

On the 20th Anniversary of the Discovery of MgB₂ Superconductor

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1. Introduction

2021 is the 20th anniversary of the discovery of MgB₂. So, the 20th anniversary symposium has been planned in many places. After the discovery of MgB₂, I had the ambition to search for a new superconductor with a higher-T_c, and had little desire to investigate the physical properties of MgB₂ itself or to apply it. At the early stage of its application, I heard the news that J_c and H_c of MgB₂ seems to be not so high and I was pessimistic with respect its application. After the 20 years has passed, the application of MgB₂ has steadily been developed, even just looking at the table of contents of the recent symposium. I am surprised at the improvement of its quality and its wonderful application to various fields. Twenty years seem to be short, but I am amazed at its progress. Here, it's a little personal impression, but I would like to look back on 20 years ago.

2. Prehistory of MgB₂ discovery

As is well known, superconductivity was discovered in 1907 by Kamerlingh Onnes in mercury (Hg). After that, the new superconductors have been discovered by various peoples, and during that time, B. Matthias carried out the most vigorous and systematic investigation from single element to two-element system. Figure 1 shows the well-known superconducting transition temperature (T_c) vs. its year of discovery. Looking at this figure, T_c vs. its year of discovery is almost straight and rising slowly until the discovery of high temperature superconductor by Bednorz and Müller in 1986. The main materials of these were discovered by Matthias and his group. I don't guarantee the truth, but according to the story I heard, one of the students told to Matthias, "Professor, if this straight line is extended, room temperature superconductor will be realized in about XX years." However, Matthias replied, "No, these are the materials I found, so if I die, T_c will not be raised." In fact, it is true that after the discovery of Nb₃Ge in around 1970, T_c was not improved till 1986.

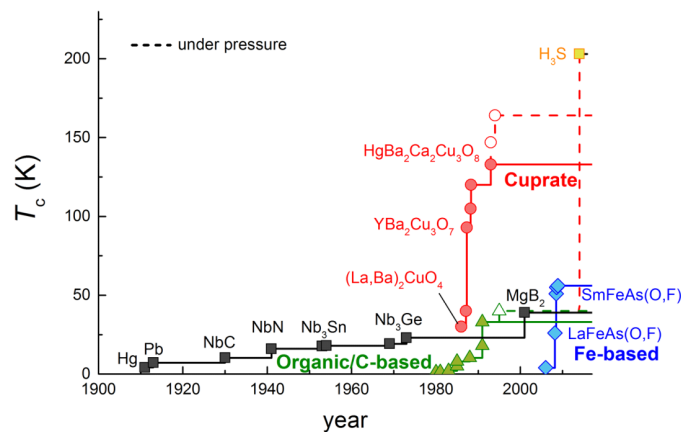


Fig.1. History of superconductor T_c

The next break-through came in 1986. It was the discovery of "cuprate superconductors" by Bednorz and Müller. This was a discovery that brought a new paradigm to the world of

solid-state physics, and then T_c also rapidly rose to around 135K at $\text{Hg}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8$. I also followed the flow of this discovery and found more than 10 new superconductors (Table 1). Among these, we found a new type of superconductor on 1996, being called "ladder-type superconductor" that has an intermediate structure between one- and two-dimensional [1].

3. Discovery of MgB_2

However, I became aware that cuprate superconductor was almost completely searched for, so I decided to go back to metal superconductors and look for it with a new eye. I focused on metal superconductors, especially boron-based superconductors. I chose the Mg-Ti-B system. I let Jun Nagamatsu an undergraduate student, do this theme. He received the cooperation of Yuji Zenitani, assistant professor, Takahiro Muranaka, doctor course student, and Norimasa Nakagawa, master course student. Then finally, the superconductivity with $T_c \cong 39\text{K}$ of MgB_2 was ascertained. Surprisingly, however, little MgB_2 was found by X-ray diffraction at first, and only a small amount of Mg was found (Fig.2). However, we succeeded in manufacturing single phase during the New Year holidays, so we presented it at the New Year's study group before writing an academic paper. To my surprise, the News spread all over the world, and I was surprised to receive more than 10 emails asking me to send a paper. So, I was in a hurry to try to submit the paper to the Journal of Physical Society of Japan. However, I heard the rumor that the next paper has already been submitted to Nature. So, I submitted the paper to Nature

Table 1. Cuprate new superconductors discovered in Akimitsu laboratory

Year	Superconductor	T_c (K)
1987	Bi-Sr-Ca-O	6
1988	Nd-Ce-Sr-Cu-O	28
1989	(Eu,Ce)-(Ba,Ln)-Cu-O (Ln=Nd,Sm,Eu)	43
1992	(Y,Ca)-Sr-Cu(CO ₃)-O	63
1992	(Bi,Pb)-Sr-Cu(CO ₃)-O	41,54
1993	Sr-Ca-Cu-(CO ₃)-(BO ₃)-O	33, 55, 105, 115
1993	Tl-(Ba,Sr)-Cu-(CO ₃)-O	70
1993	Hg-Ba-Sr-Cu-(CO ₃)-O	66
1994	Ba-Ca-Cu-(CO ₃)-(BO ₃)-O	120
1994	(Ca,Na)-Ca-Cu-O-Cl	49
1995	(Ca,A)-Cu-O-Br(A=Na,K)	19
1996	Ba-Ca-Cu-O-F	28,106,108
1996	Sr-Ca-Cu-O(14-24-41)	12
1998	Cu-Sr-(Y,Ce)-Cu-O	43
1999	Ru-Sr-Y-Cu-O	40

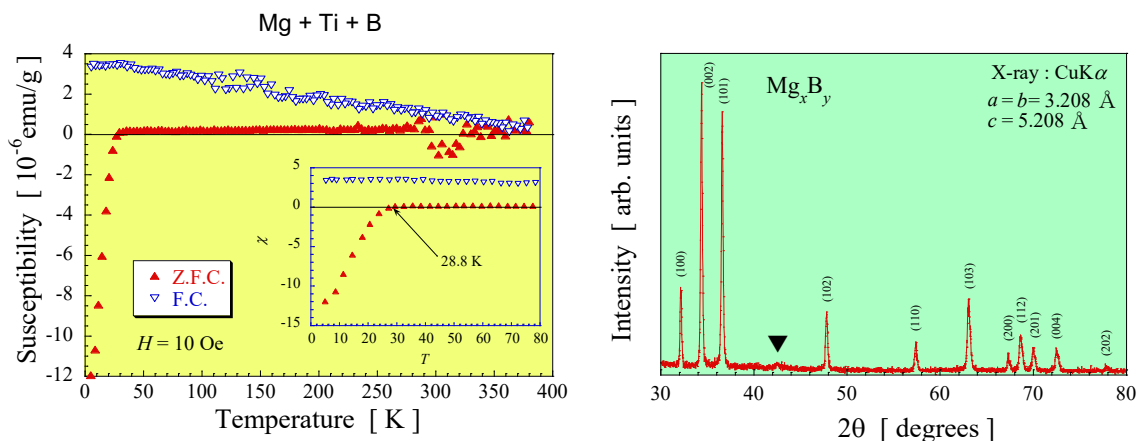


Fig.2. Discovery of MgB_2 superconductor

[2]. Nature's referee commented at that time it was very impressive. "Nature" is very lucky to get it. This author might submit to the Japanese journal."

There were some interesting episode about this material. I would like to introduce some of them.

- 1) Surprisingly, this material has been sold as a commercial product. Nature introduced under the title of "Genie in a bottle" (Fig. 3). I was impressed by the fact that it was a good expression, but it was actually the title of a song sung by a young woman.
- 2) Second surprise happened at the Matthias Prize ceremony. If my memory is correct, Chairman of Matthias Prize, Professor Paul Chu said that Matthias had been checking superconductivity of MB₂ series materials, but he didn't check the superconductivity of MgB₂. Nobody could understand why he didn't check it. Professor Chu said "Jun, you are lucky".



Fig.3. Nature News and View

After that, many calculations and experiments such as band calculation were performed, and it was gradually clarified that it would be the highest T_c material among the materials described by the conventional electron-phonon theory (Fig.4).

Later, it was discovered that hydrogen-based superconductors with high T_c under high pressure. Perhaps the hydrogen system is also a material described by electron-phonon interaction theory.

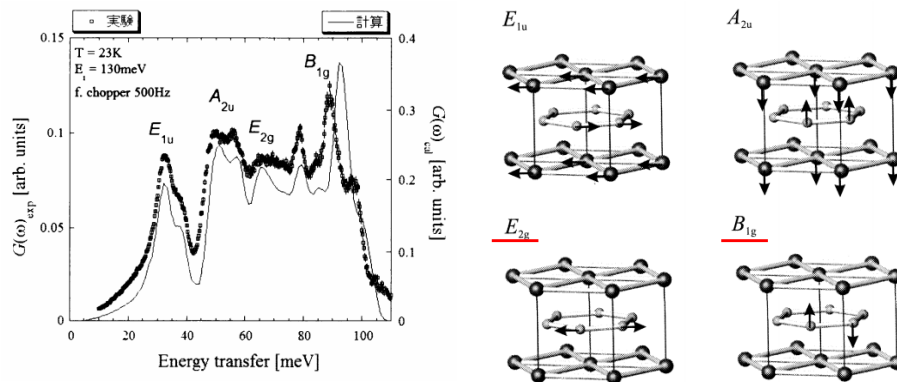


Fig.4. Superconductivity mechanism of MgB₂: Electron-Phonon interaction
 Left hand side: Experimental result and theoretically calculated phonon DOS in MgB₂
 Right hand side: calculated phonon modes Arrows show the direction of atom vibration.

4. Special features of MgB₂

I would like to introduce special features of superconductivity by the MgB₂ research.

- 1) The first is a characteristic of the band structure that comes from the crystal structure. Figure 5 shows the results of our X- ray experiments at Spring-8, and it can be imagined that the boron elements form a two- dimensional network and are covalently bonded [3]. The Takahashi group at Tohoku University found this band structure by photoelectron spectroscopy [4] (Fig. 6). The conclusion obtained here is that there are two bands, one is

the band that flows through the boron layer and is called the σ (sigma) band. The other is the π band that connects Mg and B. In other words, MgB_2 is a two-gap superconductor with two bands.

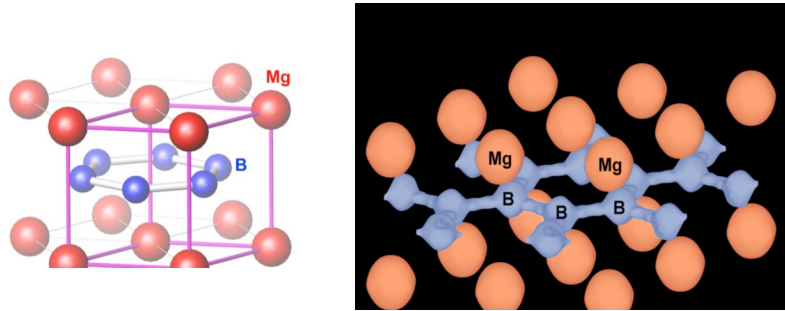


Fig.5. Electron density distribution [3]

- 2) The second major feature is that the superconducting mechanism of MgB_2 can be explained by the electron - phonon interaction caused by the B atom (Fig.4). Furthermore, the superconducting symmetry of these bands has s- wave symmetry.

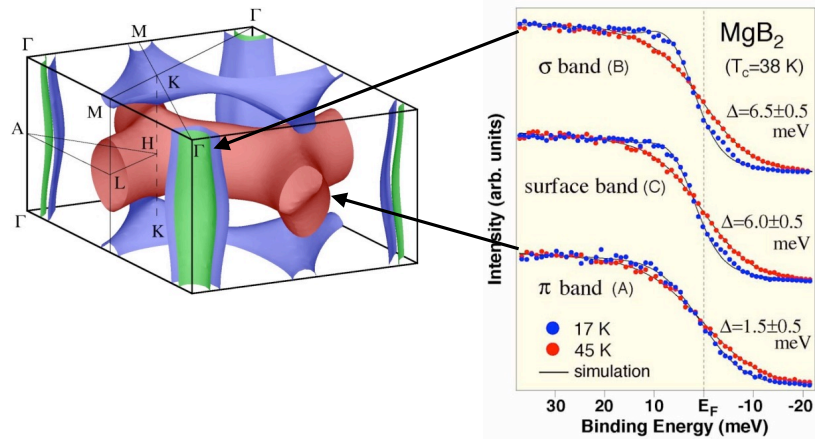


Fig.6. Band structure of MgB_2 [4,5]

5. Application of MgB_2

Finally, the recent application of MgB_2 is shown here. Many applications are considered, but the most popular application at present is the magnet. This is used as a "superconducting magnet" in many laboratories, but recently, a wider range of uses has come to be considered. Here are two examples where MgB_2 is used as a popular use.

- 1) MRI: It is well known that many hospitals have MRI because it can examine the state of internal organs including the brain in detail. Currently, MRI using MgB_2 is being prepared (as far as I know) by ASG in Europe, Hyper Tech in the United States, and HITACHI in Japan (Fig.7). Unfortunately, H_c and J_c are slightly lower than those of conventional superconductivity, but since it can be used at 10



Fig.7. MgB_2 wires and MRI application

to 20K, it has the advantage of being economically cheaper, and is expected to become widespread in the future.

- 2) Accelerator: Indeed, CERN in the second phase has a plan to use MgB_2 feeder line connecting between magnets. This is now under construction (Fig. 8).



Fig.8. MgB_2 Feeder cable for accelerator (By courtesy of Prof.A.Yamamoto(KEK))

In addition, B is being considered for use as a neutron detector because it absorbs a large amount of neutrons, but this is also an issue for the future (Fig. 9).

Finally, a list of metallic superconductors we have found is shown (Tables 2).

Table 2. Metal based new superconductors discovered in Akimitsu laboratory

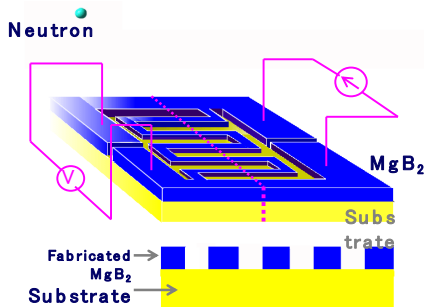


Fig.9. MgB_2 neutron detector (By courtesy of Prof.T.Ishida)

Year	Superconductor	Tc (K)
1984	$(Nb,Ta)Se_3$	4
2001	MgB_2	39
2003	Re-B	5
2004	Y_2C_3	18
2006	$(W,Mo)-Re-(B,C)$	7,8
2007	NaAlSi	7
2007	SiCB	1.4
2008	SiC:Al	1.5
2008	AlN_x	2.8
2009	W_5Si_3	2.8
2010	YSn_3	7
2010	$Y_3Pt_4Ge_6$	2.6
2011	W_5SiB_2	5.8
2012	$(Ta,W)_5SiB_2$	6.5
2012	KAIX(X=Si,Ge)	3.5,4
2012	$AE(TM,Si)_2$ (AE=Ca,Sr,Ba, TM=Ni,Pd,Pt,Cu,Ag,Au)	0.9-3.5
2013	KSn_2	3.2
2013	$A_8(Al,Ge)_{46}$	4,4.4
2013	Ln_2SnC	5
2014	Cn_2Re_3B	6

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