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Development of Superconducting Materials (1911-2017)

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***Abstract*— The discovery of high-temperature superconductors, whose mechanism remains as elusive as the cuprates discovered in 1986, has injected a new energy into superconductivity field. From the beginning of 2008, the birth of iron based superconductors was provided with the opportunity of interacting with those who have enjoyed a long history in superconductivity. Many believe that it helps to understand the 100 years question of what cause to bind the pair of electrons in superconducting state at high temperature. Amid chemical doping and magnetic field, an external pressure is one of a key factor to explore that exotic phenomenon in high Tc superconductors like copper oxide and recent iron based compounds. Furthermore, the recent discovery of H2S shows highest Tc around 203 K at 150 GPa. Moreover, superconductors appear to be extremely flexible in terms of chemical composition and applied magnetic field, as they belong to a comprehensive class of materials, where many chemical substitutions are possible, and their layered structure allows a high upper critical field and designing new composite structures**

Keywords*— High Temperature superconductors, High pressure effect, Pnictides, H_2S compounds.

DEVELOPMENT OF SUPERCONDUCTORS

Superconductivity was discovered by H. Kamerlingh-Onnes in Holland in 1911 as a result of his investigations leading to the liquefaction of helium gas. In Onnes' time superconductors were simple metals like mercury [1], lead, bismuth etc. These elements become superconductors only at the very low temperatures of liquid helium. During the 75 years that followed, great strides were made in the understanding of how superconductors worked. Over that time, various alloys were found that were superconductors at somewhat higher temperatures. Unfortunately, none of these alloy superconductors worked at temperatures much more than 23 Kelvin. Thus, liquid helium remained the only convenient refrigerant that could be employed with these superconductors. Since this initial discovery, many more elements have been discovered to be superconductors. In 1912, Pb was found to be a superconductor at 7 K and 9.3 K for niobium (Nb) has the highest T_c among the element. And, some other elements shows the superconducting in particular forms: carbon (C) in the form of nanotubes, chromium (Cr) as thin films, palladium (Pd) after irradiation with alpha particles, and platinum (Pt) as a compacted powder. It is worth noting that copper (Cu), silver (Ag) and gold (Au), three elements that are excellent conductors at room temperature, do not become superconductors even at the lowest temperatures that are attainable.

In 1928, the compound niobium-germanium called as binary alloys, with the formula of Nb_3Ge (A-15 compounds) shows T_c = 23.2 K, was then the highest of all materials were found by Matthias *et al*. The fact that this transition temperature is less than one third of the liquid nitrogen boiling point 77 K caused most specialists in the field to believe that the possibility was indeed very remote of ever finding a material to superconduct above, or even close to, the magic value of 77 K [2]. During the mid 1980's all known superconductors operated at temperatures far below the boiling point of liquid nitrogen, which is 77 K. In 1979, in violation of another Matthias rule, the superconductivity was discovered in the magnetic material $CeCu_2Si_2$ as the first representative of a new class named '**heavy fermion**' superconductors where the magnetism is responsible for the Cooper pair formation. In the late 1980's, the amount of research effort in the field of superconductors increased dramatically due to the discovery of so-called 'high temperature' superconductors by Bednorz and Muller in 1986. Their findings were thought to be so important that it was only a year later that they were awarded the Nobel Prize in Physics by the Royal Swedish Academy of Sciences. There are several advantages in using liquid nitrogen instead of liquid helium. Firstly, the 77 Kelvin temperature of liquid nitrogen is far easier to attain and maintain than the chilly 4.2 Kelvin of liquid helium. Liquid nitrogen also has a much greater capacity to keep things cold than does liquid helium. Most importantly, nitrogen constitutes 78% of the air we breathe, and thus unlike liquid helium, for which there are only a few limited sources, it is relatively much cheaper. Until 1986, the highest temperature a superconductor operated was 23 K, and so they all had to be cooled by liquid helium (boiling temperature ~ 4 K). This, of course, made any use of superconductors extremely expensive.

The discovery of a barium-doped lanthanum copper oxide ($La_{2-x}Ba_xCuO_4$) or Bednorz and Muller molecules (LBCO), which became superconducting at 35 K led to a flood of new high temperature superconductors some of which were superconducting above the boiling temperature of nitrogen (77 K) [3]. The discovery was particularly surprising because this material is an insulator at room temperature. The following year they received the Nobel Prize for Physics 'for their important breakthrough in the discovery of superconductivity in ceramic materials' (Nobel Prize citation), and the unprecedented rapidity with which the prize followed publication of their results reflects the importance. As a result of this breakthrough, a scientific bandwagon started to roll and many other Scientists began to examine similar materials and over 50 high temperature superconductors, almost all containing copper oxide layers, are now known. Wu and Chu found a maximum T_c of 90 K from YaBaCuO and later Maeda *et al*. discovered first 100 K superconducting transition temperature in BiSrCaCuO compound. A highest T_c reached by using these class compounds are ~ 130 K at ambient pressure from HgBaSrCaCuO and ~ 164 K at high external pressure of 30 GPa [4]. Since these materials superconducting at a significantly higher temperature, they are called as High Temperature Superconductors (HTS). The past three decades have also seen the discovery of other unexpected types of superconductors. A few types of low temperature superconductivity have been observed in organic polymers, and alkali metal doped C_{60}. Then, the maximum attained T_c of ~ 40 K was found metal (K, Rb and Cs) intercalated in between C_{60} molecule layers. In 2001, a record temperature of 40 K for the onset of conventional superconductivity was observed in MgB_2 set a first compound of type I superconductors having T_c more than 30 K in the intermetallic compounds [5]. However, this temperature level is not enough for liquid nitrogen cooling as a low cost product than liquid helium. Though a theory to explain high-temperature superconductivity still eludes modern science, clues occasionally appear that contribute to our understanding of the exotic nature of this phenomenon.

The most recent "family" of superconductors to be discovered is the "pnictides". These iron-based superconductors were first observed by a group of Japanese researchers in 2006. Like the high-T_c copper-oxides, the exact mechanism that facilitates superconductivity in them is a mystery. The new superconductor LaFePO based on the strong Fe ferromagnetic metal with T_c of ~ 3 K was found by Hideo Hosono *et al* [6]. Since after, the maximum attained T_c = 26 K in 2008 has been observed from $LaFeAsO_{1-x}F_x$ compound by the same group. Then, more than 70 new superconductors have been discovered within several months, with the highest T_c of up to 55 K being observed in Sm based FeAs superconductor and it shows the importance of iron based superconductors than other known high T_c superconductors. However, with T_c's over 50K, a great deal of excitement has resulted from their discovery.

As introduced above, two kinds of "layered materials" have contributed to the development of high-T_c superconductors. However, there are not the only layered superconductors which have provided us with some hints on how to understand the physics of unconventional superconductivity.

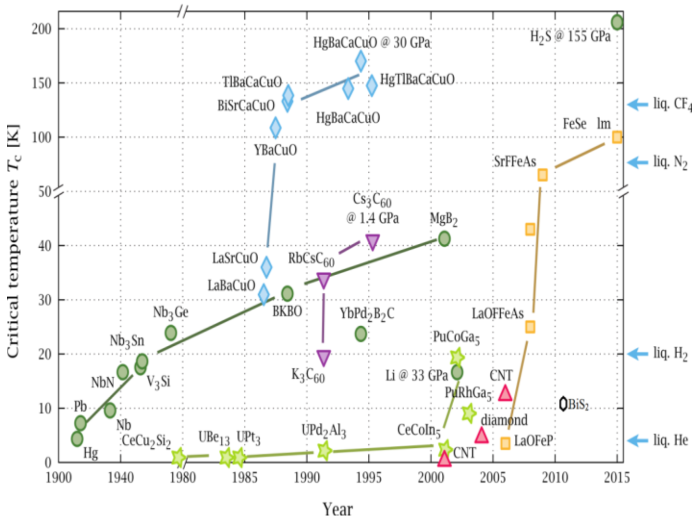

Figure 1: T_c vs. year of discovery of some important superconductors over the last 105 years (ref-13).

In this regard, the discovery of new layered superconductors is one of the most important issues for the realization of a T_c approaching room temperature. In 2012, Yoshikazu Mizuguchi was discovered novel layered superconductors which have a crystal structure similar to those of the Cu-oxide and Fe-based superconductors. The characteristic structure is an alternate stacking of superconducting BiS_2 layers and blocking layers. In the conduction plane, the Bi and S atoms are alternately aligned and form a Bi–S square plane. The new superconducting family "**BiS_2-based superconductors**"[7,8]. So far, many superconductors have been discovered in this family, and the highest record of T_c is 11 K in $LaO_{0.5}F_{0.5}BiS_2$ [9]. In addition, we should mention the Bi-oxide superconductor $B_{1-x}K_xBiO_3$ with a T_c of ~30 K [10, 11]. On the basis of these similarities of crystal structure and composing elements to the layered high-T_c superconductors, we consider that the T_c can be increased by optimizing the structure of superconducting layers and/or blocking layers in the BiS_2 family. Figure.1. clearly indicates the T_c vs. year of discovery of some important superconductors. As follows, the groups are start by looking at the proposed compounds with important properties of BiS_2 based superconductors family that was discovered nearly three years ago.

Recently, sulfur hydride, where a T_c of 80 K has been predicted. This system transforms to a metal at a pressure of approximately 90 GPa. On cooling, the signatures of superconductivity: a sharp drop of the resistivity to zero and a decrease of the transition temperature with magnetic field, with magnetic susceptibility measurements confirming a T_c of 203 K (150 GPa). The phase responsible for high-T_c superconductivity in this system is likely to be H_3S, formed from H_2S by decomposition under pressure. These findings raise hope for the prospects for achieving room-temperature superconductivity in other hydrogen-based materials [12]. The interest in the new superconductors continues to mount. Many Governments, Corporations and Universities are investing large sums of money in this field to investigate this major breakthrough that many have hailed as important as the invention of the transistor and other application based SC's materials.

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