years we obtained beautiful results from optical measurements. Based on those results, we proposed a new band model for $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ that could explain the metal-semiconductor transition. As for the mechanism of superconductivity, we thought that the electrons' strong interaction with the breathing-mode phonons, which was proposed by Leonard Mattheiss (AT&T Bell Laboratories), might be a plausible explanation for Cooper pairing of the electrons. Toward the spring of 1986, our research on superconductivity in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ appeared to be coming to an end. We shifted our interests to investigating the properties of semiconducting BaBiO_3 and to finding new oxide superconductors.

After November 1986

In November 1986, we read the paper of Georg Bednorz and Alex Müller (IBM Zurich).⁷ In this paper Bednorz and Müller reported on the possibility of superconductivity up

to 30 K in a mixed-phase sample of Ba-La-Cu-O. We decided to study their material. We had no problem in making the sample, as we already had acquired lot of experience in making oxide materials. The experiment started on 6 November, and on 13 November, we observed a large diamagnetic susceptibility—an encouraging sign for the existence of superconductivity. So we concentrated our efforts on identifying the true superconducting phase. Our first report, on the observation of the Meissner effect, was submitted for publication on 22 November; in the second paper, submitted on 8 December, we reported our success in identifying the superconducting phase $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$. The critical temperature for onset of superconductivity in our single-phase sample of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ exceeded⁸ 30 K. The figure on this page shows our susceptibility measurements.

For the past several years, the theoretical group of the New Superconducting Materials project has organized a meeting on novel mechanisms of superconductivity every year. At the 1986 meeting, held in Ajiro City, Hidetoshi Fukuyama strongly recommended that I present our preliminary results on the new oxide superconductor. I gave a short talk on "a new ceramic superconductor" on 19 November, and this opened the floodgates for research on the new high- T_c superconductors in Japan.

In early December, Kitazawa attended the Materials Research Society meeting in Boston and gave an invited talk on the unusual properties of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. Somehow, a rumor circulated at this meeting that our group had found a new high-temperature superconductor. A news story on some of our results that appeared on 28 November may have been responsible for the rumor. One of the session chairs at the meeting urged Kitazawa to report on our results. In a telephone conversation, Kitazawa asked me to give him permission to discuss our results. I gladly agreed, and Kitazawa gave the talk on 5 December. This talk awakened worldwide interest in the new superconducting oxide of Bednorz and Müller.

After my presentation of 19 November, several Japanese groups rushed to investigate the new superconducting materials. Fueki's group at the University of Tokyo joined our group and we succeeded in making new materials, $[\text{La},\text{Sr}]_2\text{CuO}_4$ and $[\text{La},\text{Ca}]_2\text{CuO}_4$, on 22 December.

Participants in special research projects supported by

the Ministry of Education must meet once a year and make public the results they obtained during the year. The meeting of the New Superconducting Materials project was held at the University of Tokyo on 19-21 January 1987. The organizers expected the attendance to be around 100. But more than 300 researchers actually attended. Besides our group, Masatoshi Sato of the Institute for Molecular Science, Toshizo Fujita's group from Hiroshima University, Yoshio Muto's group from Tohoku University and Hideo Ihara of the Electrotechnical Laboratory reported about their results. Some theorists also talked about the possible mechanisms for superconductivity in these materials.

Since the beginning of this year, "high-temperature superconductivity fever" has gripped the whole of Japan. Newspapers have carried stories every day about some development related to superconductivity. This must be the first time in Japanese science when laymen know what is happening at the frontiers of research in superconductivity. The situation was greatly intensified by the announcement in *The New York Times* on 16 February that a group led by Paul C.W. Chu had found a new superconductor with a T_c above 90 K.

A small meeting to discuss the oxide superconductors was held in Itoh City on 18 and 19 February. The meeting was sponsored as an activity of the New Superconducting Materials project, and 40 scientists attended. At the end of the meeting, Kagoshima announced that S. Hikami of his group had discovered a new superconductor, the critical temperature of which was above 80 K. Hikami's material was Y-Ba-Cu-O, the same as Chu's, but he made his discovery quite independently of Chu's. Later, Fujio Izumi of the Research Institute of Inorganic Materials did beautiful work in determining the crystal structure of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ by neutron diffraction experiments.

After the now famous marathon session on high- T_c superconductivity in New York on 18 March, a similar meeting was held in Nagoya by the Physical Society of Japan on 28 March. About 2000 physicists attended, and it ended at 11 o'clock at night. Furthermore, the Japan Society of Applied Physics held a symposium on 1 April that more than 1000 physicists attended.

The editorial board of the *Japanese Journal of Applied Physics* decided in the middle of January to publish a special issue of *Japanese Journal of Applied Physics Letters* on high-temperature superconductivity, to help disseminate the available information and accelerate the research in Japan. The editorial board was encouraged in this decision by the fact that the first five papers from our group were all submitted to *JJAP Letters*. It seems that the editorial board made the right decision, for the number of papers submitted to the journal exceeded 200 by the end of March. Most of the papers on high-

temperature superconductivity in Japan since then have also been submitted to *JJAP Letters*. The figure on page 54 shows fairly well the situation regarding research papers on high- T_c superconductivity. In this figure, the number of such papers published in *JJAP Letters* is plotted against the months in 1987. Since the peak of 112 papers in the May issue, about 30 papers have been submitted to this journal every month.

Movements in the government

The Japanese government responded to this unusual situation in research. At present, about 30 scientists are working on the new superconductors at the Electrotechnical Laboratory of the Ministry of International Trade and Industry; the numbers of scientists and engineers at the National Institute for Research on Inorganic Materials and the National Institute of Metals are about 30 and 50, respectively. The Electrotechnical Laboratory has had a long history of work on developing superconducting magnets for magnetohydrodynamic generators and on Josephson devices. A group at the National Institute of Metals is now quite famous for its work on developing superconducting wire for high-field magnets. Several groups at the National Institute for Research on Inorganic Materials are studying the structure and properties of perovskites.

The Ministry of Education, Science and Culture has decided to extend for a year the New Superconducting Materials project, originally scheduled to be terminated in March 1987. The ministry has also decided to start a new research project on high- T_c oxide superconductors in April 1988. The new project is expected to go on for three years. The ministry is also planning to begin in 1988 a new project on applications of superconductivity.

The Science and Technology Agency established last February a committee for research in superconductivity. The committee organized its first symposium on new superconducting materials on 1 May. It is now organizing a workshop, open to public, every two months. The Agency is planning to begin in 1988 the Multi-Core Project, and this project is aimed at strengthening the research capabilities of its own two laboratories (National Institute for Research in Inorganic Materials and National Research Institute for Metals) and at improving the laboratories' cooperation with industry.

MITI formed a consultative committee on superconductivity last April. Many industrial companies are planning to establish an association for developing superconductor technology. It is expected that about 100 companies will join this association, and the association might set up a small research laboratory of its own for developing the basic technology, and probably for investigating the trends in future technology. I think that it is important for this association to assume international

Role of the 'New Superconducting Materials' Program

The late K. Yasukochi felt in the early 1980s that the time was ripe to start a systematic program of research into the possibility of obtaining superconductivity at high temperatures. He invited me—I was then director of the Institute for Solid State Physics at the University of Tokyo—to organize a team of scientists to work together toward higher T_c . Shoji Tanaka and Hideroshi Fukuyama joined the team at an early stage and participated actively in its organization.

The group organized two workshops, one each in 1981 and 1982, to chart out its course. Global trends in basic research activities were critically reviewed at the first workshop; at the second, key experimenters in the group talked about their own activities and future plans. In the past, development of new superconducting materials had almost always raised the possibility of novel mechanisms of superconductivity, and the workshop participants recognized this as a significant feature also of some recent advances. For instance, Cooper pairing of electrons competes with other phenomena such as the formation of spin density waves or of charge density waves in some organic and inorganic superconductors, and with Anderson localization in superconducting amorphous films.

On the basis of discussions at the two workshops, a three-year research program called New Superconducting Materials commenced in April 1984. The immediate goal of the program was to investigate the mechanism controlling the T_c in different classes of superconducting materials, and to raise the T_c if possible. More than 30 senior scientists, mostly from universities, took part in the program. The Ministry of Education, Science and Culture provided about 2×10^8 yen per annum in financial support for the project. Some active scientists from the Electrotechnical Laboratory and the Nippon Telephone and Telegraph Laboratories also joined the project while continuing to be supported by their companies.

The research program was divided into five groups. These were to focus on:

- ▷ theory
- ▷ intermetallic compounds and magnetic superconductors
- ▷ inorganic superconductors
- ▷ organic materials and salts
- ▷ development of new technologies for synthesis of superconducting materials.

The last group was to be headed by Yasukochi, but he unfortunately passed away at the very beginning of the

program.

A meeting was held at the end of each fiscal year, to review the whole program. The reports of the review committees are available in a collected English translation under the title *Research Report on New Superconducting Materials*. (The three volumes may be obtained by writing to Kunimitsu Uchinokura, Department of Applied Physics, University of Tokyo.) More than 300 research papers reporting the activities of various members were published in archival journals.

To say the least, the program was very effective in training a strong team of scientists in Japan to work on superconducting materials with modern equipment. The program also trained young researchers in the theoretical aspects of superconductivity. However, many felt that the scope of the program was a little too wide. Consequently, the budget as well as manpower was reduced in each of the five divisions. It became difficult to dig deeply for one particular possibility.

Early in November 1986, the standing external committee reviewed the program and advised the Ministry of Education, Science and Culture not to support the program after March 1987, when its initial three-year term would expire. Soon after this recommendation was made, Tanaka's group, in collaboration with those of Koichi Kirazawa and Kazuo Fukei at the University of Tokyo, succeeded in identifying the crystal structure of the superconducting phase in La-Ba-Cu-O, discovered by Georg Bednorz and Alex Müller (IBM Zurich Research Laboratory) in early 1986. This research at Tokyo was done independently of the ongoing work in Zurich. The Japanese group also independently obtained superconductivity at 40 K in La-Sr-Cu-O. These results, together with results obtained at Tohoku University, the Electrotechnical Laboratory, the Institute for Molecular Science, and Hiroshima University, were reported at a special session on high- T_c oxides, at the third annual meeting of the special program held on 19 January 1987. This was probably the first meeting at which the so-called superconductivity fever prevailed.

In view of the Japanese participation in this dramatic breakthrough, the Ministry of Education decided to extend the program for one year. This one-year extension will support only a small number of experts on high- T_c oxides.

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character and be open for membership to any company in the world. The thinking in MITI also favors international cooperation in this field, because, the reasoning goes, the high- T_c superconductors might give birth to a major new technology, one on which the future of the world may depend.

MITI has decided to start two projects in 1988. One is for the development of a new superconducting generator and the other for the development of superconducting materials and new electronic devices. The former was planned two years ago and was expected to use Nb₃Sn wires. Because the situation has now changed, the possibility of employing wires made of the new oxide will also be considered.

The 18th International Conference on Low Temperature Physics was held in Kyoto on 20–26 August. The Yamada Conference on Superconductivity in Highly Correlated Fermion Systems was held in Sendai from 31 August to 2 September. Besides these international conferences, both the Physical Society of Japan and the Japanese Society of Applied Physics held their autumn meetings recently. Both the meetings were well attended.

On 22 September the Science and Technology Agency reported its study on the future of science and technology.

In the agency's estimate, liquid nitrogen superconductors will be in practical application in 1994 and the magnetic levitation high-speed train will begin to run in 2001. So research and development in superconductivity is quite active in Japan, at least at present. One wonders, however, how many Japanese scientists will still be active in basic research in this field after five years.

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