

# **Creative Research Initiatives**

## **새로운 초전도 연구**

Study of the New Superconductivity

Pohang Superconductivity Center  
Pohang University of Science and Technology

Ministry of Science & Technology

## 제 출 문

과학기술부 장관 귀하

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## 보고서 초록

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연구책임자	이 성 익	해당단계 참여연구원수	총 : 16 명 내부 : 16 명 외부 :    명	해당단계 연구비	정부: 1,780,000 천원 기업:            천원 계: 1,780,000 천원
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요약(연구결과를 중심으로 개조식 500자 이내)				보고서 면수	77
<p>1단계인 1997년도-2000년도에는 많은 시간을 장치 제작, 설치에 소모. 2단계에서는 이 장비들을 이용하여 소기의 목적을 달성함.</p> <p>첫 번째로 언급할 초전도체는 MgB<sub>2</sub>. 다른 사람들이 모래알 같이 부서지기 쉬운 초전도체를 만든 반면 우리는 고압 GPa 영역에서 매우 단단한 시료를 만듦. 다른 연구들이 어려움을 겪고 있을 때 우리는 이 시료를 이용하여 여러 성질을 독점적으로 측정할 수가 있었음. 이외에도 어느 누구도 MgB<sub>2</sub> 박막을 만들어 내지 못할 때, 우리는 이 물질의 성질을 즉시 파악하여 전 세계에서 처음으로 이 박막을 만들어 내는데 성공. 우리는 제조 즉시 한국, 미국, 독일, 영국, 일본 5개국에 특허 청구를 하였고, 곧이어 Science, PRL, APL, PRB 등에 논문을 게재함. 이 초전도 박막은 초전도 전자 소자 (조셉슨소자, SQUID 전자연결, 전류차단기, 작은 초전도자석, 마이크로파 통신장비) 제조 시 핵심이 될 것임. 우리는 또한 MgB<sub>2</sub> 초전도 단결정 제조에도 성공. 고압시료, 박막, 단결정 세 종류의 MgB<sub>2</sub> 시료를 전 세계에서 처음으로 제조하는데 성공하였음.</p> <p>두 번째, 우리가 만든 초전도체는 전자로 구성된 무한층 Sr<sub>(1-x)</sub>Ln<sub>x</sub>CuO<sub>2</sub> (Ln= La, Cd, Su)이 있음. 이 초전도체는 이전에도 제조는 되었으나 초전도 용적률이 10%정도였는데 우리가 처음으로 고압(4GPa)과 고온(1000°C)에서 용적률이 100%에 가까운 단일상을 만드는데 성공하였음. 마지막으로 Na가 들어간 CaCuO, Tl-2212, Tl-2201, RNi<sub>2</sub>B<sub>2</sub>C 제조에도 성공한 세계 몇 안 되는 연구팀이 되었음.</p>					
색인어 (각 5개 이상)	한 글	초전도, 조셉슨 소자, 양자 간섭계, 마이스너 효과, 마그네슘다이보라이드			
	영 어	Superconductivity, Josephson Junction, SQUID, Meissner Effect, MgB <sub>2</sub>			

# 요 약 문

## I. 제 목

새로운 초전도 연구

## II. 연구개발의 목적 및 필요성

20세기 초 처음으로 초전도현상을 발견한 당시에는 전기 저항이 없어지는 초전도체의 응용이 대단할 것으로 생각되어 학계는 물론 산업 응용의 측면에서 관심이 집중되었으나 그 전이 온도가 낮아 여러 어려움이 제기 되어왔다. 이후 20세기 말에 들어와 계속하여 초전도현상을 보이는 새로운 물질을 찾아내면서 현재는 액체질소의 끓는점(77K)보다 훨씬 높은 온도인 135K에서도 초전도 현상이 나타나기에 기존 초전도체를 사용하는데 문제점으로 제기되었던 비용에 관한 여러 문제점을 상당히 해소 시켰다. 그 후 임계 온도를 상온까지 올리려는 노력과 새로운 초전도 제조 및 이의 이해에 대한 노력이 세계 각국에서 이루어지고 있다.

## III. 연구개발의 내용 및 범위

고온, 상압에서 제조되는 대부분의 초전도체는 현재까지 많은 시도가 있었음에도 불구하고 그 종류가 다양하지 않다. 그러나 고온, 고압이라면 좀더 새롭고 다양한 초전도체를 만들어낼 수 있다. 이러한 환경 속에서는 탄소도 다이아몬드로 변할 수 있다. 이러한 기술을 가지고 있는 곳이 전 세계에 몇 군데 없는데 그 중 하나가 우리 연구단이다. 본 초전도 연구단은 각고의 노력 끝에 20 GPa의 고온 고압장비를 성공적으로 설치하였고, 연이어 세계 최고의 초전도체를 만들어 내는데 성공하였다. 이렇게 제조한 초전도체의 성질을 이해하기 위하여 저고자장 하에서의 자성 측정 장치, 고분해능을 갖는 홀 효과 측정 장치, 미세 패턴 형성 장치 등을 개발하여 새로운 초전도 제조, 분석, 소자 개발까지 가능케 하고 있다.

## IV. 연구개발 결과

1단계인 1997년도-2000년도에는 고온 고압장치를 제작, 설치하는데 많은 시간을 보냈으나 2단계에 들어와 이 장비들을 이용하여 다양한 연구를 시작할 수 있었다

첫 번째로 언급할 초전도체는  $MgB_2$ 이다 다른 사람들이 모래알 같이 부서지기 쉬운 초전도체를 만들고 있을 때 우리는 고압 GPa 영역에서 매우 단단한 시료를 만들 수 있었고 또한 이 시료를 이용하여 여러 성질을 독점적으로 측정할 수가 있었다. 이외에도 어느 누구도  $MgB_2$  박

막을 만들어 내지 못할 때, 우리는 이 물질의 성질을 즉시 파악하여 전 세계에서 처음으로 이 박막을 만들어 내는데 성공하여 제조 즉시 한국, 미국, 독일, 영국, 일본 등 5개국에 특허 청구를 하였고, 곧이어 Science, PRL, APL, PRB 등에 논문을 게재하였다. 이 초전도 박막은 초전도 전자 소자 (조셉슨소자, SQUID 전자연결, 전류차단기, 작은 초전도 자석, 마이크로파 통신장비) 제조 시 핵심이 될 것이다. 우리는 또한  $MgB_2$  초전도 단결정 제조에도 성공하여 고압시료, 박막, 단결정 세 종류의  $MgB_2$  시료를 전 세계에서 처음으로 제조하는데 성공하였다.

두 번째, 우리가 만든 초전도체는 전자로 구성된 무한층  $Sr_{(1-x)}Ln_xCuO_2$  ( $Ln = La, Cd, Sm$ )이다. 이 초전도체는 이전에도 제조는 되었으나 초전도 용적률이 10% 정도였는데 우리가 처음으로 고압(4GPa)과 고온(1000°C)에서 용적률이 100%에 가까운 단일상을 만드는데 성공하였다.

그 외에도 Na가 들어간  $CaCuO$ , Tl-2212, Tl-2201,  $RNi_2B_2C$  등 여러 종류의 단결정 제조에도 성공을 하였다. 이들은 최상의 시료로 이들을 제조할 수 있는 그룹은 몇 되지 않는다. 본 연구단은 이러한 양질의 시료와 뛰어난 측정과 분석 능력으로 세계적인 초전도 분야를 이끌어가고 있다.

## V. 연구개발결과의 활용계획

상온에서도 사용할 수 있는 초전도체가 개발이 된다면 이로 인하여 제3의 산업혁명을 기대할 수 있을 것이다. 이는 반도체에 의한 제2의 산업혁명을 보면 짐작할 수 있다. 초전도체의 응용으로는 자기부상열차, 자기부상선박, 자기공명진단 (MRI), 마이크로파의 통신, 초고속 인터넷, 조셉슨 소자에 의한 혁명적인 전자 기구, 차세대 위성통신, 양자 컴퓨터 등이 있다. 현재  $MgB_2$ 의 박막의 마이크로파의 통신이 가장 빨리 산업화가 될 것으로 생각하고 있다.

## S U M M A R Y

For the first stage (1997-2000), we spent much times setting up the instruments. Equipped with these instruments, in a second stage, we accomplish our goals. The first superconductor we would like to mention is the magnesium diboride ( $\text{MgB}_2$ ). While the samples produced by other researchers had been very brittle, like sand, our  $\text{MgB}_2$ , synthesized under high-pressure conditions (a few GPa), was very hard and dense. While others had difficulties, we could measure quite a number of the transport properties. In addition, nobody in the world could produce  $\text{MgB}_2$  thin films, which are essential for superconducting electronic device application and for the study of basic superconducting properties. We asked ourselves "why people in the world could not produce  $\text{MgB}_2$  thin films?" Very soon, we had the answer and could synthesize  $\text{MgB}_2$  thin films. We immediately applied patterned (Korea, U.S.A., Germany, British, Japan) and published papers after papers (Science, P.R.L, A.P.L. and P.R.B.). These thin films will be used for the superconducting electronic devices. For example, this thin film can be used for making Josephson Junctions, SQUID, micro-electronic interconnection, fault current limiters and local superconducting magnet, and filters used for microwave communication. We also produced  $\text{MgB}_2$  single crystals for the first time in the world. We are the only group that has synthesized three different forms (high-pressure bulks, thin films and single crystals) of  $\text{MgB}_2$ .

The second superconductor we produced was an electron-doped cuprate  $\text{Sr}_{(1-x)}\text{Ln}_x\text{CuO}_2$  ( $\text{Ln} = \text{La, Gd, Sm}$ ) infinite layer superconductor. Despite their importance, these cuprate superconductors are very difficult to synthesize, and the lack of single-phased compounds with high volume-fractions of superconductivity hindered research efforts until our recent breakthrough. Using high-pressure ( $\sim 4$  GPa) and high-temperature ( $\sim 1000$  C) annealing conditions, we were able to routinely achieve single-phase of these compounds. We are the only group in the world that can produce 100% of these superconductors.

Finally, we produced various kinds of single crystals, such as Na doped  $\text{CaCuOCl}$ , Tl-2212, Tl-2201, and  $\text{RNi}_2\text{B}_2\text{C}$ . Quality-wise, these are the worlds best, and only a few groups in the world can even produce these compounds.

Because of our exceptional ability in measurements and phenomenological analysis, we will be successful and will remain as one of the leading groups in superconductivity research.

# C O N T E N T S

- I. Research development
- II. Domestic and foreign development
- III. Research Results
- IV. Achievement and Contribution
- V. Application of the research
- VI. Information obtained during the research
- VII. Reference

# 목 차

## 제 1 장 연구개발과제의 개요

- \* 연구개발의 목적, 필요성 및 범위 등을 기술

## 제 2 장 국내외 기술개발 현황

- \* 국내·외 관련분야에 대한 기술개발현황과 연구결과가 국내·외 기술개발현황에서 차지하는 위치 등을 기술

## 제 3 장 연구개발 수행 내용 및 결과

- \* 이론적, 실험적 접근방법, 연구내용, 연구결과를 기술

## 제 4 장 목표달성도 및 관련분야에의 기여도

- \* 연도별 연구목표 및 평가착안점에 입각한 연구개발목표의 달성도 및 관련분야의 기술 발전에의 기여도 등을 기술

## 제 5 장 연구개발결과의 활용계획

- \* 추가연구의 필요성, 타 연구에의 응용, 기업화 추진방안을 기술
- \* 연구기획사업 등 사업별 특성에 따라 목차는 변경 가능함

## 제 6 장 연구개발과정에서 수집한 해외과학기술정보

## 제 7 장 참고문헌

- \* 보고서 작성 시 인용된 모든 참고 문헌을 열거 한다



## 제 1 장 연구개발과제의 개요

20세기 초 처음으로 초전도현상을 발견한 당시에는 전기 저항이 없어지는 초전도체의 응용이 대단할 것으로 생각되어 학계는 물론 산업 응용의 측면에서 관심이 집중 되었으나 그 전이온도가 낮아 여러 어려움이 제기 되어왔다. 이후 20세기 말에 들어와 계속하여 초전도현상을 보이는 새로운 물질을 찾아내면서 현재는 액체질소의 끓는점(77K)보다 훨씬 높은 온도인 135K에서도 초전도 현상이 나타나기에 기존 초전도체를 사용하는데 문제점으로 제기되었던 비용에 관한 여러 문제점을 상당히 해소 시켰다. 그 후 임계 온도를 상온까지 올리려는 노력과 새로운 초전도 제조 및 이의 이해에 대한 노력이 세계 각국에서 이루어지고 있다.

이에 따라 2 단계 연구는 아래와 같이 수행 하였다.

### Research Goal for the second phase

	Research Goal	Research Scope
First Year (2000)	<ul style="list-style-type: none"> <li>-Synthesis of infinite layer superconductor.</li> <li>-Synthesis of newly doped or Mercury based superconductor in High pressure condition and study their superconductivity</li> <li>-Synthesis of the thin film form of mercury based superconductors.</li> </ul>	<ul style="list-style-type: none"> <li>-Study of the mechanism or gap symmetry of the superconductor</li> <li>-Synthesis of the Mercury based superconductor</li> <li>-Magnetic properties of the Mercury based superconductor</li> <li>-NMR, High Pressure Study, Specific Heat,</li> </ul>
Second Year (2001)	<ul style="list-style-type: none"> <li>-Synthesis of the of the MgB<sub>2</sub> in Bulk, single crystal and thin film form</li> <li>-Basic Properties of the MgB<sub>2</sub></li> <li>-Synthesis and study of the Tl based cuprate superconductors</li> <li>-Synthesis and study of the infinite layer superconductor</li> </ul>	<ul style="list-style-type: none"> <li>- Transport of MgB<sub>2</sub> single crystals</li> <li>-Study of the Hall effect in mixed state</li> <li>-Transport study of the MgB<sub>2</sub> thin film</li> <li>-Growth of the MgB<sub>2</sub> thin film</li> <li>-Magnetic Properties of the MgB<sub>2</sub></li> <li>-Transport properties of Tl based Cuprate superconductor</li> <li>-Magnetic properties of the Tl based cuprate superconductor</li> <li>-Study of the infinite layer superconductors</li> </ul>

<p>Third Year (2002)</p>	<ul style="list-style-type: none"> <li>-Improve the quality of MgB<sub>2</sub> thin film and single crystal</li> <li>-Study of the application of MgB<sub>2</sub></li> <li>-Study of the gap symmetry and magnetic impurity in electron doped superconductors</li> <li>-Synthesize and improvement of the Thallium based superconductors.</li> <li>-Synthesize the new superconductor in high pressure condition</li> </ul>	<ul style="list-style-type: none"> <li>-Transport of the MgB<sub>2</sub> single crystal ( Anisotropic G-L theory)</li> <li>- Microwave properties and Josephson effect of MgB<sub>2</sub> thin film.</li> <li>-Hall effect and transport in a high magnetic field condition</li> <li>-Study of the quantum impurity in MgB<sub>2</sub> and infinite layer superconductor</li> <li>-Vortex dynamics in thallium based high temperature superconductors</li> </ul>
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## 제 2 장 국내외 기술개발 현황

초전도 연구의 가장 획기적인 사건은 2001년도 1월 MgB<sub>2</sub>가 초전도성을 가진다는 사실이 밝혀진 것이다. 이 초전도체는 T<sub>c</sub>=39K로서 고온 초전도체 보다는 전이온도가 매우 낮지만 여러 가지 장점을 가지고 있다. 우선 MgB<sub>2</sub>의 원료인 Mg와 B는 지상에 매우 풍부하게 존재하기 때문에 쉽게 구할 수 있고 화학적으로 안정이 되어 있어 제조 과정 또한 매우 쉽다는 장점을 가지고 있다. 39K의 초전도 전이 온도는 현재 많이 쓰이고 있는 Nb<sub>3</sub>Ge보다 그 온도가 15K 정도 높아서 응용성이 매우 높다는 것이다. 따라서 환경 친화적인 물질이다. 또한 이 물질은 임계 전류가 매우 높아 1 cm<sup>2</sup> 면적의 도선에서 저항 없이 흘릴 수 있는 전류가 100만 ampere가 넘는다. 이 물질을 박막화하면 마이크로파의 통신 혁명을 일으킬 수 있을 것 같다. 예를 들어 인터넷 송수신 속도를 100배 이상 빠르게 할 뿐 아니라 그 통신 주파수를 현재보다 10-100배 이상 상승시켜 통신 가입자 수를 그만큼 더 높일 수 있다. 그런데 이러한 통신을 가능하게 하는 우리의 MgB<sub>2</sub> 박막은 그 전이 온도와 임계 전류 등에서 전 세계에서 으뜸이다. 본 연구팀은 이 분야에서 세계의 정상 위치를 유지하기 위하여 부단히 노력을 할 것이다.

## 제 3 장 연구개발 수행내용 및 결과

### I. Accomplishments

#### 1. Research objectives and evaluation criteria

##### A. Proposed objectives

Our research goal is to synthesize new superconductors and to understand their superconductivity. The competition in synthesizing new superconducting materials is fierce. Therefore, new methods should be used to succeed in synthesizing high temperature superconductors. So far, most of the people in the world use the conventional solid-state reaction technique. With this method superconductors can be produced by an appropriate heat treatment. However, the number of materials which can be synthesized by this technique is very limited. In order to increase the possibility of success in synthesizing new materials, another degree of freedom is very important and it is a pressure.

We have successfully set up a high-pressure furnace which can pressurize samples up to 0.2 million atmospheric pressure during heating treatment. There are only few institutes in the world, which have the high pressure system and can use this technique to make superconducting materials. But the temperature of other people's synthesis is not as much as stable or uniform as our system is. The temperature stability and uniformity of our high-pressure furnace is less than 2 degree. The freedom of applying pressure is essential to make single-phase superconducting materials. So far we have produced world best-quality superconducting materials under high pressure and highly stabilized temperature condition.

In the second stage, we proposed to synthesize three different superconducting materials and to study physical properties of these materials. These were magnesium diboride ( $\text{MgB}_2$ ) superconductor, infinite layer superconductor and thallium (Tl)-based superconducting single crystals. We believe that the qualities of these samples are the world best.

In 2001, we have published our research results about the synthesis of  $\text{MgB}_2$  superconducting thin film in *Science*. This great news was broadcasted in the TV networks and reported in most newspapers.

In 2002, we were invited to give a 36 minute-talk at American Physical Society (APS) Meeting. This is a **first invitation of APS for the Korean experimental work** performed in Korea in the

history of Korean Physical Society. The APS appreciated the PSC (Pohang Superconductivity Center) in synthesizing  $MgB_2$  thin films and single crystals of for the first time in the world.

Japanese scientists first reported on January, 2001 that magnesium diboride had superconductivity with a relatively high transition temperature ( $T_c$ ) of 39 K. This report has generated a flurry of activity in  $MgB_2$  since then. Studies are now aimed at establishing the mechanism, teasing out possible routes for boosting the  $T_c$  and developing more practical preparation techniques. For the application, we need this material in a form of thin film. Fortunately we were able to synthesize  $MgB_2$  thin films for the first time in the world. The PSC team has reported that our thin films exhibit a sharp  $T_c$  of 39 K and can sustain large current densities. This current is record high as far as the superconducting critical current density is concerned. But lots of details in this material still remain to be studied. For example, surface morphology, improvement of the critical current densities, investigation of fundamental mechanism of superconductivity are important research topics we would study in a near future.

In the second stage, we had ambitious plans to do research of new  $MgB_2$  materials as well as other superconductors. We proposed the following research topics in the second stage. Since we became one of the leading groups in this area, we have tried very hard to keep this position.

- Transport study of  $MgB_2$  single crystals
- Study of the Hall effect in mixed state of  $MgB_2$
- Growth of the  $MgB_2$  thin film
- Transport study of the  $MgB_2$  thin film
- Magnetic Properties of the  $MgB_2$
- Transport properties of Tl-based cuprate superconductor
- Magnetic properties of the Tl-based cuprate superconductor
- Study of the infinite layer superconductors

### **Study of $MgB_2$**

We have been able to produce world-best quality  $MgB_2$  thin films and single crystals. We are also an expert in measuring and in analyzing the basic superconducting properties of this new material. Since we could monopolize the high quality  $MgB_2$  samples, we have an advantage to obtain information on this material in advance. In the second stage, we have measured most of the basic physical properties such as magnetization, transport, Raman and infrared spectroscopy, Hall effect in mixed state, gap measurement, microwave properties, and so on.

Proposed Research : The high superconducting transition temperature of 39 K with conventional

electron phonon interaction was quite unexpected in this superconductor. So Simple MaMillan and the Allen-Dynes treatments of the BCS theory may or may not be able to describe the  $T_c$  value. Also most of the physical properties of  $MgB_2$  could be quite different from conventional superconductors. So we proposed experiments mentioned below.

- Transport of  $MgB_2$  single crystal : We predicted a large fluctuation effect and related phenomena similar to the high temperature superconductors. The existence of the vortex liquid state and fluctuation conductivity were observed in this material .

- Study of the Hall effect in mixed state of  $MgB_2$  : The Hall effect was found to be totally different from the conventional superconductor or the cuprate superconductors. This material became an ideal system to study the Hall effect in a vortex state including anomalous Hall effect.

- Growth of  $MgB_2$  thin film : We have continuously improved the quality of the  $MgB_2$  thin films. Since the first synthesis of the  $MgB_2$  thin film at PSC at last year, nobody in the world has produced the  $MgB_2$  thin film as good as ours. Still we are the world best. Using this film, we have collaborated with about 30 famous groups in the world.

- Transport study of  $MgB_2$  thin film : We measured the transport properties of the  $MgB_2$  thin film and found out that anisotropic Ginzburg-Landau theory can be satisfied only at a certain range of temperature. In this work, we investigated the origin of enormously large pinning strength and critical current density in this  $MgB_2$  thin film.

- Magnetic Properties of  $MgB_2$  : The low thermal conductivity and the high Debye temperature made this superconductor unstable against the magnetic field penetration. So the beautiful phenomenon called a dendritic growth of the magnetic fluxes was discovered.

### **Study of infinite layer superconductors**

The study of the high  $T_c$  superconductors was concentrated in the hole-doped case and T prime n-type case, because the synthesis of the ideal electron-doped superconductor  $La_{0.9}Sr_{0.1}CuO_2$  was too difficult to make. However, we overcame this difficulty. For last several years, we have tried to make this superconductor in various conditions and finally succeeded in producing high quality samples. The superconducting volume fraction of our sample is almost 100 %, which is several times higher than those of other frontier research teams' in the world. We are the only one who knows every detailed secrets of the synthesis condition. Moreover the quantity of the superconductors produced in one run is around 200 mg, which is about five times more than that of other advanced countries.

We have performed magnetic and non-magnetic doping effect on the superconductivity in this electron-doped superconductor. We have found that the superconductivity of this material is very much different from the case of hole-doped superconductors. We proposed the study of the gap symmetry of the superconductivity, impurity effect on the superconductors. These are the key experiments to understand the basic mechanism of high temperature superconductivity.

### **Proposed Research of electron-doped superconductors**

Proposed Assumption : Superconductivity of electron-doped cuprate could be quite different from that of the hole-doped superconductors. There is no electron-hole symmetry for the cuprate superconductor. We predicted that the gap symmetry may not be same as d-wave. It turned out to be right .

The pair breaking effect of non-magnetic and magnetic impurity on the superconductors followed the conventional superconducting behavior that is totally different from the hole-doped high temperature superconductors.

### **Study of TI-based superconductor**

Despite the extensive study over the preceding decade, a fundamental understanding of the high temperature superconductivity still remains as a challenge for the physicists. Many peculiar properties of the high temperature superconductors are attributed to the strong interactions between grains. The electric properties of these materials over the last few years have been mainly studied on either thin film or polycrystalline forms. Since extrinsic factors are inevitably included in these forms, single crystal is an ideal form to understand the intrinsic properties of the superconductivity. The effort to synthesize single crystals of TI-based cuprate superconductor has not been very successful for the last several years. Recently we were able to synthesize this material in a single crystalline form. This achievement is marvelous since **we are one of the very few groups in the world who could produce this single crystal at this moment. Now we could clarify whether the already accepted facts obtained from YBCO and BSCCO are truly intrinsic or not.**

**The equilibrium magnetization of TI based superconductors will give information of the intrinsic superconducting parameters and will replace the information obtained so far from the thin film. The high irreversibility of the thin film caused from defects gives less accurate intrinsic superconducting properties .**

Actually PSC has been recognized as one of the best centers as far as superconductivity research is concerned. As you can easily find at the self-evaluation at next chapter, many world-famous papers

have been published by the PSC. Moreover, the number of collaborators in worldwide keeps increasing and recently it is more than 40. This is possible due to the fact that we became internationally famous for producing several world-best superconducting materials. We are also good at measurements and understanding of physics.

## 2. Progress analysis

### A. Degree of objectives fulfillment

In the second stage, we had more ambitious plans to do the research of new  $MgB_2$  material as well as other superconductors. In this sense, we proposed the following research topics. Since we became one of the leading groups in this area, we have worked hard and smartly to keep this position. **All of these topics were thoroughly investigated.**

- Transport of  $MgB_2$  single crystals
- Study of the Hall effect in mixed state of  $MgB_2$
- Growth of  $MgB_2$  thin film
- Transport study of  $MgB_2$  thin film
- Magnetic Properties of  $MgB_2$
- Dynamic vortex behavior of TI-based cuprate superconductor
- Equilibrium magnetization of TI-based cuprate superconductor
- Study of infinite layer superconductors

published Journal	Oct/1/2000 to Sep/30/2001	Oct/1/2001 to Sep/30/2002	Oct/1/2002 to Sep/30/2003
Science	1		
Physical Review Letter	2	2	3
Applied Physics Letter	2	2	
Physical Review B	7	19	16
Physica C	11	9	12
J. of Korean Physical Society	2	2	2
Solid State Comm.	1	1	
Supercond. Sci. Technol.	2		5
the others	4	6	14
<b>Total</b>	<b>39</b>	<b>35</b>	<b>52</b>

For the second stage, we have been quite successful because we were able to produce world best quality  $MgB_2$  thin films as well as  $MgB_2$  single crystals and continuously upgraded the quality of these samples. We also produced  $MgB_2$  the infinite layer n-type cuprate and Tl-based cuprate superconducting single crystals. This success was the fruit of our hard work in setting up new sample fabrication systems. In order to produce higher quality samples, we have devoted a couple of years to set up several systems including a high-pressure synthesis furnace for polycrystalline and single crystal growth, a laser ablation system for thin film fabrication and a superconducting magnet system for the transport measurement. After a few years of struggle, we were able to produce several superconducting samples of which quality is world's best. One example is a production of the high quality infinite layer superconductors. The superconducting volume fraction of this sample is 10 to 100 times higher than that of the superconductors produced elsewhere. The superconductivity of this electron doped infinite layer system shows the properties that are quite different from the hole-doped cuprate superconductivity. Usually the hole-doped superconductor shows d-wave gap symmetry, but this infinite layer superconductor shows s-wave gap symmetry.

After synthesizing these materials, we collaborate with the world-class research groups. The numbers of the collaborators are currently more than 40. These include Caltech, Argonne National Laboratory, Brookhaven National Laboratory, Los Alamos National Lab, Univ. of Illinois, Jet Propulsion Lab, Univ. Of Oslo, Max Planck institute at Stuttgart, Univ. of Zagreb, Univ. of Paris etc.

### 3. Method for the research

At the second stage, we proposed two major hypotheses 1) superconductivity of electron doped infinite layer superconductor could be quite different from that of the hole doped high temperature superconductors. 2) The controlling of the inert gas atmosphere and controllability of the Mg should be the essence of high quality of  $MgB_2$  thin film. Amazingly both hypotheses turn out to be true. First assumption was proved to be true and published at PRL. For the second assumption, people have still not figured out the details, so nobody in the world was able to produce  $MgB_2$  thin film as good as ours until now.

#### **Synthesis and study of the infinite layer superconductors**

**We believed that the origin of superconductivity in the infinity layer superconductor is not the same as that of other hole doped high temperature superconductors. The gap symmetry of this infinite layer superconductor could be different from typically known d-wave.**



All the high-Tc cuprate superconducting materials are composed of two components, a charge reservoir block and CuO<sub>2</sub> superconducting planes. For instance, the highest Tc superconductor HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8</sub> (Hg-1223) consists of one HgBa<sub>2</sub>O<sub>3</sub> charge reservoir block and three CuO<sub>2</sub> planes. Intrinsic properties, such as superconducting transition temperature and critical current density, depend critically on the alternating stacking of charge reservoir blocks and CuO<sub>2</sub> planes. But due to the complicated intermixed contribution of the two components, how to enhance these properties for application is not yet fully understood. In order to increase the potentials of cuprate HTS, we need to understand the role played by each component separately. Since the infinite layer superconductor does not have the charge reservoir block, the crystalline and electronic structures are relatively simple, thus its understanding would be critical for version up of the possibility of HTS. But the study on this compound has remained at poor level because of low sample quality. We have already succeeded in making samples for this compound whose quality was found to be far better than any samples synthesized until now unprecedented. We also found the quality of our samples just reached to the level which makes any rigorous studies on intrinsic properties for this compound possible. We believe that the mechanism of superconductivity in this material is quite different from that of other high temperature superconductors. The mechanism or gap symmetry of the superconductivity of this material will be further studied. As previously explained, we will study the low temperature behavior of the penetration depth to get information about the gap symmetry that will help to understand the mechanism of superconductivity.

In this research, we proved that n-type cuprate reveals that the pairing symmetry, pseudo gap phenomenon and spin fluctuations are in fact not universal. The only ubiquitous features among all cuprate appear to be the strong electronic correlation and nearest-neighbor Cu<sup>2+</sup>-Cu<sup>2+</sup> antiferromagnetic interaction in the CuO<sub>2</sub> planes. We have also substituted magnetic Ni and nonmagnetic Zn impurities at Cu sites in order to probe the nature of this superconductor. We found that non-magnetic impurity does not suppress the superconductivity much but magnetic impurity kills the superconductivity drastically which is very similar to that of s-wave conventional superconductors. This is quite different from typical holed-doped d-wave cuprate superconductors.

### **The growth of the MgB<sub>2</sub> superconducting thin films**

**Controlling of atmospheric environment and doping configuration is the key secret to optimize the quality of the new superconducting thin films.**

Since the large size single crystal is not available yet, fabrication of high quality thin film is crucial to study all physical properties prior to other groups. If we could grow a thin film form of new superconductors, we will be able to obtain lots of information for those materials from the most

physical property measurements, such as magnetization, transport, Raman and infrared spectroscopy, and so on. Thus, we have extensively studied the growth of thin films using a pulsed laser deposition method. One of the remarkable research results we have achieved previously is the fabrication of the Hg-based superconductors with the highest  $T_c$  (135 K) and a single phase. We have made the world's best Hg-based superconducting thin films by two-step method using a pulsed laser deposition system. Because Hg-free precursor is very sensitive to  $H_2O$  and  $CO_2$  in moisture, we have recently developed a special vacuum chamber to transport precursor film from a main growth chamber to a dry box without exposing the precursor to air in our pulsed laser deposition system. In this way, we can avoid a possible contamination of the precursor from the moisture and make high quality thin films. In order to make mercury gas diffuse into the precursor thin film, we have to use a specially designed configuration. Maximization of the mercury content in a thin film is the key factor for the quality of thin films.

When the  $MgB_2$  was discovered, we realized that the method to synthesize a  $MgB_2$  thin film was nearly the same as that of Hg-based high  $T_c$  superconductors. For the case of the Hg-based superconductors, since the evaporation temperatures of Hg and the rest of compound are so different as  $500^\circ C$  and  $3000^\circ C$ , respectively, in situ growth of the Hg-based superconducting thin film by the laser ablation technique didn't work. Therefore we usually made a precursor thin film without Hg by the laser ablation first. Then we diffused Hg gas into the precursor film and it resulted in high quality thin films. This was a key secret for synthesizing the world best quality Hg-based superconducting thin films. This method is called a two-step method. The same two-step method was applied to the growth of the  $MgB_2$  thin film. Evaporation temperature of boron (B) is about  $4000^\circ C$ . Magnesium (Mg) evaporates at about  $1100^\circ C$ . Due to this huge difference in evaporation temperatures the traditional laser ablation method can not be applied for producing the  $MgB_2$  thin films. While all the rest of the world tried the traditional method to grow  $MgB_2$  thin films, we adopted the two-step method and as a result, produced the world best quality  $MgB_2$  thin films for the first time. So far 1.5 years have been passed since we produced the  $MgB_2$  thin film, but nobody in the world could produce the  $MgB_2$  thin films as good as ours.

## 4. Results

### A. Research details

#### 1) Study of the $MgB_2$

Now we produced world best quality thin films and single crystals. We are also expert in measuring and analyzing the basic superconducting properties of the new materials. Since we could monopolize the high quality  $MgB_2$  samples, we are in a highly advanced stage to obtain information for those materials in advance. In this year, we measured, in advance, the most of the basic physical property, such as magnetization, transport, and infrared spectroscopy, Hall effect in mixed state, gap

measurement, microwave properties, and so on.

**The high superconducting transition temperature of 39K with conventional electron phonon interaction is quite unexpected in this superconductor. So Simple MaMillan and the Allen-Dynes treatments of the BCS theory may or may not describe the value of  $T_c$ . Also the most of the physical properties of  $MgB_2$  could be quite different from the conventional superconductors. So we proposed experiments mentioned below.**

**- Study of the Hall effect in mixed state of  $MgB_2$  :** The Hall effect is found out to be totally different from the conventional superconductor or the cuprate superconductors. This material becomes ideal to study the Hall effect in a vortex state including anomalous Hall.

**-Transport of  $MgB_2$  single crystals:** We predict the large fluctuation effect and related phenomena, which were observed in high temperature superconductors. The existence of the vortex liquid state and fluctuation conductivity were observed in this material.

**- Transport study of the  $MgB_2$  thin film:** We measured the transport properties of the  $MgB_2$  thin film and found out that anisotropic Ginzburg-Landau theory is satisfied only at the certain range of the temperature. In this work, we investigate the origin of enormously large pinning strength (critical current density) in this  $MgB_2$  thin film.

**- Growth of the  $MgB_2$  thin film:** We continuously improve the quality of the  $MgB_2$  thin film. Even after one and half years of the first synthesis of  $MgB_2$  thin film at PSC, nobody in the world produced the  $MgB_2$  thin film as good as ours. Still we are the best. Using this film, we could collaborate about 30 groups in the world.

**- Magnetic Properties of the  $MgB_2$ :** The low thermal conductivity and high Debye temperature makes this superconductor unstable against the magnetic field penetration. So the beautiful phenomena called dendritic growing of the magnetic fluxes was discovered.

## **2) Study of the infinite layer superconductors**

The study of the high  $T_c$  superconductors is concentrated in the hole-doped case and T prime n-type case, because the synthesis of the ideal electron doped superconductor is too difficult to make. However, this obstacle has been removed from us. For last several years, we tried to make electron-doped superconductor  $La_{0.9}Sr_{0.1}CuO_2$  in a various conditions and finally produced high quality samples. The superconducting volume fraction of ours is almost 100 %, which is several times higher than the case of other frontier research teams in the world. **We are the only one who knows**

**every detailed secret of the synthesis condition.** Moreover the quantity of the superconductors produced in one run that is around 200 mg, which is about five times higher than that of the case of other advanced countries.

We have performed the magnetic and non-magnetic doping effect to the superconductivity in this electron doped superconductor. **Then we realized that there is a possibility that superconductivity of this material is very much different from the case of hole-doped superconductors.** We proposed the study of the gap symmetry of the superconductivity, impurity effect on the superconductors. These are the key experiments to understand the basic mechanism of high temperature superconductivity.

### **Proposed Research of electron doped superconductors**

**Proposed Assumption:** Superconductivity of electron-doped cuprate could be quite different from that of the hole doped superconductors. There is no electron-hole symmetry for the cuprate superconductor. We predicted that the gap symmetry could not be same as d wave. It turns out to be right.

**The pair breaking effect of non-magnetic and magnetic impurity on the superconductors follows conventional superconducting behavior that is totally different from the hole doped high temperature superconductors.**

### **3) Study of the Tl based superconductor**

Despite the extensive study over the preceding decade, a fundamental understanding of the high temperature superconductivity is still a challenge for the physicists. Many peculiar properties of this high temperature superconductivity are attributed to strong interactions between the grains. The electric properties of this material over the last few years still need high quality single crystals. It enables one to deal with extremely accurate special environment such as single crystals. These single crystals are essential to understand the basic understanding of the superconductivity. The effort to synthesize the single crystal lined form of Tl based cuprate superconductor was not very successful for the last several years. However, recently we were successful to synthesize this in a single crystalline form. **This is marvelous since we are one of the several groups in the world who could produce this single crystal at this moment. Now we could clarify the already known experimental results obtained by YBCO and BSCCO, whether these are intrinsic properties or not.**

**Detailed investigation of the Dynamic behavior of the vortex motion specially near at the second peak in a magnetic hysteresis. If this behavior is somewhat average of the YBCO or BSCCO, this is intrinsic effect.**

The equilibrium magnetization of Thallium based superconductors will give information of the intrinsic superconducting parameters and will replace the information obtained so far from the Thallium based superconducting thin film. The highly irreversible property of the thin film from defect gives less accurate intrinsic superconducting properties.

#### **4) The growth of the MgB<sub>2</sub> superconducting thin films**

Controlling of the atmospheric environment and the configuration of doping is the key secret to maximizing the quality of the new superconducting thin films.

#### **Synthesis and study of the infinite layer superconductors**

We believed that the origin of superconductivity in the infinity layer superconductor is not the same as that of other hole doped high temperature superconductors. The gap symmetry of this infinite layer superconductor could be different from typically known d-wave.

We proved that n-type cuprate reveal that the pairing symmetry, pseudo gap phenomenon and spin fluctuations are in fact not universal. The only ubiquitous features among all cuprate appear to be the strong electronic correlation and nearest-neighbor Cu<sup>2+</sup> - Cu<sup>2+</sup> antiferromagnetic interaction in the CuO<sub>2</sub> planes. We also have substituted magnetic Ni and nonmagnetic Zn impurities at Cu sites, in order to probe the nature of this superconductor. We found that non-magnetic impurity does not suppress the superconductivity much but magnetic impurity kill the superconductivity drastically which is very similar to that of s wave conventional superconductors. This is quite different from typical holed-doped d-wave cuprate superconductors.

### **B. Research results**

#### **Growth and transport properties of c-axis-oriented MgB<sub>2</sub> thin films**

We report the growth of high-quality c-axis-oriented MgB<sub>2</sub> thin films on Al<sub>2</sub>O<sub>3</sub> substrates by using a pulsed laser deposition technique. The thin films show an onset transition temperature of 39.2 K with a sharp transition width of 0.15 K. X-ray diffraction patterns indicate a c-axis-oriented crystal structure perpendicular to the substrate surface. We observed high critical current densities (J<sub>c</sub>) of 16 MA/cm<sup>2</sup> at 15 K and under self-field, which is comparable to or exceeds those of cuprate high-temperature superconductors. The extrapolation J<sub>c</sub> at 5 K was observed to be ~ 40 MA/cm<sup>2</sup>, which is the highest record for MgB<sub>2</sub> compounds. At a magnetic field of 5 T, the J<sub>c</sub> of ~ 0.1 MA/cm<sup>2</sup> was detected at 15 K, suggesting that this compound is very promising candidate for the practical applications at high temperature with lower power consumption. As a possible explanation

for the high current-carrying capability, the vortex-glass transition is considered.

**The discovery of superconductivity in MgB<sub>2</sub> compound [1] with a remarkably high transition temperature  $T_c = 39$  K has attracted great both basic scientific interest [2-6] and practical application [7-16]. The strongly linked nature of the inter-grains [7] with high charge carrier density [6] in this material is further advantages for use in technological applications. Recently, the upper critical field ( $H_{c2}$ ) of 29 - 39 T [8,9], which is much higher than that of previous reports, was observed, suggesting that MgB<sub>2</sub> is of considerable for practical application in superconducting solenoids using mechanical cryocoolers such as closed cycle refrigerators. In addition to higher  $T_c$  and  $H_{c2}$  in MgB<sub>2</sub>, the magnitude of critical current density ( $J_c$ ) is also very important factor for use in practical applications. Indeed, successful fabrication of Fe-clad MgB<sub>2</sub> tape has been reported [10]. This tape showed  $J_c$  of  $1.6 \times 10^4$  A/cm<sup>2</sup> at 29.5 K and under 1 T, encouraging the practical application of MgB<sub>2</sub>.**

To explain the complex phase in the vortex state for cuprate high- $T_c$  superconductors (HTS), Fisher *et al.* [11] proposed the theory of a vortex-glass superconductivity by considering both pinning and collective effects of vortex lines. According to this theory, a diverging coherence length ( $\xi$ ) near vortex-glass transition ( $T_g$ ) can be described by  $\xi \sim |T-T_g|^{-\nu}$  and coherence time scale  $z$ , where  $\nu$  is the static exponent and  $z$  is the dynamic exponent; thus  $I$ - $V$ -curves can be expressed by a universal scaling function. For HTS, experimental evidences of vortex glass phase have been reported [12]. Moreover, a vortex glass transition was observed in an untwinned single crystal of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> after inducing a sufficiently high pinning centers, suggesting that a vortex glass phase is one of origins for high  $J_c$  [13].

In here, we report high current-carrying capability in high quality MgB<sub>2</sub> thin films, which is confirmed by direct current-voltage ( $I$ - $V$ ) measurements as functions of magnetic fields and temperatures. As a possible origin of this high  $J_c$  in MgB<sub>2</sub> thin films, the vortex glass phase will be considered. By using pulsed laser deposition (PLD) system containing a load-rock sample preparation chamber, we are able to fabricate very high quality MgB<sub>2</sub> thin films.

The MgB<sub>2</sub> thin films were grown on R-plane Al<sub>2</sub>O<sub>3</sub> single crystals in a high vacuum condition at  $\sim 10^{-7}$  Torr by using PLD and post annealing techniques, which were reported in our earlier paper [14]. The PLD system used in the present study is especially designed for growth of metallic thin films without oxygen contamination. Furthermore, this system is able to transfer the precursor B films from the growth chamber to a very clean dry box without exposure in air. We found that preparation of pure B film is a very crucial point for the fabrication of high quality c-axis-oriented MgB<sub>2</sub> thin films. Typical dimensions of the samples were 10 mm in length, 10 mm in width and 0.4 mm in thickness. In order to measure  $I$ - $V$  characteristics, thin films were patterned into microbridge shape with the strip dimension of 1 mm long and 65  $\mu$ m wide by the standard photolithography technique, and then chemically etched in the acid solution with HNO<sub>3</sub> (50%) and pure water (50%). To obtain good

ohmic contacts ( $< 1 \text{ ohm}$ ), we coated Au film on the contact pad after cleaning the film surface with an Ar ion-beam milling. This patterning process didn't reduce the superconducting properties of  $\text{MgB}_2$  thin film.

Fig. 1 shows the low-field magnetization at  $H = 4 \text{ Oe}$  for both the zero-field-cooled (ZFC) and field-cooled (FC) states of an  $\text{MgB}_2$  thin film. A very sharp diamagnetic transition is observed. X-ray diffraction analysis indicates that the  $\text{MgB}_2$  thin film had a highly c-axis-oriented crystal structure and that the sample purity exceeded 99% (inset of Fig. 1). These results indicate that the  $\text{MgB}_2$  films used in the present study are homogeneous and of very high quality.

Fig. 2 shows (A) the plane-view and (B) the cross-sectional view taken by scanning electron microscopy techniques of  $\text{MgB}_2$  thin films grown on  $\text{Al}_2\text{O}_3$  substrates having a thickness of  $0.4 \text{ m}$ . Very smooth and shiny surface morphology can be observed except for the triangle or hexagonal shape single crystals that are embedded on the surface. We confirmed that these crystals are  $\text{MgB}_2$  compound from the analysis of energy dispersive x-ray spectroscopy. In the cross-sectional view of our thin films (Fig. 2B), we observe no grain boundaries, indicating that our thin films are very dense and have well-connected crystal structures

Fig. 3 shows the typical temperature dependence of the resistivity of  $\text{MgB}_2$  thin film. The onset transition temperature of  $39.2 \text{ K}$  with a very sharp transition of  $\sim 0.15 \text{ K}$ , determined from 90% to 10% of the normal-state resistivity, was observed. The resistivity at  $300 \text{ K}$  of  $10.4 \text{ cm}$  in the thin film is similar to that in polycrystalline  $\text{MgB}_2$  wire [15] whereas a residual resistivity ratio ( $\text{RRR} = 300\text{K}/40\text{K}$ ) of 3, which is much smaller than the value observed in  $\text{MgB}_2$  wire, is observed. This large difference of RRR value depending on various synthesis methods is still under debate [6, 17]. A very small (less than 0.5%) magnetoresistance was observed at  $5 \text{ T}$  and  $40 \text{ K}$ .

We measured the magnetization ( $M$ - $H$ ) hysteresis loops of a  $\text{MgB}_2$  thin film in the field range of  $-5 \text{ T} \leq H \leq 5 \text{ T}$  with parallel to the c-axis by using a superconducting quantum interference device magnetometer. Fig. 4 shows the  $M$ - $H$  curves of the thin film at temperatures of  $5$  and  $15 \text{ K}$ . The magnetization at low field decreases below  $T = 10 \text{ K}$  with decreasing temperature (lower panel of Fig. 3), indicating the dendritic penetration of vortices. This is explained a thermo-magnetic instability in the flux dynamics [18]. Therefore, we may not apply the Bean critical state model in this temperature region.

Fig. 5 shows the  $J_c$  estimated from  $M$ - $H$  loops (open symbols) and measured directly by transport method (solid symbols), as functions of temperatures and magnetic fields. The transport  $J_c$  was determined by using a voltage criterion  $1 \text{ V/mm}$ . From the  $M$ - $H$  curves, we calculated the values of  $J_c$  using Bean critical state model ( $J_c = 30M/r$ ), where  $M$  is the height of  $M$ - $H$  loop. Here, we used  $r = 1.784 \text{ mm}$ , the corresponding radius to the total area of sample size. With this sample size, the  $J_c$  curves obtained from  $M$ - $H$  loops and  $I$ - $V$  measurements are well coincided, indicating strongly linked nature of the inter-grains on the thin film, but different from the behavior of the HTS [19].

Under self-field, the  $J_c$  was observed to be  $16 \text{ MA/cm}^2$  at  $15 \text{ K}$  and then slightly decreases to  $12$

MA/cm<sup>2</sup> at 5 K. As mentioned before, since the temperature region below 15 K cannot be applied critical state model, the transport  $J_c$  at 5 K is probably higher. From the  $I$ - $V$  measurements region using polycrystalline thin films, the monotonous increase of critical current density with decreasing temperature at low temperature was observed [20]. The extrapolation value of  $J_c$  at 5 K was estimated to be 40 MA/cm<sup>2</sup>, which is the highest record for MgB<sub>2</sub> superconductors and is comparable to that of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> thin film [21] or even exceeds those of other HTS, such as Hg- and Bi-based superconductors [22,23]. The high  $J_c$  of  $\sim 0.1$  MA/cm<sup>2</sup> at 37 K in self-field suggests that MgB<sub>2</sub> thin film has very high potential for applications of electronic devices operating high temperature, such as microwave devices and portable SQUIDS sensors by using miniature refrigerators with low cost. At  $H = 5$  T, the current carrying capability of 0.1 MA/cm<sup>2</sup> at 15 K, is also of considerable for practical application in superconducting solenoids using mechanical cryocoolers with low power consumption if we fabricate high quality MgB<sub>2</sub> thick films or tapes.

In order to investigate the vortex phase diagram of MgB<sub>2</sub> thin film, we have measured  $I$ - $V$  characteristics for various magnetic fields as shown in Fig. 6. The  $I$ - $V$  curves in the inset of Fig. 6 are very similar to typical behavior of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> superconductor [12] around vortex-glass transition temperature  $T_g$ . According to the vortex-glass theory [11],  $I$ - $V$  curves show positive curvature for  $T > T_g$ , negative curvature for  $T < T_g$ , and a power-law behavior at  $T_g$ , which is in good agreement with our results with  $T_g = 26.15$  K at  $H = 3$ . Furthermore, these  $I$ - $V$  curves can be expressed by a universal scaling function near  $T_g$  with two common variables given by

$$V_{sc} = V / I |T - T_g|^{\nu(z-1)} \quad (1)$$

$$I_{sc} = I / T |T - T_g|^{2\nu}, \quad (2)$$

All  $I$ - $V$  curves collapse onto above scaling functions with static exponents of  $\nu = 1.0$  and dynamic exponents of  $z = 4.5$ , which were in good agreement with the theoretical prediction for a three-dimensional (3D) system. This scaling behavior is well satisfied all  $I$ - $V$  curves measured at other fields from 1 to 5 T. We find that the vortex-glass region of MgB<sub>2</sub> is wide, implying that the pinning force is very strong at low temperature. We suggest that the high current carrying capability of MgB<sub>2</sub> superconductor is probably originated from the 3D vortex-glass phase with strong pinning disorders and with higher charge carriers [6]. Indeed, the vortex glass phase of untwined YBCO single crystal was observed only for highly disordered samples after proton irradiations whereas the vortex lattice melting transition was observed in pristine samples [13].

By using PLD system with a load-rock sample preparation chamber, we have successfully fabricated very high quality MgB<sub>2</sub> thin films. SEM images show that our thin films are very dense and have well-connected crystal structures. We have measured  $J_c$  in MgB<sub>2</sub> thin film by both transport



property and  $M$ - $H$  hysteresis curves. We find these two data are quite well coincided into one curve for entire temperature region, indicating that the Bean's critical-state model is well consistent with this material. We observed high  $J_c$  of  $16 \text{ MA/cm}^2$  at 15 K and under zero-field, which is comparable to those of HTS. At a magnetic field of 5 T, the critical current density of  $\sim 0.1 \text{ MA/cm}^2$  was detected at 15 K, suggesting that this compound is very promising candidate for the practical applications at high temperature, such as a liquid-He-free superconducting magnet system and superconducting electronic devices by using mechanical or miniature cryocoolers with lower power consumption. We have suggested the 3D vortex-glass phase as a possible origin for high current-carrying capability of  $\text{MgB}_2$ .

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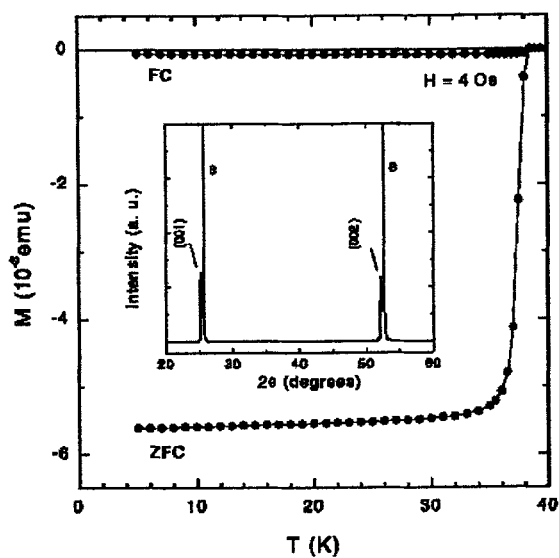


Fig. 1. Magnetization at  $H = 4$  Oe in the ZFC and FC states of  $\text{MgB}_2$  thin films grown on  $\text{Al}_2\text{O}_3$  substrates. A very sharp diamagnetic transition was observed. The inset shows the X-ray diffraction patterns, indicating a highly c-axis-oriented crystal structure normal to the substrate surfaces. S denotes the substrate peaks.

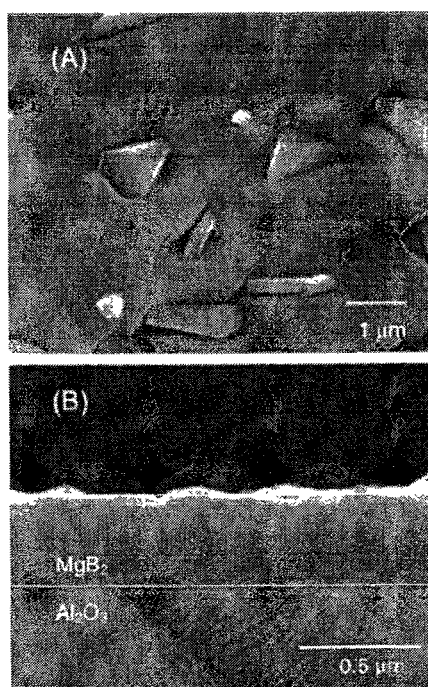


Fig. 2. (A) Plane-view and (B) cross-sectional view of SEM pictures of  $\text{MgB}_2$  thin films grown by pulsed laser deposition system on  $\text{Al}_2\text{O}_3$  substrates.

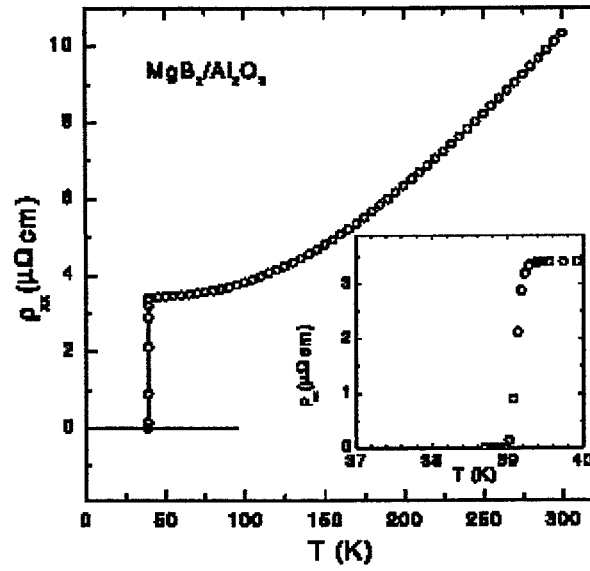


Fig. 3. Temperature dependence of resistivity for MgB<sub>2</sub> thin film.

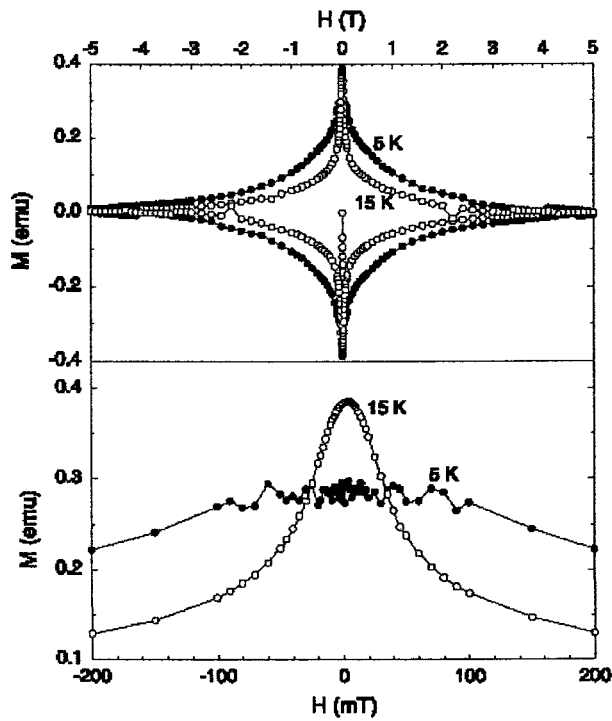


Fig. 4. The upper part shows the  $M$ - $H$  hysteresis loop at 5 K (solid circle) and 15 K (open circle). The lower is the magnified view for low field region at 5 and 15 K.

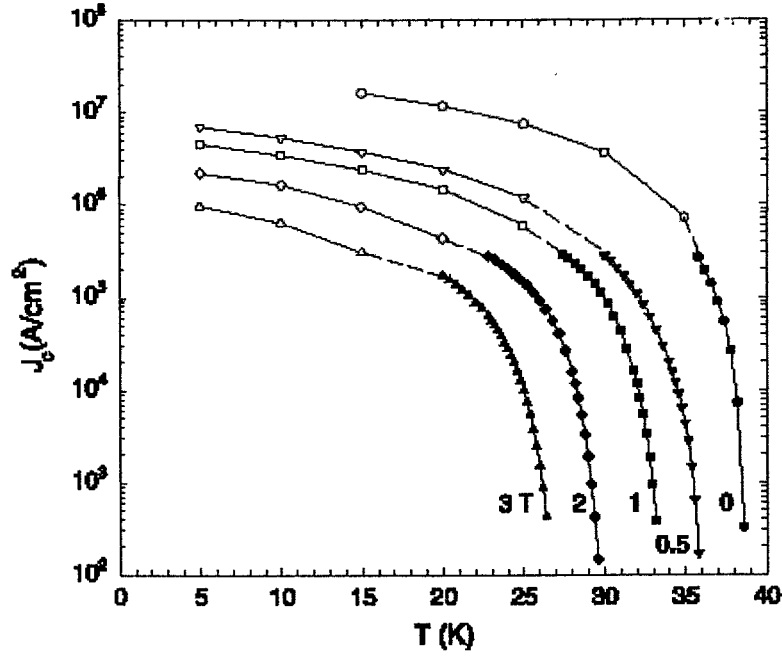


Fig. 5. The temperature dependence of critical current density of MgB<sub>2</sub> thin film for  $H = 0 - 5$  T, extracted from the  $M-H$  (open symbols) and the  $I-V$  (solid symbols) curves, respectively.  $J_c = 0.1$  MA/cm<sup>2</sup> is a common benchmark for practical application.

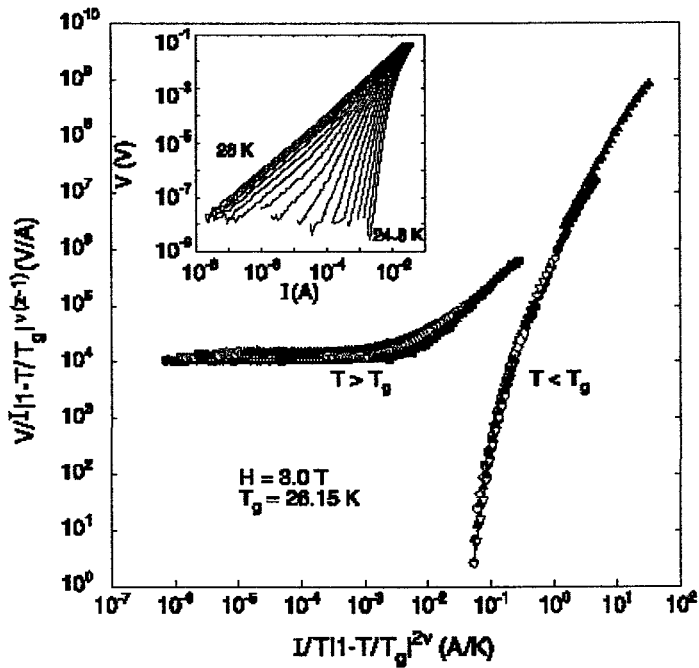


Fig. 6. Vortex-glass scaling behavior. The inset shows  $I-V$  characteristics at  $T = 24.8 - 28$  K in 0.2 K step under  $H = 3$  T.

## Energy gap, penetration depth and surface resistance of MgB<sub>2</sub> thin film determined by microwave resonator measurements

We have measured the temperature dependence of the microwave surface impedance  $Z_s = R_s + i\omega\mu_0\lambda$  of two c-axis oriented MgB<sub>2</sub> films at a frequency  $\omega/2\pi$  of 17.9 GHz employing a dielectric (sapphire) resonator technique. Apart from small deviations close to  $T_c$ , the temperature dependence of the magnetic field penetration depth  $\lambda$  can be fitted by the standard BCS expression assuming the reduced energy gap  $\Delta(0)/kT_c$  to be as low as 1.03 and 1.13 for two different samples. For the penetration depth at zero temperatures, values between 115 nm and 136 nm were determined from the fit. Our results clearly indicates the s-wave character of the order parameter. The temperature dependence of the surface resistance  $R_s$  below  $T_c/2$  is consistent with the low value of the energy gap. The surface resistance below 8 K was found to be below the resolution limit of  $100\mu\Omega$  for our measurement technique.

The question about the energy gap in a particular superconducting material is of fundamental importance for the understanding of the relevant pairing mechanism and for the determination of its application potential. The recently discovered superconductivity in MgB<sub>2</sub> [1] raises this question with particular emphasis.

According to initial findings, MgB<sub>2</sub> seemed to comprise a high transition temperature with superconducting properties resembling that of conventional superconductors rather than that of high temperature superconducting cuprates [2-4]. In particular, the strong anisotropy of superconducting properties, the short coherence length and the unconventional order parameter being apparent for high temperature superconducting cuprates have turned out to be a burden for many applications. Consequently, such burdens are expected not to be present or at least less pronounced in MgB<sub>2</sub>.

Recent experiments have brought some clarifications about the gap features of MgB<sub>2</sub>. According to tunneling spectroscopy [5], point contact spectroscopy [6-7], photoemission[8], Raman scattering [9], specific heat [10-11], and optical conductivity spectra [12] there is evidence for an s-wave symmetry with two distinct gaps possibly associated with the two separate segments of the Fermi surface being present in MgB<sub>2</sub> [13]. The absolute values of these two gaps were determined to be around 1.5 to 3.8 meV and 5.5 to 8 meV consistently by these different methods.

On the other hand, the temperature dependence of the penetration depth  $\lambda(T)$  is quite controversial. Quadratic, linear and exponential dependence are reported in the literature [14-19]. Quadratic and linear dependence might be an indication for unconventional superconductivity, similar to high temperature superconducting cuprates [20]. However, the observation of an exponential dependence would be clear indication for a nodeless gap, i.e. for an order parameter comprising s-wave symmetry. Hence, a very high measurement accuracy for temperature changes of  $\lambda$  at  $T \ll T_c$  for high quality samples is required to distinguish between a power-law and an exponential temperature dependence.

Microwave surface impedance measurements have proved to be the most sensitive tool to determine the temperature dependence of the magnetic field penetration depth of both thin film [21] and bulk single crystal samples [22]. In particular, they have been employed successfully to attain significant information about the symmetry of the order parameter in the high temperature superconducting cuprates. Therefore, microwave resonator techniques are most appropriate to be used for high-precision  $\lambda(T)$  measurements on high quality MgB<sub>2</sub> samples.

Apart from the penetration depth the microwave surface resistance,  $R_s$  is an important figure of merit for microwave applications. According to BCS theory, the expected  $\exp(-\Delta/kT)$  dependence of  $R_s$  below  $T_c/2$  might result in very low  $R_s$  values at temperature attainable with low-power cryocoolers.

MgB<sub>2</sub> thin films were fabricated using a two-step method by pulsed laser deposition. The detailed process is described in [23] and [24]. The films deposited on a plane parallel [1102] oriented sapphire substrate of 10x10 mm<sup>2</sup> in size exhibit a sharp resistive and inductive transition at  $T_c = 39$  K. The film thickness was 400 nm for both samples. X-ray diffraction analysis indicates a high degree of c-axis-orientation perpendicular to the substrate surface and no detectable amount of MgO or any other crystalline impurity phases. The microwave surface impedance was determined using a sapphire dielectric resonator technique described elsewhere [25]. The cavity with part of one end plate replaced by the thin film sample was excited in the TE<sub>018</sub> - mode under weak coupling conditions. The unloaded quality factor  $Q_0$  and resonant frequency was recorded as a function of temperature. The real part of the effective surface impedance, the effective surface resistance  $R_s^{eff}$  was determined according to

$$R_s^{eff}(T) = G \left[ \frac{1}{Q_0(T)} - \frac{1}{Q_{NbN}(4.2K)} \right] \quad (1)$$

with  $G$  being a geometrical factor determined by numerical simulation of the electromagnetic field distribution in the cavity and  $Q_{NbN}(4.2\text{ K}) = 108,440$  representing the unloaded quality factor measured by employing a high-quality NbN thin film as sample. The notation "effective" indicates an enhancement of  $R_s$  and due to the film thickness  $d$  being of the order of  $\lambda$  [26]. For temperatures below 30 K Eq. 1 allows for the determination of  $R_s^{eff}$  with a systematic error of about 0.1 mΩ, which is due to neglecting the temperature dependent background losses of the cavity and the small microwave losses ( $R_s \approx 10^{-5}\Omega$ ) of the NbN film.

$$\delta\lambda^{eff}(T) = \frac{G}{\pi\mu_0} \frac{f(T) - f(5K)}{f^2(5K)} \quad (2)$$

The temperature dependence of the effective penetration depth was determined from the temperature dependence of the resonant frequency  $f(T)$  using with  $\mu_0 = 1.25610 \cdot 10^{-6}$  Vs/Am. There is a systematic error due to frequency changes caused by thermal expansion, the temperature dependence

of the skin depth of the cavity wall material (copper) and the temperature dependence of the dielectric constant of sapphire. To account for these effects, we recorded the temperature dependence of the resonant frequency employing a copper sample. From this measurement we found that the systematic error is less than 1 nm for  $T < 15$  K and less than 2.5 nm for  $T > 25$  K, which is at least one order of magnitude lower than the observed temperature changes of  $\lambda$  for our MgB<sub>2</sub> sample. Therefore, Eq. 2 was applied without correction for our investigation.

In general, microwave resonator measurements do not allow for the determination of absolute values of  $\lambda$  because the resonator dimensions are only known with a precision of several ten micrometers. However, absolute value  $\lambda$  can be extracted by comparing the measured temperature dependence with existing models.

Fig. 1 shows temperature dependence of  $R_s^{eff}$  and  $\delta\lambda^{eff}$  (sample B) as determined by Eq. 1 and Eq. 2, respectively. The inset shows  $R_s^{eff}(T)$  value at low temperatures. The solid line represents the resolution limit of our setup. Below 8 K,  $R_s^{eff}$  is below the resolution of our technique ( $100\mu\Omega$ ). Scaling to 10 GHz by assuming an  $\omega^2$  law results in a corresponding value of less than  $30\mu\Omega$ . To our knowledge, this is the lowest value reported for wires, pellets and thin films of MgB<sub>2</sub> [17,27-29].

Fig.2 shows the measured temperature dependence of  $\delta\lambda^{eff}$  determined from  $f(T)$  according to Eq. 2 in a  $\log \delta\lambda$  versus  $1/T$  representation. The nearly linear dependence in this representation clearly indicates an exponential dependence as predicted by BCS theory [20]. In contrast, a double logarithmic plot of the same data indicates that a power law does not fit the data at low temperatures. The occurrence of an exponential behaviour of  $\delta\lambda^{eff}(T)$  at  $T < T_c / 2$  is a clear indication for a finite energy gap in all directions of the Fermi surface without nodes. The solid lines represent BCS calculations based on the standard BCS integral expression[20]

$$\frac{1}{\lambda^2(T)} = \frac{1}{\lambda^2(0)} \left[ 1 - 2 \int_{\Delta(T)}^{\infty} -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \frac{\varepsilon}{\sqrt{\varepsilon^2 - \Delta^2(T)}} d\varepsilon \right] \quad (3)$$

with  $f(\varepsilon) = [\exp(\varepsilon/kT) + 1]^{-1}$  representing the Fermi function and  $\Delta(T)$  the temperature dependence of energy gap. The quantities  $\Delta(0)/kT_c$  and  $\lambda(0)$  are used as fit parameters. For the temperature dependence of  $\Delta(T)/\Delta(0)$  values tabulated in Ref [30] were used. The  $\delta\lambda_{BCS}$  values calculated from Eq. 3 are multiplied with  $\coth(d/\lambda_{BCS})$  to account for the finite film thickness [26]. As a result, the fits of Eq. 3 to the  $\delta\lambda_{eff}(T)$  data (full lines in Fig. 2) yield  $\Delta(0)/kT_c = 1.13$  ( $\Delta(0) = 3.8$  meV) and  $\lambda(0) = 115$  nm for sample A,  $\Delta(0)/kT_c = 1.03$  ( $\Delta(0) = 3.5$  meV) and  $\lambda(0) = 136$  nm for sample B. For comparison, the same analysis was performed for a NbN thin film, which is a well-known s-wave superconductor with a relatively high  $T_c$  of 15.8 K. The fit parameters are  $\Delta(0)/kT_c = 2.3$  and  $\lambda(0) = 265$  nm, respectively, which is similar to literature data [31]. The  $\Delta(0)/kT_c$  values obtained for the MgB<sub>2</sub> samples are similar to the value of  $3.5 \pm 0.5$  meV determined by scanning tunneling microscopy [5]. The  $\lambda(0)$  values are also in the range of corresponding values determined by other techniques [14,17,32,33]. In contrast to



tunneling experiments, which are very sensitive to a possible modification of the surface, microwave surface impedance measurement probe almost the entire volume of a thin film sample with thickness of the order of  $\lambda$ . Therefore, surface degradation can be ruled out as a possible reason for the small values of  $\Delta/kT_c$ . In fact, some tunneling data exhibit  $\Delta/kT_c$  values even lower than ours, indicating that surface degradation effects may play some role there [3,4].

The other possible explanation is that the small gap represents the smallest component of a double-or multigap or a strongly anisotropic gap. In this case the temperature dependence of  $\lambda$  at  $T \ll T_c$  would be determined by its minimum value, because  $\lambda(T)$  probes the thermal excitations with the lowest activation energy. However, the existence of a second larger gap should have a significant impact on  $\lambda(T)$  at higher temperatures. Fig.3 shows the temperature dependence of  $\lambda^2(0)/\lambda^2(T)$ , which represents the normalised superfluid density. Sample A exhibits an almost perfect agreement with BCS theory, sample B exhibits slight deviations above  $0.6 T_c$ . Similar to sample A, the NbN film exhibits perfect agreement over the entire temperature range. The latter indicates, that the effects of strong coupling on  $\lambda(T)$  can be modelled just by assuming  $\Delta/kT_c$  being larger than the BCS-value of 1.76[34].

In order to test a possible two gap scenario, we tried fits of

$$\frac{1}{\lambda^2(T)} = \frac{1}{\lambda_{BCS}^2(T, \Delta_{min}/kT_c)} + \frac{1}{\lambda_{BCS}^2(T, \Delta_{max}/kT_c)}$$

representing two independent components of the superfluid with different values of the energy gap. Employing  $\Delta_{min}/kT_c$  as determined before from the low temperature  $\lambda(T)$  data we could not attain any improvement of our fit for any value of  $\Delta_{max}/kT_c$   $\Delta_{min}/kT_c$  and for any possible combination of  $\lambda(0)$  values for the "small" and "large" energy gap superfluid component. From this result we can rule out that a second independent superfluid component with a larger energy gap provides a significant contribution to our experimental results. However, since the films have a high degree of c-axis orientation and since the rf current induced by the resonator field are "in-plane", we cannot exclude a strongly anisotropic gap. In fact, a study of the c-axis microwave response on bulk single crystals would be an experiment worth to be done.

Another possible reason for the fact that a two-gap fit does not work is that thermal excitations from the low energy gap "smear" the effects of the large energy gap in the quasi particle density of states. In this case the independent two-fluid picture is no longer appropriate. To prove such an hypothesis, more advanced theoretical modelling of a two-gap superconductor would be necessary. The absence of second energy gap was also found for SIS junction[7,35]. It is believed that the persistent and clear observation of only small energy gap is due to the much higher probability of tunneling into the 3d band, where only the small energy gap exists [7].

Fig. 4 shows temperature dependence of the  $R_s^{eff} - R_s^{eff}(4.2 K)$  data of our samples The full lines indicates fits of an  $\exp(-\Delta/kT)$  dependence with  $\Delta/kT_c$  values as determined from  $\lambda(T)$ . According to

Fig. 4, the data are consistent with the fit.

In conclusion, our experimental finding represents clear evidence for the existence of a finite gap with  $\Delta(0)/kT_c$  values around 1.1. The temperature dependence of  $\lambda$  can be fitted by BCS theory in the entire temperature range below  $T_c$ . The very low  $R_s$  value ( $<100\mu\Omega$  at 4.2K and  $270\mu\Omega$  at 15K and 17.9GHz ) obtained for one sample implies that  $MgB_2$  is a promising material for microwave applications.

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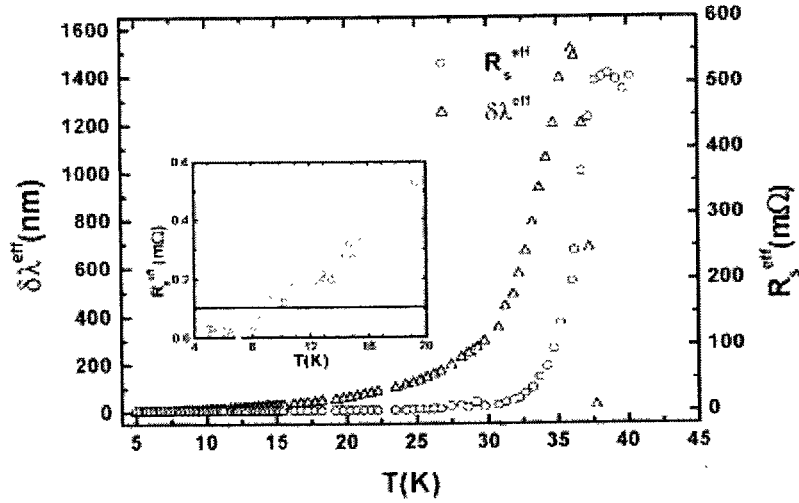


Fig. 1: Temperature dependence of  $R_s^{eff}$  and  $\delta\lambda^{eff}$  of a  $MgB_2$  thin film recorded at 17.9 GHz using a dielectric resonator technique. The inset shows the  $R_s^{eff}$  (T) values below 8K and our measurement resolution of  $100\mu\Omega$ .

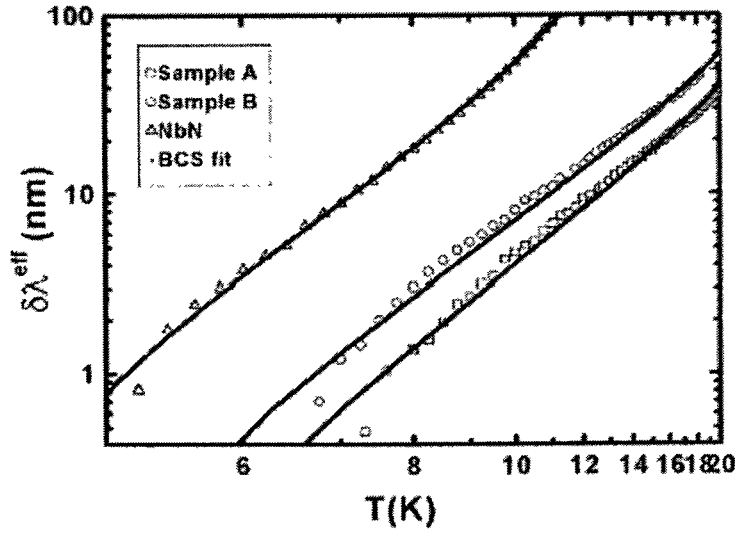


Fig. 2:  $\delta\lambda^{eff}$  dependence on temperature below 20K ( $T_c/2$ ) for two  $MgB_2$  samples and a NbN thin film for comparison. The solid line represents BCS fits with parameters as described in the text.

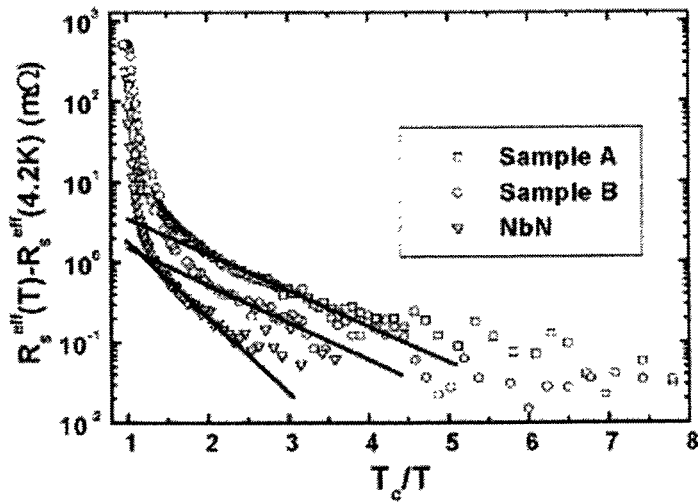


Fig. 3:  $\lambda^2(0)/\lambda^2(T)$  dependence for the samples shown in Fig. 2. The full lines represent BCS fits using  $\Delta(0)/kT_c$  as fit parameter. The predictions by two fluid model (dashed) , quadratic (dashed-dotted) dependence and standard BCS model with  $\Delta(0)/kT_c = 1.76$  (dotted) are also drawn.

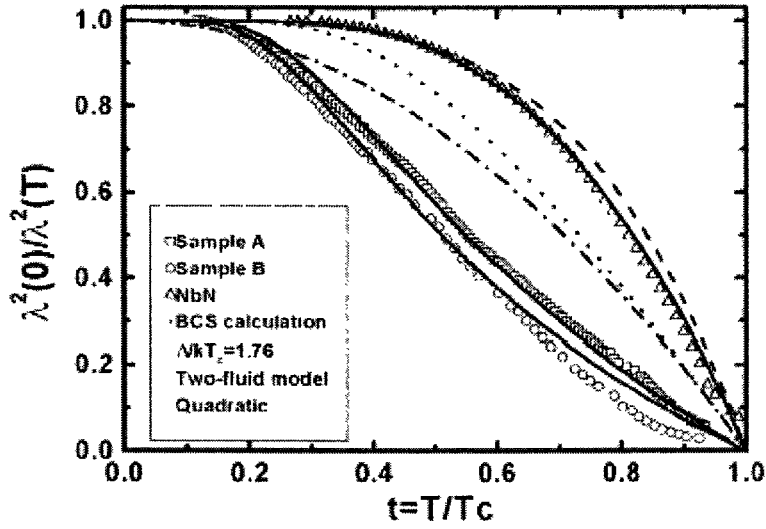


Fig.4:  $R_s^{eff}(T) - R_s^{eff}(T = 4.2 \text{ K})$  plotted versus  $T_c/T$  for the samples shown in Fig. 2. The full lines correspond to fits of  $\exp(-\Delta(0)/kT_c)$  to the experimental data.

### Effect of pressure on the superconductivity and magnetism of $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$

We have studied the pressure effect on the superconductivity and the magnetism of  $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$  for  $x=0.1$  and  $x=0.4$  by measuring its transport properties. While the superconducting transition temperature  $T_c$  lies above the Neel temperature  $T_N$  for  $x=0.1$ , the  $T_c$  lies below the  $T_N$  for  $x=0.4$ . The pressure changes the magnetic exchange integral,  $J_{sf}$ , and controls the pair breaking effect. In the case of the  $x=0.1$  sample, increasing pressure decreases  $T_c$ , which can be explained by the pressure-induced change of the magnetic exchange integral  $J_{sf}$  within the Abrikosov-Gor'kov's theory. On the other hand, the pressure does not influence the  $T_c$  of the  $x=0.4$  sample. Also, we measured the pressure dependence of the upper critical field. These results support the phenomenological theory of multiband superconductivity in an antiferromagnetic state.

The intermetallic compounds  $\text{RNi}_2\text{B}_2\text{C}$  ( $R = \text{Y, Lu, Tm, Er, Ho, and Dy}$ ) [1-4] have attracted much interest because they are ideal for studying the competition between superconductivity and magnetism[5]. Depending on the rare-earth element  $R$ , these compounds show various types of magnetic structures. In this system, the localized spins from  $4f$  orbitals are indirectly coupled with each other through the conduction electrons, i.e., through the RKKY interaction. Based on the band

calculations [6,7], the electrons form complicated multiband structure near the Fermi level, and the superconductivity is thought to be mainly from the Ni 3d band. Other bands also contribute, however. According to the Abrikosov-Gor'kov (AG) theory, the magnetic moments at rare-earth ions generate the pair-breaking field of superconductivity and suppress the superconducting transition temperature by an amount  $T_c = T_c - T_{c0}$ , which is proportional to  $J_{sf}^2 (gJ-1)^2 J(J+1)$  [8]. Here,  $J_{sf}$  is the exchange interaction between the conduction electron spin and the localized momentum of the f orbital, and  $(gJ-1)^2 J(J+1)$  is the so-called de Gennes factor (dG). This series of compounds also roughly follows the de Gennes scaling in the AG theory of  $T_c$  suppression[9-13]. However, very notably, for  $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$ , the de Gennes scaling is broken severely [14]: For increasing concentration, x, the  $T_N$  increases with dG, and the  $T_c$  decreases when  $T_c > T_N$  however, after  $T_c$  drops below  $T_N$ ,  $T_c$  remains almost constant. The AG theory, which is based on the paramagnetic state, is not suitable for explaining this case, i.e., the superconductivity in an ordered magnetic state. This anomalous behavior was explained using competition between two superconducting order parameters from two different bands [15]. As seen in Fig. 1, the field at the Ni site in the commensurate antiferromagnetic order of the rare-earth atoms is cancelled, and its effect on the Ni site is suppressed because the Ni sites are located at the centers of tetrahedra consisting of nearest-neighboring rare-earth atoms. Thus, if we assume that one of the bands originates from the Ni d-orbital, that band is hardly influenced by the commensurate antiferromagnetic order. This assumption is also supported by the Mossbauer spectroscopy[16] which shows a vanishingly small local magnetic field at the Ni site in  $\text{HoNi}_2\text{B}_2\text{C}$  below the Neel temperature. Experimental studies to test this idea and to understand the magnetic pair breaking phenomena for various x are underway.

Unfortunately, it is not simple to study the effects of magnetic order on superconductivity by substituting rare-earth ions. Since the magnetic structure depends on the rare-earth ion R in  $\text{RNi}_2\text{B}_2\text{C}$ [17], the substitution can change not only the dG but also the magnetic structure. Among nickel borocarbides, Ho and Dy are the only pair that have a similar magnetic order but different dG. Thus the mixing of Ho and Dy does not disturb the magnetic structure. However, for other pairs of rare-earth ions, mixing causes complicated magnetic structures[18] as for  $\text{Er}_{1-x}\text{Tb}_x\text{Ni}_2\text{B}_2\text{C}$  [19,20], and makes it difficult to study the pair-breaking effect.

The  $T_c$  suppression,  $T_c$  in the AG theory, and  $T_N$  in the RKKY theory are both proportional to  $J_{sf}^2 dG$ . Thus, the pair-breaking strength can be controlled by  $J_{sf}$ , as well as by dG. Since  $J_{sf}$  is determined by the overlap of the f-orbital and the wave function of conduction electrons, it is sensitive to the external pressure. The pressure decreases the distance between atoms and increases the overlap of the orbitals. Up to linear terms, the dependence of the  $J_{sf}$  on the pressure can be written as  $J_{sf}(p) = J_{sf0} + (dJ_{sf}/dp)p$ . Michor *et al.* [21] reported that  $J_{sf0} = 31$  meV and  $dJ_{sf}/dp \sim 1.0$  meV/GPa are common values for  $\text{R}_{1-x}\text{R}'_x\text{Ni}_2\text{B}_2\text{C}$  with  $\text{R} = \text{Y, Lu}$  and  $\text{R}' = \text{Dy, Ho, Tb, Gd}$ . Here, pressure doesn't change the composition, so it is simpler to study the effects of magnetic order than it is when substituting of rare-earth elements.

The purpose of this article is to investigate the interaction between magnetism and superconductivity for a magnetically ordered state by controlling  $J_{sf}$  by changing the pressure without changing the composition and to show how differently the  $T_c$  responds to the pressure for  $T_c > T_N$  and  $T_c < T_N$ . For this purpose, we adopted two pseudo-quatary compounds,  $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$  with  $x=0.1$  and  $x=0.4$ , which have values of  $T_c$  slightly higher and slightly lower than  $T_N$ , respectively. The experiments reveal that pressure (or  $J_{sf}$ ) suppresses the  $T_c$  following the AG theory in the paramagnetic region ( $T_c > T_N$ ), and that the  $T_c$  is almost constant for  $T_c < T_N$ . Actually, the  $T_c$  increases very weakly with pressure. The pressure dependences of the  $T_c$  and the upper critical field  $H_{c2}(T)$  lines for  $x=0.1$  strongly suggest that the superconductivity, which is insensitive to the magnetism below  $T_N$ , originates from cancellation of the pair-breaking fields at the Ni sites. Since our pressure experiments are quite similar to those for the substitution effect in  $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$  [14], the two-band phenomenological theory [15] for  $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$  is also applicable to our experiments.

Single crystals of  $\text{Ho}_{0.9}\text{Dy}_{0.1}\text{Ni}_2\text{B}_2\text{C}$  ( $x=0.1$ ) and  $\text{Ho}_{0.6}\text{Dy}_{0.4}\text{Ni}_2\text{B}_2\text{C}$  ( $x=0.4$ ) were grown by using the high temperature  $\text{Ni}_2\text{B}$  flux method [22-24]. The obtained single crystals which were plate shaped, were cut by using a wire saw and were then ground into a bar shape with dimensions  $1.7 \times 0.6 \times 0.2 \text{ mm}^3$  for  $x=0.1$  and  $1.7 \times 0.6 \times 0.3 \text{ mm}^3$  for  $x=0.4$ . Then, the crystal bars were annealed at 950C for 6 hours to remove possible internal stresses introduced during the polishing process. The electric resistances of these samples were measured from  $T= 2 \text{ K}$  to  $20 \text{ K}$  for hydrostatic pressures up to  $2.0 \text{ GPa}$ . The magnetic field effect was also investigated, especially for  $x=0.1$ , for fields up to  $5 \text{ kOe}$  at pressures of  $0.1 \text{ GPa}$  and  $2.0 \text{ GPa}$ .

Figure 2 shows the temperature dependence of the in-plane electrical resistivity ( $T$ ) under various pressures up to  $2.0 \text{ GPa}$  for the temperatures in the range  $2 \text{ K} < T < 15 \text{ K}$ . For  $x=0.1$  [Fig. 2(a)], at  $p = 0.1 \text{ GPa}$ , the  $T_c$  is measured as  $8.2 \text{ K}$ . The  $T_N$  cannot be determined from the resistivity measurement below  $T_c$ . For  $p = 1.0 \text{ GPa}$ , the  $T_N$  can be measured due to the reentrance behavior which appears near  $6 \text{ K}$ . The reentrance behavior of ( $T$ ) occurs due to the maximum fluctuation of the magnetic ordering. Thus, the  $T_N$  is determined from the maximum of the ( $T$ ) in the reentrance region. Reentrance behavior does not appear in our  $x=0.1$  sample at zero and low pressures, while it was reported previously [14]. The reentrance at this concentration seems to be delicate and strongly sensitive to the inhomogeneity and magnetic scattering induced by some structural defects or disorders. At  $p = 1.0 \text{ GPa}$  and  $1.5 \text{ GPa}$ , the ( $T$ ) peaks occur at near  $6 \text{ K}$ , and the values of  $T_N$  are indicated by the arrows in the figure. The resistivity at  $p = 1.5 \text{ GPa}$  drops near  $7.5 \text{ K}$ , but does not go completely to zero because of either severe reentrance behavior or fluctuating vortex states. Therefore, under this pressure, the  $T_c$  is uncertain, but it is estimated to be between  $6.1 \text{ K}$  and  $7.5 \text{ K}$ .

The former value was determined from zero resistance, and the latter value was from linearly extrapolating the resistance data around  $7.5 \text{ K}$  to zero resistance. As the pressure increases, the  $T_c$  decreases, but the  $T_N$  increases, and at  $p = 2.0 \text{ GPa}$ ,  $T_N$  exceeds  $T_c$ . For  $p=2.0 \text{ GPa}$ , there is a preceding drop of ( $T$ ) near  $6.5 \text{ K}$ , which is above  $T_c$ , since the antiferromagnetic ordering suppresses

the paramagnetic scattering. Thus,  $T_N$  is determined as 6.5 K. A weak decrease of  $(T)$  is also observed below 8.5 K. The origin of this might be related with a weakly developing magnetic order, such as the spiral and a-axis modulation found in  $\text{HoNi}_2\text{B}_2\text{C}$  [17]. A detailed study of this would require neutron or x-ray scattering information of the magnetic structure.

For  $x=0.4$  [Fig. 2(b)],  $(T)$  for  $p = 0.1$  GPa shows the typical temperature dependence for a magnetic superconductor with  $T_c < T_N$  as  $T$  decreases,  $(T)$  first decreases at  $T_N = 7.2$  K and then goes completely to zero at  $T_c = 6.0$  K. The sharp nature of  $(T)$  near the  $T_N$  becomes gradual for  $p = 1.0$  GPa. Therefore, the determination of  $T_N$  is not easy. Instead of specifying  $T_N$ , we distinguish  $T_M^{\text{mid}}$  and  $T_M^{\text{onset}}$ . Here,  $T_M^{\text{onset}}$  is the onset of the resistivity drop and  $T_M^{\text{mid}}$  is the mid point of the resistivity values at  $T_M^{\text{onset}}$  and just above the superconducting transition. Since  $T_M^{\text{mid}}$  follows the RKKY theory well, it was used for our analysis and is indicated by the arrows in the Fig. 2 (b).

The external magnetic field dependency for  $x=0.1$  was measured at low pressure  $p=0.1$  GPa [Fig. 3(a)] for  $T_c > T_N$  in zero field and at high pressure  $p = 2.0$  GPa [Fig. 3(b)] where  $T_c < T_N$ . For  $p=0.1$  GPa, the  $T_c$  decreases abruptly from 8.5 K to 5.3 K when a rather weak field of 0.1 T is applied. This weak field enhances the reentrance region around 5.8 K and is enough to destroy the upper superconductivity between 6 K and 7.5 K. When  $T_c < T_N$ , the  $T_c$  decreases linearly. Unlike the case of  $p=0.1$  GPa, for the pressure  $p=2.0$  GPa, the R-T curves show a rather simple behavior from the start as the field varies; the  $T_c$  decreases linearly as the field increases, and the  $T_N$  is slightly suppressed by the field. These behaviors are similar with those for  $\text{DyNi}_2\text{B}_2\text{C}$  which has a  $T_c$  lower than its  $T_N$ .

The pressure dependence of  $T_c$  and  $T_N$  (the  $T_M^{\text{mid}}$  is used for  $x=0.4$  sample), determined from Fig. 2, are plotted in Fig. 4. The behavior of the  $T_c$  and the  $T_N$  for  $x=0.1$  follows the AG theory and the RKKY theory, respectively, as was expected from the fact that the pressure increases the exchange coupling  $J_{sf}$ . According to the AG theory, the  $T_c$  decreases with increasing pair-breaking parameter,  $J_{sf}^2 dG$ . Thus, the pressure, by increasing  $J_{sf}$ , will suppress the  $T_c$  ( $p$ ). The observed initial slope,  $dT_c/dp = -0.64$  K/GPa, is roughly consistent with the value,  $-0.49$  K/GPa, estimated by assuming the linear pressure dependence in Eq. (1), and by adopting the values  $J_{sf0} \cong 31$  meV and  $dJ_{sf}/dp \cong 1.3$  meV/GPa reported in Ref. 21. The increase of the  $T_N$  can be understood easily since  $T_N \propto J_{sf}^2 dG$  in the RKKY theory. The slope of the  $T_N$  ( $p$ ) is measured to be  $d T_N / d p \cong 0.48$  K/GPa. This is quite consistent with the estimated value  $dT_N/dp = 2[T_N(0)/dJ_{sf0}](dJ_{sf}/dp) \cong 0.482$ . Figure 4(a) shows the experimental  $T_N$  values and the estimated values.

For  $T_N > T_c$ , i.e., for  $p = 2$  GPa in case of  $x=0.1$  and for  $x=0.4$  sample, the behaviors of the  $T_c$  ( $p$ ) and the  $T_N$  ( $p$ ) are quite different from those of  $x=0.1$  sample for  $p < 2$  GPa. As seen in Fig. 4 (b), the  $T_c$  ( $p$ ) is not much affected by the pressure. As the pressure increases, the  $T_c$  does not decrease; it even increases very slightly. We suggest that the superconductivity from the Ni band is not affected due to the cancellation of the pair-breaking field at the Ni sites in the Neel state [15]. From this interpretation, the  $T_c$  given by the Ni bands alone is at most about 6 K. Since the  $T_c$  is near 8 K when  $x=0.1$  and  $p=0$  GPa, there should be an additional second band which is sensitive to the magnetic pair



breaking. The superconductivity of the second band becomes suppressed as the pressure increases, and finally vanishes while that of the Ni bands survives when  $T_N > T_c$ . Moreover, as the  $T_N$  goes up and moves away from the  $T_c$ , the fluctuation of the magnetic order decreases, thus enhancing the superconductivity weakly. On the other hand, the  $T_M$  onset increases very rapidly with pressure. The change of the  $T_M$  onsite is far more rapid than that of  $T_M$  mid estimated from the same set of parameters,  $J_{sf}0$  and  $dJ_{sf}/dp$  (line in Fig. 4 (b)). The drop of the resistivity at  $T_M^{\text{onset}}$  is so gradual that it is hard to regard it as the antiferromagnetic transition. The  $T_M^{\text{mid}}$  determined from the midpoint in the resistivity roughly follows our  $T_N$  line estimated from RKKY theory. From this fact, we presume that the antiferromagnetic transition occurs not near the  $T_M^{\text{onset}}$  but near the  $T_M^{\text{mid}}$ . Thus, the de Gennes scaling is still valid for the magnetic properties of this sample.

The behavior of the two superconductivities from the different bands can be made clearer if we compare the  $Hc2(T)$  curves for  $T_c > T_N$  and for  $T_c < T_N$ . Figure 5 shows the  $Hc2(T)$  and the  $T_N$  (H) for  $x=0.1$  at 0.1 GPa and 2.0 GPa, which were determined from Fig. 3. Since the magnetic field was applied along the c-direction, which is perpendicular to the preferred direction of Ho and Dy spins, the changes of  $T_N$  (H) due to a magnetic field should not be severe. The  $Hc2(T)$  curve for 0.1 GPa for  $T < T_N$  is very similar to that for 2.0 GPa at which the  $T_c$  is lower than the  $T_N$ . The difference appears at  $T > T_N$ . This means that the superconducting state at  $T < T_N$  is insensitive to magnetic pair breaking no matter the value of the  $T_c$ . This supports the idea that the superconductivity is governed by the Ni band which is not affected by the pair-breaking field. However, at  $T > T_N$ , the superconductivity is suppressed by the pressure through the second band which is sensitive to the pair breaking field.

In conclusion, we measured the resistance of  $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$  with  $x=0.1$  and  $x=0.4$  under high pressure, to study the superconductivity and the magnetism. Basically, the pressure controls the pair breaking effect by changing the magnetic exchange integral,  $J_{sf}$ , as in the case of direct changing of the elements with different de Gennes factors. The effects of  $J_{sf}$  on the superconductivity, both in paramagnetic and ordered magnetic states, was thoroughly studied. In the paramagnetic state, the  $T_c$  decreases as the pressure increases, and follows the AG theory. However, in the ordered state, the  $T_c$  doesn't change much and even increases slightly.

The upper critical field  $Hc2$  was also measured for  $x=0.1$  and showed that  $Hc2(T)$  for both  $p=0$  and  $p=2.0$  GPa below  $T_N$  were the same. The superconducting state below  $T_N$  did not depend on the strength of the magnetic pair-breaking field. This supports the idea that, due to the cancellation of the magnetic pair-breaking fields at the Ni-sites, the Ni band becomes the only source of the superconductivity below the  $T_N$  in  $\text{HoNi}_2\text{B}_2\text{C}$  and  $\text{DyNi}_2\text{B}_2\text{C}$ . The breakdown of the de Gennes scaling with pressure can be basically understood by the phenomenological theory of two superconducting order parameters [14] as for substitution experiments [15]. We expect that the pressure experiment can be a powerful tool to study the pair-breaking effect in the borocarbides of general magnetic structures as in our result of  $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$ .

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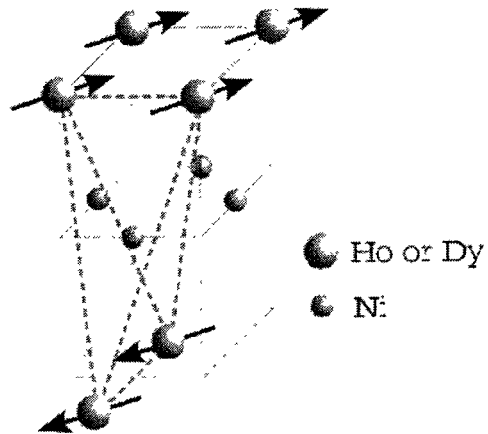


FIG. 1. The arrows attached to the Ho or the Dy indicate the directions of the magnetic moments of the rare-earth atoms in Néel states. The nickel is located at the center of the tetrahedron (dashed line) formed by the four nearest rare-earth atoms.

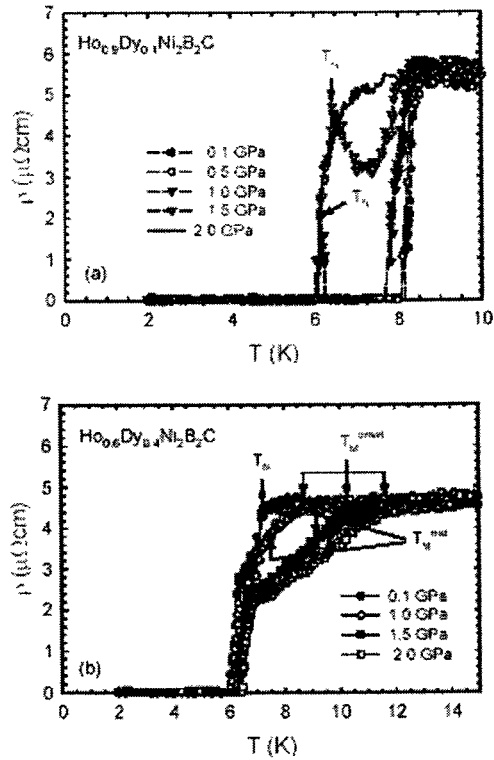


FIG. 2. Temperature dependences of the resistivity under various pressures for (a)  $x=0.1$  and (b)  $x=0.4$ .

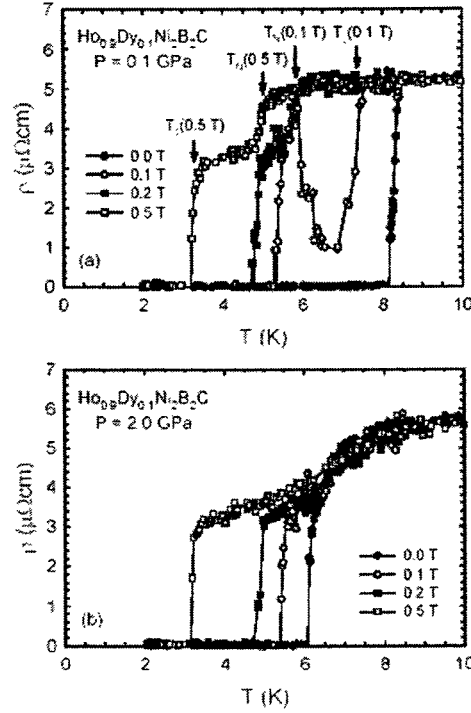


FIG. 3. Temperature dependences of the resistivity for various magnetic fields for the  $x=0.1$  sample under pressures of (a) 0.1 GPa and (b) 2.0 GPa.

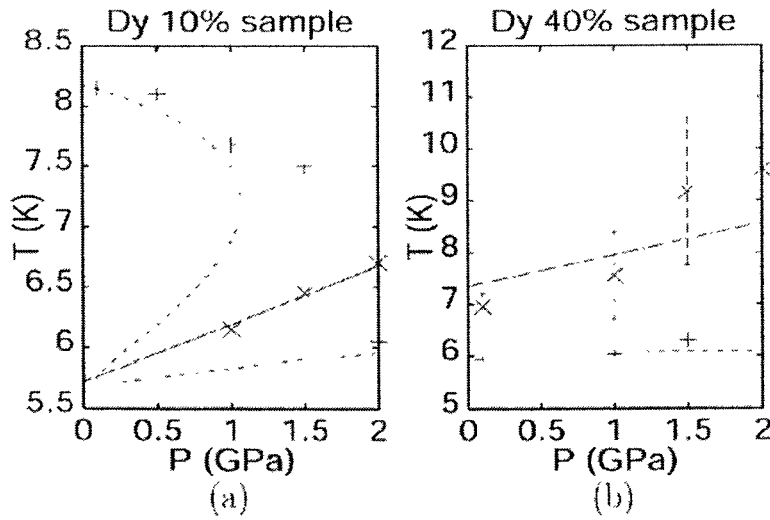


FIG. 4. Phase diagrams of the  $T_c$  and the  $T_N$  (the  $T_M^{\text{mid}}$  is used for  $x=0.4$  sample) vs. pressure. The symbol  $+$  denotes the  $T_c$ , and the symbol  $\times$  denotes the  $T_N$ . The dotted line is a rough sketch of the phase boundary of superconductivity based on the Ref. [17]. The solid line is the pressure dependence of the  $T_N$  estimated from  $T_N$  in the Eq. (1).

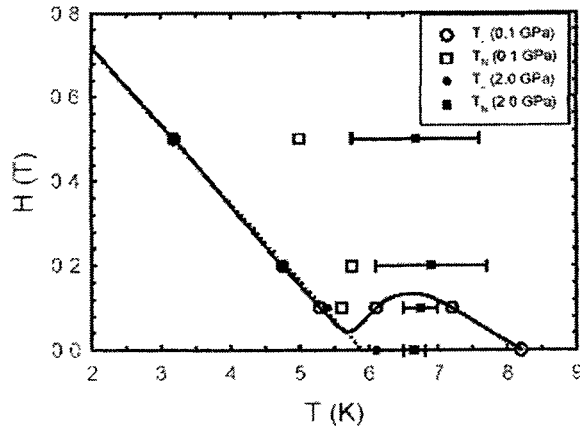


FIG. 5. Magnetic field dependences of the  $T_c$  and the  $T_N$  for low (0.1 GPa) and high (2.0 GPa) pressures. Filled symbols denote the transition temperatures for high pressure and empty symbols denote those for low pressure. The circles indicate the  $T_c$ , and the squares indicate the  $T_N$ . The solid line is a rough estimate of  $H_{c2}$  for low pressure, and the dotted line is that for high pressure.

### Reversible magnetization of MgB<sub>2</sub> single crystals

We present reversible magnetization measurements on MgB<sub>2</sub> single crystals with  $T_c \cong 38$  K and with the magnetic field parallel to the crystal's  $c$ -axis. This magnetization is analyzed in terms of the Hao-Clem model, and various superconducting parameters, such as the critical fields [ $H_c(0)$  and  $H_{c2}(0)$ ], the characteristic lengths [ $\xi(0)$  and  $\lambda(0)$ ], and the Ginzburg-Landau parameter, are derived. In the temperature range we investigated,  $\lambda(T)$  could be well fitted by using both the two-fluid model and the two-gap model.

## I. Introduction

MgB<sub>2</sub> with a superconducting transition temperature ( $T_c$ ) of 39 K [1] has attracted great attention because it has several notable features compared to other conventional superconductors. First, its  $T_c$  of 39 K may be too high to be explained within the conventional electron-phonon mechanism. Therefore, an unconventional pairing mechanism [2] was proposed as a possible candidate of theoretical description. However, an early isotope experiment ruled out the unconventional theory and showed that the main driving force for the superconductivity is electron-phonon coupling [3,4]. Furthermore, it was suggested that the anisotropy in the electron-phonon coupling plays an important role in the

unusually high  $T_c$  [5-7].

Another notable feature of  $\text{MgB}_2$  is its multi-gap property. A number of theoretical [5, 6, 8] and experimental investigations [9-15] suggest that  $\text{MgB}_2$  has two different superconducting gaps: a larger gap originating from a two dimensional cylindrical Fermi surface with an average gap value of 6.8 meV and a smaller gap associated with a Fermi surface of three-dimensional tubular networks with an average gap value of 2.5 meV. Recently, direct evidence for two superconducting gaps was obtained from several measurements, such as specific heat [16], penetration depth [17, 18], tunneling [19, 20], point-contact spectroscopy [21] and photoemission spectroscopy [22, 23] on good quality  $\text{MgB}_2$  single crystals and thin films.

Third,  $\text{MgB}_2$  is a very interesting system regarding vortex problems. Like high- $T_c$  and some conventional superconductors which show various vortex phases and vortex phase transitions,  $\text{MgB}_2$  is reported to have surface superconductivity [24] and peak effects [25, 26]. In this sense,  $\text{MgB}_2$  may offer a unique opportunity to study the interplay between the various vortex phases and the two superconducting gaps. If these behaviors are to be understood, a study of the equilibrium magnetization which characterizes the material's thermodynamic parameters, such as the thermodynamic critical field and the magnetic penetration depth, is a prerequisite. The determination of superconducting parameters, however, was hindered by the strong pinning in  $\text{MgB}_2$  bulks and thin films [27]. On the other hand, the pinning is orders of magnitude lower in single crystals [28, 29]; thus, a study of the superconducting parameters for single crystals is urgently needed. Previously, those parameters were obtained exclusively within the London model [30]. Since the London model only considered the free energy from electromagnetic contributions and ignored the free energy associated with the core parts, which becomes quite important in low- $\kappa$  ( $= \lambda/\xi$ ) materials such as  $\text{MgB}_2$ , a description within the London model has inevitable limitations. Therefore, a more complete model which considers the free energies both from the electromagnetic part and from the core part is needed.

In this paper, we present reversible magnetization measurements on  $\text{MgB}_2$  single crystals with  $T_c \cong 38$  K. The weak pinning property of our single crystals enabled us to have a wide reversible region in the magnetization data. To calculate more reliable superconducting parameters, we applied the Hao-Clem model based on the Ginzburg-Landau (GL) theory to the magnetization. Using applied fields up to 1 T parallel to the  $c$ -axis, we obtained superconducting parameters such as the critical field  $H_c(0)$  and the penetration depth  $\lambda(0)$ .

## II. Experiment

Single crystals were grown by using a high-pressure technique [28, 29]. A 1:1 mixture of Mg and amorphous B powders was well ground and pressed into a pellet. The pellet was put in a BN

container and then placed in a high-pressure cell equipped with a graphite heater. Heat treatment was done inside a 14-mm cubic multi-anvil-type press (Rockland Research Corp.) under 3.5 GPa. The heating temperature of 1400 - 1500 C was maintained for 60 minutes and then was slowly lowered to 800 - 900 C, which was followed by a fast cool to room temperature.

Two sets of single crystals were investigated using magnetization measurements. In the first set, we collected 10 relatively hexagonal-shaped single crystals [28], with typical dimensions of 200 x 100 x 25  $\mu\text{m}^3$  on a substrate without an appreciable magnetic background and with their  $c$  axes aligned perpendicular to the substrate surface. The total volume of the collected single crystals was carefully calculated based on the images obtained using a polarizing optical microscope (POM). In the second set, we mounted a shiny and flat, but not hexagonal-shaped single crystal with dimensions of 800 x 300 x 60  $\mu\text{m}^3$  on a substrate with its  $c$ -axis aligned perpendicular to the substrate surface. The values of  $T_c$  and the transition width  $\Delta T_c$  determined from the low-field magnetization data were 36.8 K and 1.5 K for the first set and 37.9 K and 0.7 K for the second set, respectively. Regardless of slightly different values of  $T_c$ , these two sets of crystals did not show any significant differences upon further magnetization analysis.

### III. Results and Discussion

The measurement of the reversible magnetization was carried out by using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL). The background contribution from the paramagnetic substrate at high magnetic fields was properly subtracted by fitting the magnetization curves with the formula  $C_1/T + C_2$ , where  $C_1$  and  $C_2$  are constants which linearly depend on the external field, in the high temperature region of 50 K  $< T < 100$  K [31].

Figure 1 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations measured at a field of 10 G parallel to the  $c$ -axis of a  $\text{MgB}_2$  single crystal. The onset of superconducting transition is at 37.9 K with a transition width  $\Delta T_c \sim 0.7$  K. At  $T = 5$  K, the value of  $4M/H$  for the ZFC is around 3 due to a demagnetization effect. The calculated demagnetization factor is about 0.67, and this large value is consistent with the plate-like shape of our sample.

Figure 2 shows the temperature dependence of reversible magnetization,  $4\pi M(T)$ , measured in the field range 0.5 T  $< H < 1.0$  T with the field parallel to the  $c$ -axis of the sample. The reversible point was determined from the  $M(H)$  data (not shown in this paper) by using the criterion of  $[M(H^-) - M(H^+)] = 0.1$  G. The curves shift to lower temperatures as the field is increased and appear to be nearly parallel to each other. This feature is similar to that for a conventional superconductor [32] and has been observed in infinite-layer  $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$  superconductors [33]. The nearly parallel shift of the magnetization could be understood by means of the Abrikosov model [34], in which the magnetization increases linearly with the magnetic field. This mean-field behavior

indicates that the thermal fluctuation effect [35] observed in most cuprate superconductors [31, 36, 37] is not significant in this system. Even though the magnetizations,  $4\pi M(T)$ , appear to be nearly parallel to each other, the calculated slopes,  $d(4\pi M)/dT|_{T_c}$ , for a fixed field  $H$  depend on the field as shown in the inset of Fig. 2. The slope decreases to about one third as the magnetic field is increased from 0.5 T to 1.0 T, which is not expected from the Abrikosov model. This suggests that our data may deviate from Abrikosov's linear region.

In order to calculate the various thermodynamic parameters characterizing MgB<sub>2</sub>, we applied the Hao-Clem model [38] to our magnetization data. This model considers not only the electromagnetic energy outside of the vortex cores, but also the kinetic and the condensation energy changes arising from suppression of the order parameter in the core. This variational model permits a reliable description of the reversible magnetization in the entire mixed state and an accurate determination of the thermodynamic parameters [31, 36, 39].

In the Hao-Clem model, the reversible magnetization in dimensionless form,  $4\pi M'(H')$ , is a universal function for a given value of the GL parameter  $\kappa$  and is temperature independent. Here, the magnetization and the external field are defined as  $4\pi M' \equiv 4\pi M / \sqrt{2}H_c(T)$  and  $H' \equiv H / \sqrt{2}H_c(T)$ , respectively [33]. At a fixed temperature, the ratio  $4\pi M_i(H_i)/H_i$  ( $i = 1, 2, \dots$ ) for the experimental data corresponds to the ratio  $4\pi M'/H'$  at a certain point on the theoretical curve for a given  $\kappa$ . Through this correspondence, the value of  $\sqrt{2}H_c(T)$  can be determined from the ratio  $H'/H_i$  for each  $i = 1, 2$ . If the value of  $\kappa$  is appropriately chosen, the smallest error in  $\sqrt{2}H_c(T)$  is achieved. Using this procedure, we obtained  $\kappa$  as a function of temperature in the temperature range of 19 K  $T$  27 K, and its average value,  $\kappa_{av}$ , was 6.4, as shown in the upper inset of Fig. 3. This nearly temperature independence of  $\kappa$  has also been observed in many cuprate superconductors [31, 40]. The Hao-Clem fitting yields a universal curve for the  $4\pi M(H)$  curves with a scaling factor  $\sqrt{2}H_c(T)$ , as shown in the lower inset of Fig. 3, and all the data for different fields nicely collapse into a single curve. During the Hao-Clem fitting, we also checked the effect of the demagnetization correction, but since the applied field was much higher than  $4\pi M(H)$ , the results were hardly affected.

Figure 3 shows the thermodynamic critical field  $H_c$  versus temperature plot obtained from this analysis. The solid and the dotted lines represent the temperature dependence of  $H_c$  in the BCS model [41] and the empirical two-fluid model [42], respectively. The BCS result for  $H_c(T)$  yields  $H_c(0) = 0.25$  T and  $T_c = 37$  K, which correspond to a slope of  $dH_c/dT = 0.012$  G/K near  $T_c$ . By using the



relation  $H_{c2}(T) = \sqrt{2\kappa}H_c(T)$ , we calculated the upper critical field slope as  $(dH_{c2}/dT)_{T_c} = 0.10$  T/K. Since  $H_{c2}(T)$  for  $H // c$  determined from the  $4\pi M(H)$  data shows a nearly linear behavior near  $T_c$ , similar to the previous reports on single crystals [24, 30], we used the Warthamer-Helfand-Hohenberg (WHH) formula [43] to estimate  $H_{c2}(0)$ . In the WHH formula,  $H_{c2}(0) = 0.5758(\kappa_1/\kappa)T_c|dH_{c2}/dT|_{T_c}$  and  $\kappa_1/\kappa$  is 1.26 and 1.20 in the clean and the dirty limits, respectively.  $H_{c2}(0)$  and  $\xi(0)$  were estimated to be 2.87 T and 10.7 nm in the clean limit and 2.73 T and 11.0 nm in the dirty limit. These low  $H_{c2}(0)$  values may be underestimated due to the fact that the WHH formula considers a weak saturation of  $H_{c2}$  as the temperature approaches zero. The predicted weak saturation of  $H_{c2}(T)$ , however, was observed neither in this study nor in previous results for single crystals down to 5K [24, 44].

Employing the values of  $H_c(T)$  and  $\kappa_{av}$  obtained from the Hao-Clem fitting, we calculated the magnetic penetration depth,  $\lambda(T)$  from the relation  $\lambda(T) = \kappa[\phi_0/2\pi H_{c2}(T)]^{1/2}$ , where  $\phi_0$  is the flux quantum, as plotted in Fig. 4. The temperature dependence of  $\lambda$  has been controversial so far, and quadratic, linear, and exponential dependences have been reported [18, 45-48]. We tried to fit our data with the two-fluid model  $\lambda(T) = \lambda(0)/[1 - (T/T_c)^4]$ , as shown by the solid line in the figure, and the optimized fitting curve with  $\lambda(0) = 93$  nm and  $T_c = 35$  K follows our data reasonably well.

Even though the two-fluid model gives a relatively good fit with our data, since MgB<sub>2</sub> is found to have two different gaps with different gap values, we should try to fit our  $\lambda(T)$  data with the two-gap model. For a system like MgB<sub>2</sub>, the existence of a larger gap should have a significant impact on  $\lambda(T)$  at higher temperatures while the temperature dependence of  $\lambda$  for  $T \ll T_c$  would be determined by the smaller gap. Since the temperature region we investigated for the Hao-Clem fitting is rather high ( $T > 0.5T_c$ ), we applied the two-gap model [17] to fit our  $\lambda(T)$  and to estimate  $\lambda(0)$ . Here, the theoretical  $\lambda(T)$  was calculated using

$$\lambda^{-2}(T)/\lambda^{-2}(0) = 1 - 2 \left[ c_1 \int_{\Delta_s}^{\infty} \left( -\frac{\partial f}{\partial E} \right) D_s(E) dE + (1 - c_1) \int_{\Delta_L}^{\infty} \left( -\frac{\partial f}{\partial E} \right) D_L(E) dE \right], \quad (1)$$

where  $c_1$  is a parameter which determines the contribution of the small gap,  $\Delta_s$  is the small gap,  $\Delta_L$  is the large gap,  $f$  is the Fermi-Dirac distribution function, and  $D(E) = E/[E^2 - \Delta^2]$ . The dotted line in Fig. 4 is a fit to the two-gap model using Eq. (1). This fit is also relatively good over the whole temperature region investigated, and the parameters are  $\lambda(0) = 82$  nm,  $c_1 = 0.14$ ,  $\Delta_s = 23$  K,  $\Delta_L = 86$

K, and  $T_c = 36$  K. The values of these parameters are in ranges similar to those in Ref. 17. The lower values of  $T_c$  in the fits with the two-fluid model and the two-gap model may be due to the lack of data points near  $T_c$ . All the parameters derived from the Hao-Clem model are summarized in Table 1. The total error of the superconducting parameters obtained from the Hao-Clem fitting, including the error in measuring the volume of a single crystal, are estimated to be much less than 5%.

#### IV. Summary

The reversible magnetization of a MgB<sub>2</sub> single crystal was measured for magnetic fields up to 1 T with the field parallel to the crystal's *c*-axis. The reversible magnetization was well described using the Hao-Clem model. From this analysis, various superconducting parameters, such as the penetration depth  $\lambda(0)$ , the coherence length  $\xi(0)$ , the Ginzburg-Landau parameter  $\kappa(T)$ , and the critical fields [ $H_{c1}(0)$  and  $H_{c2}(0)$ ], were derived. In the temperature range we investigated, the temperature dependence of  $\lambda$  could be well fitted by using both the two-fluid model and the two-gap model.

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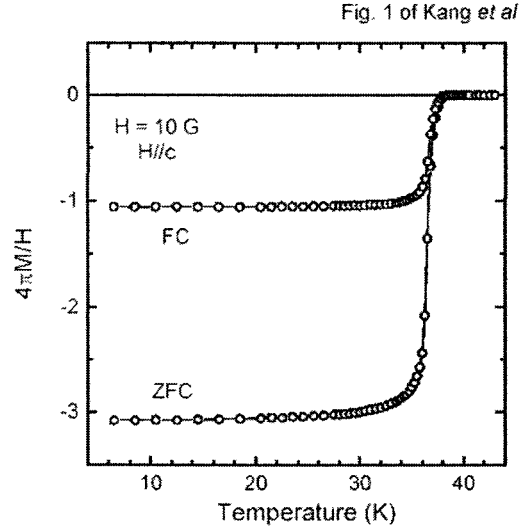


Fig.1. Temperature dependence of low-field magnetization,  $4\pi M / H$ , of a  $\text{MgB}_2$  single crystal for  $H = 10$  G parallel to the crystal's  $c$ -axis,  $T_c = 37.9$  K, and  $\Delta T_c \sim 0.7$  K.

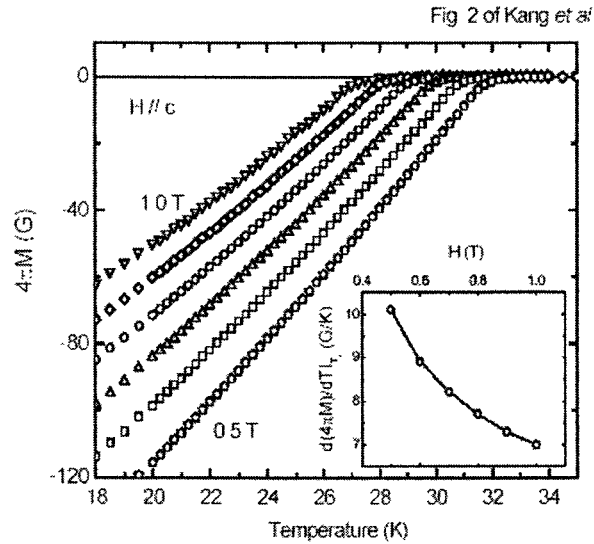


Fig. 2. Temperature dependence of the reversible magnetization,  $4\pi M(T)$ , in the field range 0.5 T  $H$  1.0 T in 0.1 T steps parallel to the  $c$ -axis. Inset: The calculated slope  $d(4\pi M) / dT|_{T_c}$  for a fixed field,  $H$ , as a function of the magnetic field. The slope decreases as the magnetic field is increased, indicating that our data may deviate from Abrikosov's linear region.

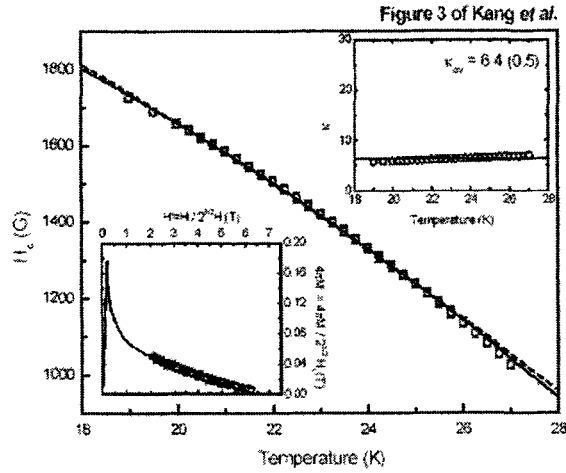


Fig. 3. Temperature dependence of the thermodynamic critical field,  $H_c(T)$ . The solid and the dotted lines represent the BSC temperature dependence and the two-fluid model, respectively. Upper inset: the temperature dependence of the Ginzburg parameter  $\kappa(T)$  extracted from the Hao-Clem model.  $\kappa(T)$  shows a very weak temperature dependence and  $\kappa_{av} = 6.4$ . Lower inset: Magnetization,  $-4\pi M' \equiv -4\pi M / \sqrt{2} H_c(T)$  vs. external magnetic field,  $H' \equiv H \sqrt{2} H_c(T)$ . The solid line represents the universal curve derived from the Hao-Clem model using  $\kappa_{av} = 6.4$ .

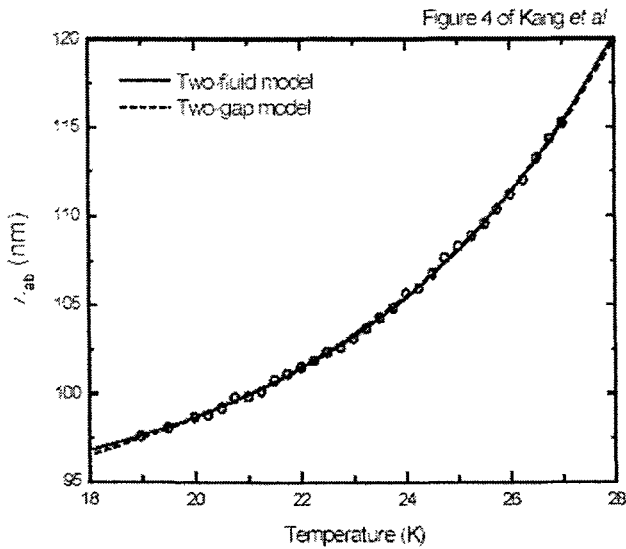


Fig. 4. Temperature dependence of the penetration depth  $\lambda$ . The solid and the dotted lines represent is to the two-fluid model and the two-gap model, respectively. The formulas for the fitting curves are given in the text.

$T_c$ (K)	$\kappa$	$dH_{c2}/dT _{T_c}$ (T/K)	$H_c(0)$ (T)	$H_{c2}(0)$ (T)	$\xi$ (nm)	$\lambda$ (nm)
37.9 $a$	6.4	0.10	0.25	2.87 $b$ 2.73 $c$	10.7 $b$ 11.0 $c$	93 $d$ 82 $e$

$a$  Low field,  $b$  BCS dirty limit,  $c$  BCS dirty limit,  $d$  Two-fluid model,  $e$  Two-gap model

Table 1. Transition temperature  $T_c$ , the Ginzburg-Landau parameter  $\kappa = \lambda/\xi$ , the thermodynamic critical field  $H_c(0)$ , the upper critical field  $H_{c2}(0)$ , the coherence length  $\xi(0)$ , and the penetration depth  $\lambda(0)$  of MgB<sub>2</sub> derived from the reversible magnetization.

## 제 4 장 목표달성도 및 관련분야에의 기여도

In this second stage, we synthesize several new superconductors and accomplished several world leading research output. The first superconductor we would like to mention is the magnesium diboride ( $\text{MgB}_2$ ). While the samples produced by other researchers had been very brittle, like sand, our  $\text{MgB}_2$ , synthesized under high-pressure conditions (a few GPa), was very hard and dense. While others had difficulties, we could measure quite a number of the transport properties. In addition, nobody in the world could produce  $\text{MgB}_2$  thin films, which are essential for superconducting electronic device application and for the study of basic superconducting properties. We asked ourselves "why people in the world could not produce  $\text{MgB}_2$  thin films?" Very soon, we had the answer and could synthesize  $\text{MgB}_2$  thin films. We immediately applied patterned (Korea, U.S. Germany, British, Japan) and published papers after papers. These thin films will be used for the superconducting electronic devices. For example, this thin film can be used for making Josephson Junctions, SQUID, micro-electronic interconnection, fault current limiters and local superconducting magnet, and filters used for microwave communication. We also produced  $\text{MgB}_2$  single crystals for the first time in the world. We are the only group that has synthesized three different forms (high-pressure bulks, thin films and single crystals) of  $\text{MgB}_2$ .

The second superconductor we produced was an electron-doped cuprate  $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_2$  ( $\text{Ln} = \text{La}, \text{Gd}, \text{Sm}$ ) infinite layer superconductor. Despite their importance, these cuprate superconductors are very difficult to synthesize, and the lack of single-phased compounds with high volume-fractions of superconductivity hindered research efforts until our recent breakthrough. Using high-pressure ( $\sim 4$  GPa) and high-temperature ( $\sim 1000$  C) annealing conditions, we were able to routinely achieve single-phase of these compounds. We are the only group in the world that can produce 100% of these superconductors.

Finally, we produced various kinds of single crystals, such as Na doped  $\text{CaCuOCl}$ , Tl-2212, Tl2201, and  $\text{RNi}_2\text{B}_2\text{C}$ . Quality-wise, these are the worlds best, and only a few groups in the world can even produce these compounds.

## 제 5 장 연구개발결과의 활용계획

Microwave surface impedance measurements have proved to be the most sensitive tool to determine the superconductivity. We used microwave resonator techniques which are most appropriate to be used for high-precision measurements on superconducting  $MgB_2$  thin film. The microwave surface resistance,  $R_s$  is an important figure of merit for microwave applications and we found this material very superior to any known superconductors as far as the microwave applications are concerned. We believe that  $MgB_2$  thin films will be used for the superconducting electronic devices. For example, this thin film can be used for making Josephson Junctions, SQUID, micro-electronic interconnection, fault current limiters and local superconducting magnet, and filters used for microwave communication. For this purpose, we studied the several microwave properties of this thin film.

## 제 6 장 Information

Japanese scientists first reported on January, 2001 that magnesium diboride had superconductivity with a relatively high transition temperature ( $T_c$ ) of 39 K. This report has generated a flurry of activity in  $MgB_2$  since then. Studies are now aimed at establishing the mechanism, teasing out possible routes for boosting the  $T_c$  and developing more practical preparation techniques. For the application, we need this material in a form of thin film. Fortunately we were able to synthesize  $MgB_2$  thin films for the first time in the world. The PSC team has reported that our thin films exhibit a sharp  $T_c$  of 39 K and can sustain large current densities. This current is record high as far as the superconducting critical current density is concerned. But lots of details in this material still remain to be studied. For example, surface morphology, improvement of the critical current densities, investigation of fundamental mechanism of superconductivity are important research topics we would study in a near future.

### Newly discovered novel superconductor, $MgB_2$

Pohang Superconductivity Center (PSC) at Pohang University of Science and Technology (POSTECH) succeeded in synthesizing the world-best superconducting thin films, which can be used for developing a fast supercomputer, microwave communications, and magneto encephalogram the researchers at PSC synthesized magnesium diboride ( $MgB_2$ ) thin films, which exhibit superconductivity at 39 K or - 234 °C. This research achievement was published in Science, the most famous American scientific journal. Now it is a time to introduce new novel superconductor,  $MgB_2$ .



## **What is MgB<sub>2</sub> superconductor?**

The magnesium diboride has been utilized for more than 40 years since its first synthesis in 1953, but its superconductivity was discovered very recently, January 2001.

This MgB<sub>2</sub> is used for obtaining elemental boron in chemical company, and this material of several kilograms is easily available commercially. Scientists are astonished by the news that this ordinary material has a superconducting transition temperature of 39 K, 15K higher than that of Nb<sub>3</sub>Ge which had shown the highest T<sub>c</sub> among metallic superconductors ever discovered. Fourteen years later, since the discovery of the cuprate superconductors with the highest transition temperature of 140 K, why does this material with a transition temperature of 39 K amaze people?

Firstly, we can find an answer from a BCS theory, for which Bardeen, Cooper, and Schriffer won a Nobel Prize in 1972. Based on this theory, the highest possible temperature for superconductivity was expected to be not higher than 30 K, but the MgB<sub>2</sub> compound exceeded this limit. Therefore, from the point of view of physics, we need to investigate the characteristics of this material and unveil the new physical laws in this material.

Secondly, this compound has a very simple structure and a good chemical stability, and is easily supplied since it is abundant not only in natural resources but also in seawater. While a cuprate superconductor is composed of more than four elements so that the synthesis and the chemical structure are so complicated, this is not the case of MgB<sub>2</sub>. In addition, there is no problem of superconductivity degradation due to environment. Once an electronic device is manufactured out of this material, it is semi permanent because its characteristics and quality remain the same in hundred years. Therefore, MgB<sub>2</sub> compound is the key to overcome the delicate difficulties in synthesis and chemical stability that the cuprate superconductors have, and furthermore to resolve the relatively more difficult problem of resources.

Thirdly, the superconducting transition temperature is much higher than those of conventional superconductors. This transition temperature is high enough to reach easily by using a simple electrical Helium gas refrigerator, not by expensive liquid Helium, so that the potential of application is unlimited. Suppose that we use superconducting devices in communicators for communication. If we need to keep the devices at low temperature by pouring liquid Helium, the maintenance is extremely laborious and costly, and even more when the communicators are in the middle of a vast expanse of desert or on the top of high peaks deep in mountains. However, it would be enormously beneficial, if it is possible to maintain the communicators by using a cryostat of electrical refrigerator, instead.

Fourth, MgB<sub>2</sub> compounds can carry superconducting currents more than any other superconductor can do. Up to now, it is revealed that there appears no resistance until the current of forty millions Ampere per 1 cm<sup>2</sup> area flows. In other words, through an electrical line one centimeter

in diameter we can transmit electricity that is consumed in the whole city of Seoul, without energy loss. Therefore, utilizing this superconductor, we can save plenty of electrical energy that is otherwise dissipated into heat in copper cables during electrical transmission.

Fifthly, there are many expectations for the new physics to be revealed in future. The secrets of this superconductor, which were revealed only for a few months since the research begun in earnest, are the tip of the iceberg, and plenty of secrets remain to be investigated near future. So, nobody can predict how much its potential for application would be. Even for now, scientists also expect that this material can be used for microwave communication and superconducting digital devices.

If the number of the base stations for communication can be reduced ten or hundred times by using this material, the retrenchment of expenditure will be great. Especially, as a country is large in size such as the United States or the Australia, many base stations should be spread, and superconducting base stations will be of considerable merit. Moreover, since a superconducting device can speed up the internet communication more than one thousand times, the research on this new superconductor is a matter of urgent.

One of the intriguing properties of this material is being somewhat metallic. This material has as high hole density as the free electrons of a normal metal, so the electrical conductivity is considerably high. We expect that this property will enables overcoming several weak points that the cuprate superconductors have. Also, we expect that the wires can be manufactured out of the compound with ease, and so the extensive research on its application is awaited. Since tremendous progress is being made in this research field, other applications of this superconductor are expected to be possible in near future.

## 특정연구개발사업 연구결과 활용계획서

사업명	중사업명	특정연구개발사업			
	세부사업명	창의적연구진흥사업			
과제명		새로운 초전도 연구			
연구기관		포항공과대학교	연구책임자	이 성 익	
총연구기간		2000년 10월 1일 ~ 2003년 9월 30일 ( 36 개월)			
총 연구비 (단위 : 천원)		정부출연금	민간부담금	합계	
		1,780,000	0	1,780,000	
기술 분야					
참여기업					
공동연구기관					
위탁연구기관					
연구결과활용 (해당항목에(√) 표시)		1. 기업화 ( )	2. 기술이전( )	3. 후속연구추진( )	4. 타사업에 활용( )
		5. 선행 및 기초연구 ( √ )	6. 기타목적활용 (교육연구)( )	7. 활용중단(미활용) ( )	8. 기타( )

특정연구개발사업 처리규정 제 31조(연구개발결과의 보고) 제 2항에 의거  
연구결과 활용계획서를 제출합니다.

첨부 : 1. 연구결과 활용계획서 1부.  
2. 기술요약서 1부

2004 년 2 월 25 일

연구책임자 :

이 성 익



과학 기술부장관 귀하

# 연구결과 활용계획서

## 1. 연구목표 및 내용

새로운 초전도체를 개발 하여, 초전도 기초 및 응용 연구에 기여 한다.

## 2. 연구수행결과 현황(연구종료시점까지)

### 가. 특허(실용신안) 등 자료목록

발명명칭	특허공고번호 출원(등록)번호	공고일자 출원(등록)일자	발명자 (출원인)	출원국
초전도 마그네슘 보라이드 (MgB <sub>2</sub> )박막 그 제조방법 및 그 장치 (Superconducting Magnesium Diboride thin film and method and apparatus for fabricating the same)	1020010014042	2001. 3. 19	강원남, 이성익 최은미, 김형진	한국
	0205654.7	2002. 03. 11		영국
	10/097,975	2002. 03. 15		미국
	2002-69018	2002. 03. 13		일본
	10212126.5	2002. 03. 19		독일

### 나. 논문게재 및 발표 실적

학술지명칭	제 목	게재일	호	발행기관	국 명	SCI 여부
Phys. Rev. Lett.	Evidence for Nodal Quasiparticles in the Nonmagnetic Superconductor YNi <sub>2</sub> B <sub>2</sub> C via Field-Angle-Dependent Heat Capacity	2003/5/2	90(17), 177001	The American Physics Society	USA	SCI
Phys. Rev. Lett.	Anomalous Coherence Peak in the Microwave Conductivity of c-Axis Oriented MgB <sub>2</sub> Thin Films	2003/9/19	91(12), 127006	The American Physics Society	USA	SCI

Phys. Rev. Lett.	Pair-Breaking and Superconducting State Recovery Dynamics in MgB <sub>2</sub>	2003/12/31	91(26), 267002	The American Physics Society	USA	SCI
Phys. Rev. B	Superconducting transition and phase diagram of single-crystal MgB <sub>2</sub>	2003/1/1	67(1), 012505	The American Physics Society	USA	SCI
Phys. Rev. B	Coherence lengths and anisotropy in MgB <sub>2</sub> superconductor	2003/1/1	67(2), 020507	The American Physics Society	USA	SCI
Phys. Rev. B	Phonon structure in I-V characteristic of MgB <sub>2</sub> point contacts	2003/1/1	67(2), 024517	The American Physics Society	USA	SCI
Phys. Rev. B	Local threshold field for dendritic instability in superconducting MgB <sub>2</sub> films	2003/2/1	67(6), 064513	The American Physics Society	USA	SCI
Phys. Rev. B	Superconducting fluctuation probed by in-plane and out-of-plane conductivities in Tl <sub>2</sub> Ba <sub>2</sub> CaCuO <sub>8+y</sub> single crystals	2003/4/1	67(14), 144502	The American Physics Society	USA	SCI
Phys. Rev. B	Angle-resolved soft x-ray spectroscopy study of the electronic states of single-crystal MgB <sub>2</sub>	2003/5/1	67(17), 174519	The American Physics Society	USA	SCI
Phys. Rev. B	Pair-breaking critical current density of magnesium diboride	2003/8/1	68(6), 064516	The American Physics Society	USA	SCI
Phys. Rev. B	X-ray absorption and optical spectroscopy studies of (Mg <sub>1-x</sub> Al <sub>x</sub> )B <sub>2</sub>	2003/9/1	68(9), 092505	The American Physics Society	USA	SCI
Phys. Rev. B	Critical flux pinning and enhanced upper critical field in magnesium diboride films	2003/9/1	68(10), 100503	The American Physics Society	USA	SCI

Phys. Rev. B	Magnetic relaxation in $Tl_2Ba_2CaCu_2O_8$ single crystals by SQUID magnetometer and micro-Hall sensor	2003/10/1	68(13), 134413	The American Physics Society	USA	SCI
Phys. Rev. B	Surface contribution to the superconducting properties of $MgB_2$ single crystals	2003/11/1	68(17), 172502	The American Physics Society	USA	SCI
Physica C	Peak anomaly and irreversible magnetization in $Tl_2Ba_2CaCu_2O_8$ single crystals	2003/2/1	384, 411-418	Elsevier	Holland	SCI
Physica C	Growth of superconducting $MgB_2$ thin films via postannealing techniques	2003	385, 24-30	Elsevier	Holland	SCI
Physica C	Superconducting phase diagram of single-crystal $MgB_2$	2003/3/1	385, 154-161	Elsevier	Holland	SCI
Physica C	Directional scanning tunneling spectroscopy in $MgB_2$	2003/3/1	385, 215-220	Elsevier	Holland	SCI
Physica C	Effect of interface pinning on dissipation, volume pinning force and measurement of upper critical magnetic field in $MgB_2$ thin films	2003/3/15	385(3), 313-321	Elsevier	Holland	SCI
Physica C	Magnetic relaxation measurement of the infinite-layer superconductor $Sr_{0.9}La_{0.1}CuO_2$	2003/4/1	385, 555-562	Elsevier	Holland	SCI
Physica C	Superconducting phase diagram of single crystal $MgB_2$	2003	387, 137-142	Elsevier	Holland	SCI
Physica C	Thermoelectric power of $MgB_2$	2003/5/15	387, 313-320	Elsevier	Holland	SCI
Physica C	Momentum-dependent scanning tunneling spectroscopy in $MgB_2$	2003/5	389, 141-142	Elsevier	Holland	SCI
Physica C	Mixed-state magnetoresistance of c-axis-oriented $MgB_2$ thin films	2003/8/15	391(2), 119-124	Elsevier	Holland	SCI
Physica C	Effect of the magnetic moments of Gd on the superconductivity in the infinite-layer superconductor $Sr_{0.9}Gd_{0.1}CuO_2$	2003/9/15	391(4), 319-325	Elsevier	Holland	SCI
Physica B	Two-band superconductivity and the effect of pressure in $Ho_{1-x}Dy_xNi_2B_2C$	2003/4	327, 438-442	Elsevier	Holland	SCI

Supercond. Sci. Technol.	MgB <sub>2</sub> : directional tunnelling and two-band superconductivity	2003/2/1	16, 156-161	Institute of Physics	UK	SCI
Supercond. Sci. Technol.	Quasiparticle state density on the surface of superconducting thin films of MgB <sub>2</sub>	2003/2/1	16, 167-170	Institute of Physics	UK	SCI
Supercond. Sci. Technol.	Upper critical magnetic fields in single crystal MgB <sub>2</sub>	2003/2/1	16, 193-198	Institute of Physics	UK	SCI
Supercond. Sci. Technol.	Synthesis of c-axis-oriented MgB <sub>2</sub> thin films and the Hall effect	2003/2/1	16, 237-240	Institute of Physics	UK	SCI
Supercond. Sci. Technol.	Interplay of dendritic avalanches and gradual flux penetration in superconducting MgB <sub>2</sub> films	2003/5/1	16, 566-570	Institute of Physics	UK	SCI
Modern Physics Letters B	Study of the Electron-Phonon Interaction in Metal Diborides MeB <sub>2</sub> (Me = Zr, Nb, Ta, Mg) by Point-Contact Spectroscopy	2003	17(10-12) 657-666	World Scientific	U.S.A	SCI
J. of the Korean Physical Society	Studies of the Pressure-Dependent Superconducting States of HoNi <sub>2</sub> B <sub>2</sub> C and DyNi <sub>2</sub> B <sub>2</sub> C	2003	43(2), 263-268	Korean Physical Society	Korea	SCI
Low Temp. Phys.	Elastic constants of borocarbides. New approach to acoustic Measurement technique	2003/1	29(1), 72-76	American Institute of Physics	U.S.A.	SCI
Journal of Low temperature Physics	Scanning Tunneling Spectroscopic Studies of the Pairing State of Cuprate Superconductors	2003/5	131(3/4), 435-444	Plenum Publishing Co.	U.S.A.	SCI
Journal of Low temperature Physics	Effects of Substituting Ni and Zn for Cu in the Electron Doped Sr <sub>0.9</sub> La <sub>0.1</sub> CuO <sub>2</sub> Superconductor	2003/5	131(3/4), 625-629	Plenum Publishing Co.	U.S.A.	SCI
Journal of Low temperature Physics	High Critical Current Density of c-Axis-Oriented MgB <sub>2</sub> Thin Films	2003/6	131(5), 1025-1031	Plenum Publishing Co.	U.S.A.	SCI
Journal of Low temperature Physics	Observation of Hall Scaling in MgB <sub>2</sub> Thin Films	2003/6	131(5), 1075-1084	Plenum Publishing Co.	U.S.A.	SCI

Journal of Low temperature Physics	Transport and Magnetic Properties in MgB <sub>2</sub> Single Crystals	2003/6	131(5/6), 1117-1127	Plenum Publishing Co.	U.S.A.	SCI
Journal of Low temperature Physics	Effect of Al Substitution on the Mg Sites in Mg <sub>11</sub> B <sub>2</sub> Prepared Under High-Pressure Conditions	2003/6	131(5/6), 1165-1173	Plenum Publishing Co.	U.S.A.	SCI
Journal of Low temperature Physics	Pressure Effect on the Coexistence of Magnetism and Superconductivity in Ho <sub>1-x</sub> Dy <sub>x</sub> Ni <sub>2</sub> B <sub>2</sub> C	2003/6	131(5/6), 1181-1186	Plenum Publishing Co.	U.S.A.	SCI
Journal of Low temperature Physics	Phase Diagram of Single Crystal MgB <sub>2</sub>	2003/6	131(5/6), 1237-1244	Plenum Publishing Co.	U.S.A.	SCI
IEEE Transactions On Applied Superconductivity	Effects of Small Magnetic Fields on the Critical Current of Thin Films	2003/6	13(2), 3699-3701	IEEE	U.S.A.	SCI
International Journal of Modern Physics B	Flux Dynamics and Vortex Phase Diagram in Tl <sub>2</sub> Ba <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub> System	2003/8/10	17, 3423-3426	Ingenta	UK	SCI
International Journal of Modern Physics B	Origin of Diversified Transport Properties of MgB <sub>2</sub>	2003/8/10	17, 3672-3674	Ingenta	UK	SCI
International Journal of Modern Physics B	Photo induced Conductivity Dynamics Studies of MgB <sub>2</sub> Thin Films	2003/8/10	17, 3675-3681	Ingenta	UK	SCI
Phys. Rev. Lett.	Strongly Correlated s-Wave Superconductivity in the N-Type Infinite-Layer Cuprate	2002/6/3	88(22), 227002(4)	The American Physics Society	USA	SCI
Phys. Rev. Lett.	Two-Band Superconductivity in MgB <sub>2</sub>	2002/10/28	89(18), 187002(4)	The American Physics Society	USA	SCI



Applied phys. lett.	Ferromagnetic properties of $Zn_{1-x}Mn_xO$ epitaxial thin films	2002/6/17	80(24) 4561(3)	The American Physics Society	USA	SCI
Applied physics letters	Current-induced dendritic magnetic instability in superconducting $MgB_2$ films	2002/6/17	80(24) 4588(3)	The American Physics Society	USA	SCI
Phys. Rev. B	Spectroscopic Evidence for Anisotropic S-Wave Pairing Symmetry in $MgB_2$	2002/1/1	65(1), 012505(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Effect of pressure on the superconductivity and magnetism of $Ho_{1-x}Dy_xNi_2B_2C$	2002/1/1	65(2), 024520(6)	The American Physics Society	USA	SCI
Phys. Rev. B	Giant persistent currents in the open Aharonov-Bohm rings	2002/1/15	65(3), 033305(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Far-infrared transmission studies of c-axis oriented superconducting $MgB_2$ thin film	2002/2/1	65(5), 052413(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Suppression of superconducting critical current density by small flux jumps in $MgB_2$ Thin Films	2002/2/1	65(6), 064512(5)	The American Physics Society	USA	SCI
Phys. Rev. B	Superconducting properties of well-shaped $MgB_2$ single crystal	2002/3/1	65(10), R100510(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Hall effect in c-axis-oriented $MgB_2$ thin films	2002/4/1	65(13), 134508(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Substitution for Cu in the electron-doped infinite-layer superconductor $Sr_{0.9}La_{0.1}CuO_2$ Ni kills superconductivity faster than Zn	2002/5/1	65(17), 172501(4)	The American Physics Society	USA	SCI

Phys. Rev. B	Structural and superconducting properties of $\text{MgB}_{2-x}\text{Be}_x$	2002/5/1	65(17), 172503(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Universal scaling of the Hall resistivity in $\text{MgB}_2$ superconductors	2002/5/1	65(18), 184520(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Anisotropy of critical current density in c-axis-oriented $\text{MgB}_2$ thin films	2002/6/1	65(21), 214521(5)	The American Physics Society	USA	SCI
Phys. Rev. B	Complicated nature of the gap in $\text{MgB}_2$ : Magnetic-field-dependent optical studies.	2002/6/1	65(22), 224519(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Gap anisotropy, spin fluctuations, and normal-state properties of the electron-doped superconductor $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$	2002/6/1	65(22), 224520(7)	The American Physics Society	USA	SCI
Phys. Rev. B	Magnetization and Microwave Study of Superconducting $\text{MgB}_2$	2002/7/1	66(1), 014505(7)	The American Physics Society	USA	SCI
Phys. Rev. B	Mg as a main source for the diverse magnetotransport properties of $\text{MgB}_2$	2002/7/1	66(2), R020506(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Reflection of a two-gap nature in penetration-depth measurements of $\text{MgB}_2$ film	2002/8/1	66(6), 064511(5)	The American Physics Society	USA	SCI
Phys. Rev. B	Energy gap, penetration depth, and surface resistance of $\text{MgB}_2$ thin films determined by microwave resonator measurements	2002/9/1	66(10), 104521(6)	The American Physics Society	USA	SCI
Phys. Rev. B	I-V characteristic measurements to study the nature of the vortex state and dissipation in $\text{MgB}_2$ thin films	2002/9/1	66(10), 104525(5)	The American Physics Society	USA	SCI

Phys. Rev. B	Equilibrium magnetization of $Tl_2Ba_2CaCu_2O_{8+\delta}$ single crystals	2002/10/1	66(13), 134508(5)	The American Physics Society	USA	SCI
Phys. Rev. B	Fluctuation study of the specific heat of $Mg_{11}B_2$	2002/10/1	66(13), 134515(5)	The American Physics Society	USA	SCI
Phys. Rev. B	Photoemission and x-ray absorption study of $MgC_{1-x}Ni_3$	2002/11/1	66(17), 172507(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Anisotropy of the upper critical field and critical current in single crystal $MgB_2$	2002/11/1	66(18), R180502(4)	The American Physics Society	USA	SCI
Phys. Rev. B	Magnetic relaxation in $Tl_2Ba_2CaCu_2O_8$ single crystals	2002/11/1	66(18), 184509(8)	The American Physics Society	USA	SCI
Phys. Rev. B	Microstructure and pinning properties of hexagonal-disc shaped single crystalline $MgB_2$	2002/11/1	66(18), 184519(5)	The American Physics Society	USA	SCI
Phys. Rev. B	Anisotropy and reversible magnetization of the infinite-layer superconductor $Sr_{0.9}La_{0.1}CuO_2$	2002/12/1	66(21), 214509(5)	The American Physics Society	USA	SCI
Physica C	Synthesis and pinning properties of the infinite-layer superconductor $Sr_{0.9}La_{0.1}CuO_2$	2002/2/1	366, 299-305	Elsevier	Holland	SCI
Physica C	Investigating the pairing state of cuprate superconductors via quasiparticle tunneling and spin injection.	2002/2/15	367, 174-180	Elsevier	Holland	SCI
Physica C	Origin of dendritic flux patterns in $MgB_2$ films	2002/3/15	369, 93-96	Elsevier	Holland	SCI
Physica C	Negligible effect of grain boundaries on the supercurrent density in polycrystalline $MgB_2$	2002/4/1	370, 13-16	Elsevier	Holland	SCI
Physica C	Microwave measurement of energy gap and penetration depth of $MgB_2$ thin film	2002/8/1	372-376, 1283-1286	Elsevier	Holland	SCI

Physica C	Effects of unreacted Mg impurities on the transport properties of MgB <sub>2</sub>	2002/8/15	377, 21-25	Elsevier	Holland	SCI
Physica C	Growth and transport properties of c-axis-oriented MgB <sub>2</sub> thin films	2002/10/15	378-381, 1246-1251	Elsevier	Holland	SCI
J. Korean Phys. Soc.	Transport Properties of c-axis oriented MgB <sub>2</sub> Thin Films	2002/3	40(3), 416-420	Korean Physical Society	Korea	SCI
J. Korean Phys. Soc.	Fluctuation of Superconductivity in MgB <sub>2</sub>	2002/5	40(5), 949-951	Korean Physical Society	Korea	SCI
JETP Letters	Superconducting energy gap distribution in c-axis oriented MgB <sub>2</sub> thin film from point contact study	2002/3/25	75(5), 238-241	American Institute of Physics	U.S.A.	SCI
Solid State Communications	Three-dimensional superconductivity in the infinite-layer compound Sr <sub>0.9</sub> La <sub>0.1</sub> CuO <sub>2</sub> in entire region below T <sub>c</sub>	2002/7/1	123, 17-20	Elsevier	Holland	SCI
Sing. J. Phys.	Superconducting properties of c-axis oriented MgB <sub>2</sub> thin films	2002	18(1), 59-65		Aingapore	SCI
Europhys. Lett.	Dendritic magnetic instability in superconducting MgB <sub>2</sub> films	2002/8/15	59(4), 599-605	EDP Sciences	Italia	SCI
Progress in Superconductivity	Hall effect in electron-doped Sr <sub>0.9</sub> La <sub>0.1</sub> CuO <sub>2</sub> superconductors	4(1), 32-36	2002/10/31	Korean Superconductivity Society	Korea	
Journal of Superconductivity: Incorporating Novel Magnetism	Effects of Small Fields on the Magnetic Response of Superconducting Thin Films of MgB <sub>2</sub>	2002/10	15(5), 479-482	Kluwer	Holland	SCI
International Journal of Modern Physics B	Mg as a Main Source for the Diverse Magnetotransport Properties of MgB <sub>2</sub>	2002/8/1	16, 3185-3188	Ingenta	UK	SCI
Science	MgB <sub>2</sub> superconducting thin films with a transition temperature of 39 Kelvin	2001/5/25	292 1521-1523	Science	U.S.A	SCI

Phys. Rev. Lett.	High current-carrying capability in c-axis-oriented superconducting MgB <sub>2</sub> thin films.	2001/8/20	87(8), 087002	The American Physics Society	U.S.A.	SCI
Phys. Rev. Lett	Optical Properties of c-Axis Oriented Superconducting MgB <sub>2</sub> Films	2001/12/31	87(27), 277001(4)	The American Physics Society	U.S.A.	SCI
Appl. Phys. Lett.	Effect of sintering temperature under high pressure in the superconductivity for MgB <sub>2</sub>	2001/6/25	78(26) 4157(3)	The American Physics Society	U.S.A.	SCI
Appl. Phys. Lett.	Hole carrier in MgB <sub>2</sub> characterized by Hall Measurements	2001/8/13	79(7), 982(3)	The American Physics Society	U.S.A.	SCI
Phys. Rev. B	Evidence for nonexistence of superconductivity in an isolated CuO <sub>2</sub> bilayer	2001/3/1	63(9) 092507(4)	The American Physics Society	U.S.A.	SCI
Phys. Rev. B	Vortex Interaction in a finite-sized array of Josephson junctions	2001/4/1	63(13) 132501(4)	The American Physics Society	U.S.A.	SCI
Phys. Rev. B	Two-dimensional nature of four-layer cuprate superconductors	2001/4/1	63(13) 134513(5)	The American Physics Society	U.S.A.	SCI
Phys. Rev. B	Magnetism and superconductivity in Y <sub>1-x</sub> BxNi <sub>2</sub> B <sub>2</sub> C single crystals	2001/4/1	63(14), 144528(7)	The American Physics Society	U.S.A.	SCI
Phys. Rev. B	Prominent bulk pinning effect in the newly discovered MgB <sub>2</sub> superconductor	2001/7/1	64(1) 012511(4)	The American Physics Society	U.S.A.	SCI
Phys. Rev. B	X-ray Photoemission Study of MgB <sub>2</sub>	2001/8/1	64(5), 052510(4)	The American Physics Society	U.S.A.	SCI

Phys. Rev. B	Magnetic relaxation and critical current density of MgB <sub>2</sub> thin films	2001/10/1	64(13), 134505(5)	The American Physics Society	U.S.A	SCI
Physica C	Temperature-and magnetic-field-dependent resistivity of MgB <sub>2</sub> sintered at high-temperature and high-pressure condition	2001/5/15	353 162-166	Elsevier	Holland	SCI
Physica C	High-pressure synthesis of the homogeneous infinite-layer superconductor Sr <sub>0.9</sub> La <sub>0.1</sub> CuO <sub>2</sub>	2001/11/1	364-365, 225-227	Elsevier	Holland	SCI
Physica C	Superconductivity of Four-layer HgBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>10+d</sub>	2001/11/1	364-365, 228-231	Elsevier	Holland	SCI
Physica C	Optical Phonons of Superconducting Infinite-Layer Compounds Sr <sub>0.9</sub> Ln <sub>0.1</sub> CuO <sub>2</sub> (Ln = La and Sm)	2001/11/1	364-365, 629-631	Elsevier	Holland	SCI
Solid State Comm.	Evidence for electron-doped(n-type) superconductivity in the infinite-layer (Sr <sub>0.9</sub> La <sub>0.1</sub> )CuO <sub>2</sub> compound by X-ray absorption near-edge spectroscopy	2001/5/22	118(7) 367-370	Elsevier	Holland	SCI
Supercond. Sci. Technol.	Dendritic flux patterns in MgB <sub>2</sub> films	2001/9	14, 726-728	Institute of Physics	UK	SCI
Supercond. Sci. Technol.	High-resolution transmission electron microscopic observation of highly dense MgB <sub>2</sub> Superconductors	2001/9/25	14, 880-883	Institute of Physics	UK	SCI
Chem. Phys. Lett.	Anisotropic superconductivity in epitaxial MgB <sub>2</sub> films	2001/8/10	343, 447-451	Elsevier	Holland	SCI
J. Phys.: Condens. Matter	X-ray photoemission study of the infinite-layer cuprate superconductor Sr <sub>0.9</sub> La <sub>0.1</sub> CuO <sub>2</sub>	2001/8/16	13, 7977-7985	Institute of Physics	UK	SCI
J. of the Korean Physical Society	Optical properties of RNi <sub>2</sub> B <sub>2</sub> C (R=Y, Lu, Ho,Er) Intermetallic Borocarbide superconductors	2001/8	39(2), 406-408	Korean Physical Society	Korea	SCI
Current Applied Physics	Synthesis and characterization of the infinite-layer superconductor Sr <sub>0.9</sub> La <sub>0.1</sub> CuO <sub>2</sub>	1(2-3), 157-161	2001/8	Elsevier	Holland	SCI

Current Applied Physics	High-pressure sintering of highly dense of MgB <sub>2</sub> and its unique pinning properties	2001/11/1	1(4-5), 327-331	Elsevier	Holland	SCI
Journal of Magnetism and Magnetic Materials	Penetration depth measurements in HoNi <sub>2</sub> B <sub>2</sub> C: competition between superconducting and magnetic order	2001/5	226-230, 301-303	Elsevier	Holland	SCI
Journal of the Physical society of Japan	Specific Heat of Field-dependent Magnetic Orderings in HoNi <sub>2</sub> B <sub>2</sub> C	2001/10	70(10), 3037-3041	Physical society of Japan	Japan	SCI
Progress in Superconductivity	Domination of glassy and fluctuation behavior over thermal activation in vortex state in MgB <sub>2</sub> thin film	2001	3(1), 23-27	Korean Superconductivity Society	Korea	
Progress in Superconductivity	Temperature and magnetic field dependent optical properties of superconducting MgB <sub>2</sub> thin film	2001	3(1), 31-35	Korean Superconductivity Society	Korea	
계	119 편					

○ 학술회의 발표 실적

강 연 일	학 회 명	강 연 제 목	학 회 규 모
May 25-30 2003	7th M2S-RIO (RIO DE JANEIRO, BRAZIL)	Superconductivity of MgB <sub>2</sub> thin film and single crystal	노벨상수상자 포함 1000 명 정도 초전도 모임 중 가장 큰 규모
Feb 2-14 2003	AMN-1 (Wellington, New Zealand)	Superconductivity of MgB <sub>2</sub> thin film and Single crystal	노벨상수상자 포함 500 명
Jan 16-21 2003	New3SC-4 (San Diego, USA)	Superconductivity of MgB <sub>2</sub> thin film and single crystal	노벨상수상자 포함 500 명
Dec 11-13 2002	RAIM02 (IITM, India)	New Superconductor MgB <sub>2</sub>	1000 명

Oct 2-4 2002	ISAMM '02 (Halong Bay, Vietnam)	Coexistence of superconductivity and magnetism in intermetallic superconductor $\text{Ho}_{1-x}\text{Dy}_x\text{Ni}_2\text{B}_2\text{C}$	200 명
Sep 25-28 2002	APCTP-ICTP Joint Conference on Condensed-Matter Physics (Pohang, Korea)	Superconductivity of $\text{MgB}_2$ thin film and single crystal Invited Talk	노벨상수상자 포함 150 명
Aug 13-18 2002	MOS2002 (Hsinchu, Taiwan)	Superconducting Properties of $\text{MgB}_2$ Single Crystal	노벨상수상자 포함 1000 명
Jul 8-11 2002	Conference of Superconducting and Related Oxides: Physics and Nanoengineering V (Seattle, Washington)	Superconductivity of $\text{MgB}_2$ thin film and single crystal	4000 명
Jun 17-19 2002	International workshop on Superconductivity in $\text{MgB}_2$ (Genoa, Italy)	Superconductivity of $\text{MgB}_2$ thin film and single crystal	80 명
May 8-10 2002	QTSM & QFS 2002 (Yonsei Uni, Korea)	Superconductivity of $\text{MgB}_2$ thin films	노벨상수상자 포함 200 명
Mar 18-22 2002	APS March meeting (Indianapolis, IN)	Growth and superconductivity of $\text{MgB}_2$ thin film and single crystal Invited Talk	8000 명
Nov 26-28 2001	EASSE2001 (Sendai, Japan)	Superconducting Properties of Well-Shaped $\text{MgB}_2$ Single Crystal	100 명
Sep 2-4 2001	Korean-Japanese International Workshop (Spring 8, Japan)	Superconducting properties of Well shaped $\text{MgB}_2$ single crystal	100 명
May 11 2001	QTSM & QFS 2001 (DongKuk Uni., Korea)	High Pressure synthesis of highly-dense $\text{MgB}_2$ and its unique pinning properties	200 명
Mar 12-16 2001	APS 2001 March meeting $\text{MgB}_2$ special session (Seattle, USA)	Superconducting Hole carrier in $\text{MgB}_2$ characterised by Hall Measurements	8000 명
Jan 15-19 2001	New 3SC conference, (Hawaii, USA)	Superconductivity of Four-layer $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+d}$	500 명
계	19 회		



3. 연구성과            해당사항 없음

#### 4. 연구결과 활용계획

##### 가. 당해연도 활용계획

새로운 초전도 박막인 MgB<sub>2</sub>로 표면 전도도를 측정, 마이크로파 통신에 활용 여부 결정

##### 나. 활용방법

새로운 초전도 박막인 MgB<sub>2</sub>로 표면 전도도를 측정, 필터로 quality factor 의 향상을 알아내어야 한다.

##### 다. 차년도 이후 활용계획

높은 온도와 좋은 성질의 초전도 개발을 한 후 이의 응용을 알아본다.

#### 5. 기대효과

The recent discovery of superconductivity in magnesium diboride(MgB<sub>2</sub>) having a superconducting transition temperature (T<sub>c</sub>) of approximately thirty nine degrees Kelvin(39K) introduced a new, simple binary intermetallic superconductor having three atoms per formula unit. MgB<sub>2</sub> has a T<sub>c</sub> that is higher by almost a factor of two of any known non-oxide and non-C60-based compound. Measurements of the boron isotope effect in MgB<sub>2</sub>, which is an indication of the extent to which phonon mediate superconductivity, and consistent with the superconductivity being mediated via electron-photon coupling. Measurements of the upper critical field, H<sub>c2</sub>(T), the thermodynamic critical field, H<sub>c</sub> (T), and the critical current, J<sub>c</sub>, indicate that MgB<sub>2</sub> is a type-II superconductor with properties that are consistent with an intermetallic superconductor that has a T<sub>c</sub> of approximately 40K.

It is believed that MgB<sub>2</sub> forms via a process of diffusion of magnesium (Mg) vapor into boron grains. Superconducting wire, tape, and film can be used for research and applied purposes. For example, superconducting wire can be used for making superconduction magnets, fault-current limiters, and for power transmission. Films can be used to make Josephson junction, SQUIDS (superconducting quantum interference devices), micro-electronic interconnects and other devices. The films can also be used to coat microwave cavities and other objects.

It is an object of the instant invention to provide a method of manufacturing magnesium diboride wires, tapes, and films. It is a further object of the instant invention to provide a method of

manufacturing magnesium diboride wire using boron filaments and films using boron films.

In view of the above objects, it is an object of the instant invention to provide a method of manufacturing magnesium diboride wire and films utilizing simple cost effective techniques.

In accordance with an embodiment of the instant invention, a method of manufacturing magnesium diboride wire or film comprises the steps of exposing boron filaments, tape, or film to Mg vapor for a predetermined time and temperature to form  $MgB_2$  wire, tape or film, removing the formed  $MgB_2$  wire, tape or film from the Mg vapor, and either quenching the  $MgB_2$  wire, tape or film to near ambient temperatures or quenching the reaction vessel to near ambient temperatures and removing the Mg B<sub>2</sub>wire, tape or film from the reaction vessel.

# 기술 요약서

## ■ 기술의 명칭

임계 온도가 높고, 마이크로파의 표면 저항이 적은 초전도 박막 MgB<sub>2</sub> 개발

## ■ 기술을 도출한 과제현황

과제관리번호	M1-0018-00-0021			
과제명	새로운 초전도 연구			
사업명	특정연구개발사업			
세부사업명	창의적연구진흥사업			
연구기관	포항공과대학교	기관유형		
참여기관(기업)				
총연구기간	2000. 10.1-2003.9.30			
총연구비	정부(1,780,000)천원    민간(        0)천원    합계(1,780,000)천원			
연구책임자	성명	이 성 익	주민번호	520630-1047516
	근무기관 부서	포항공과대학교 물리학과	E-mail	silee@postech.ac.kr
	직위/직급	교수	전화번호	054-279-2073
실무연락책임자	성명	김 경 화	소속/부서	초전도연구단
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	전화번호	054-279-5824	FAX	054-279-5299
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## ■ 기술의 주요내용

### [기술의 개요]

본 발명은 초전도 마그네슘 보라이드(Magnesium Boride:  $MgB_2$ ) 박막, 그 제조방법 및 이의 제조 장치를 제공한다. 상기 제조방법은 기판 상에 보론 박막을 형성하는 단계 및 보론 박막이 형성된 기판과 마그네슘을 열처리한 다음, 이를 냉각시키는 단계를 포함하는 것을 특징으로 한다. 본 발명에 명시된 방법으로 박막을 제조하면, 기판에 수직하게 c축 배향성을 갖는 초전도 마그네슘보라이드 박막을 얻을 수 있다. 본 발명에 의해 제조된 마그네슘보라이드 박막은 초전도체 박막을 이용하는 전자장비 예를 들어, 미세자기장을 탐지하는 초전도양자간섭소자(SQUIDS)를 이용하는 의료용 정밀진단 장비와 위성통신에서 사용되는 마이크로파 통신장비, 조셉슨 소자 등에 이용이 가능하며, 이를 이용하여 컴퓨터를 제작하면 현재의 경우보다 연산속도가 100배 이상 향상되는 컴퓨터를 제조하는 것이 가능해진다.

### <기술적 특징>

- (1) 고압조건을 유지하면서 보론 박막과 마그네슘을 반응시켜 양질의 초전도 마그네슘 보라이드 박막을 형성할 수 있다.
- (2) 빠른 열처리를 통해 마그네슘보라이드 박막과 이 박막이 형성되는 기판간의 화학반응으로 인하여 발생하는 박막 품질 저하를 최대한 막을 수 있다.
- (3) 시편을 산소와 격리시킨 상태에서 반응을 진행시켜 높은 순도와 c축 배향성을 갖는 마그네슘보라이드 결정을 성장시킬 수 있다.

### [용도 · 이용분야]

- (1) c축 배향성을 갖는 결정상과 우수한 초전도 특성을 갖는 마그네슘보라이드박막제작
- (2) 의료용 정밀 진단 장비와 위성통신에서 사용되는 마이크로파 통신 장비, 조셉슨 소자 등에 이용가능
- (3) 연산속도가 100배 이상 향상되는 컴퓨터 제조 가능



