Superconductivity in MgB_2 at 39 K—A Sensational and Curious Discovery

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Superconductivity was first observed in 1911 by Kammerlingh Onnes in mercury by cooling it with liquid helium at 4 K. Since then many metallic elements and compounds showing such a material property have been found; however, with the exception of the ceramic oxocuprate superconductors discovered in the last few years, their critical temperatures T_C all lie below 30 K. Thus it was a sensation, when Jun Akimitsu and collegues announced their discovery in January this year[1] that the metallic magnesium diboride MgB_2 becomes superconducting below the relatively moderate temperature of 39 K.[2] The interest of the authors was originally focussed on the semiconducting CaB_6, which becomes ferromagnetic on slight doping with electrons.[3] Their intention was to partially substitute Ca in this boride by the lighter homologue Mg, and it seemed evident to use MgB_2 (known since 1953)[4, 5] the boron-richest phase in the Mg/B system, as the starting material. MgB_2 is commercially available, currently costs approximately one € per gram, and is a common reactant for the syntheses of elemental boron, boranes, or transition metal borides.[6] One can imagine the astonishment of the researchers, when they discovered that a chemical which can be found in every lab cupboard becomes superconducting already at 39 K (see Figure 1).

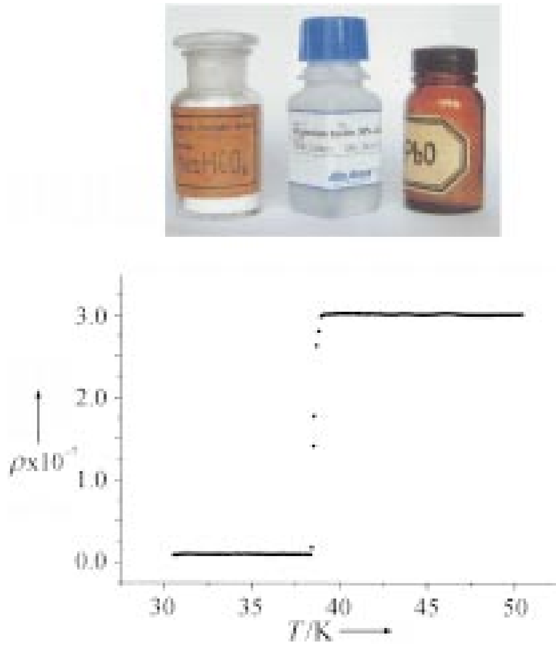

Figure 1. Temperature dependence of the electric resistance (resistivity) ρ [Ω m] (bottom) of magnesium diboride MgB_2 acquired commercially (top).

The discovery appears especially curious if one considers that generations of scientists have undertaken great efforts for almost a century to find new superconductors with higher transition temperatures. Central to these efforts was B. T. Matthias, who has prepared, doped, and tested thousands of metallic oxides, nitrides, carbides, and also numerous borides for superconductivity.[7] Nevertheless, until the middle of the 1980s a T_C value of 23 K in Nb_3Ge[8] was the upper limit, which appeared to be unsurmountable. Because the venture of reaching higher critical temperatures appeared increasingly hopeless no public research funding was given in the USA for the search for new superconducting materials for a number of years. This all changed when fifteen years ago Bednorz and Müller[9] presented the first superconducting oxocuprate with a T_C of 40 K!, for which they received the Nobel prize for physics a year later. This initialized a tremendous search for further such compounds, and has subsequently led to the discovery of the new ceramic high-temperature superconductors.[10] The best superconductor of this modern generation indeed works above 100 K, but cannot transport sufficient current for practical applications without being cooled far below its critical temperature. Conventional superconductors with higher T_C values have been found only recently, for example 33 K in $Cs_xRb_yC_{60}$,[11] 30 K in $Ba_{1-x}K_xBiO_3$,[12] and 52 K in hole-doped surfaces of C_{60} crystals.[13] MgB_2 with a transition temperature of 39 K lies in this order of magnitude and has been simply overlooked during the search for new superconductors over the past decades.

The structure of MgB_2 is hexagonal and contains sheets of B and Mg, which are alternatingly stacked along the c axis (Figure 2). The B atoms form a honeycomb net (6^3 net), similar to the arrangement of the C atoms in graphite, and each B atom is surrounded by three equidistant B atoms. The Mg atoms between the boron sheets lie above and below the centers of the benzene-like B_6 rings, which are two-dimensionally condensed. The B_2^{2-} sheet is isoelectronic to a C sheet

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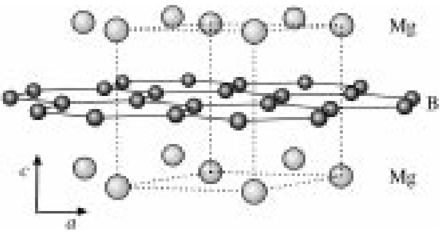


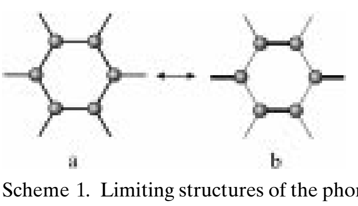
Figure 2. Crystal structure of MgB_2 together with the unit cell. The B_2^{2-} sheets are highlighted.

in graphite and also exhibits an extended π-electron sytem with sp^2-hybridized atomic orbitals at B.

What then makes the decisive difference between graphite, which does not superconduct even at lowest temperatures, and MgB_2? Through the layers of Mg^{2+} ions lying between the B_2^{2-} sheets the structure of MgB_2 is markedly more three-dimensional. According to band sructure calculations,[14] the π orbitals perpendicular to the plane (p_z) are stabilized by the Mg^{2+} ions and lowered in energy to such an extent that they lie below the p–σ orbitals. Because of this electrons from the p–σ bands are shifted to the p-π bands corresponding to a hole-doping of the p–σ bands. In other words the Fermi level crosses the p–σ bands in MgB_2, which in this case is evidently decisive for the occurrence of superconductivity. This band can be filled by substituting Mg by Al, which leads to lower T_C values when doping up to 10%, and at higher doping leads to the complete disappearance of superconductivity.[15]

Within the BCS theory (named after the discoverers Bardeen, Cooper, and Schrieffer) the critical temperature of a superconductor can be calculated according to $T_C = \omega_{ph} \exp(-1/\lambda^*)$.[16] The phonon frequency ω_{ph} corresponds to the thermal motion of the atoms, which plays the decisive role in the electron–phonon coupling process with the constant λ^* which is relevant for the attractive interaction of two electrons with spin $= \pm 1/2$ to a so-called Cooper pair with $S = 0$. The boron isotope effect, which is charateristic for conventional BCS superconductivity was measured for MgB_2:[17] The T_C value for $Mg^{10}B_2$ lies approximately 1 K higher than that for $Mg^{11}B_2$. Furthermore measurements of the heat capacity[18] and results of tunneling spectroscopy investigations[19] indicate that MgB_2 is a conventional BCS superconductor with a weak-to-moderate electron–phonon coupling.

Detailed analyses of the electron–phonon coupling in MgB_2 on the basis of quantum-mechanical calculations show[20, 21] that the p–σ electrons couple very strongly to a high-frequency B–B stretching mode, whose limiting structures can be described as "benzoid" and "quinoid" (see Scheme 1). Within such a mode the degree of overlap of the π bonding changes, as does that of the p–σ bonding, whose band lies at the Fermi level. The calculated electron–phonon coupling constant results in an expected T_C value of 40 K for MgB_2. That MgB_2 can be well described by means of reliable theoretical tools is also shown by the calculation of the pressure dependence of the elastic and electronic properties of MgB_2,[22] according to which the value of T_C should decrease by -1.4 K per GPa. This value is in good agreement with the experimental value of $-1.6\,K\,GPa^{-1}$ published shortly thereafter.[23, 24] Through application of external pressure the interatomic B–B and Mg–B distances are shortened. Consequently the phonons become harder, that is ω_{ph} becomes larger, simultaneously however, the density of states at the Fermi level becomes smaller, and also the electron–phonon coupling is weakened, so that the observed decrease of the T_C value under pressure can be well explained within the BCS scenario.



Scheme 1. Limiting structures of the phonon in a B_2^{2-} sheet in MgB_2 which is relevant for the occurrence of superconductivity: a) "benzoid" with equal B–B distances and b) "quinoid" with short (bold) and long B–B distances.

Finally the relevance of Akimitsu's discovery for possible applications is worth mentioning. Nowadays superconducting materials in the form of strong magnets are used in daily life, for example in magnetic resonance tomography in hospitals or transport based on magnetic levitation. Although MgB_2 is not the best superconductor, a great deal is expected owing to its potential for applications; it is a so-called type 2 superconductor[25] with large values for the upper critical magnetic field H_{c2}, and the critical current, at which the superconductivity disappears, is relatively high.[26] These are important quantities for applicable superconducting wires[27] or thin films,[28] which can transport large amounts of current. As MgB_2 can be used as a superconducting material slightly below its T_C value of 39 K, there is even the chance that instead of cooling with liquid helium—which is technologically demanding—it might be possible to cool with electrical aggregates.

The enormous interest in the superconductivity of MgB_2 has led to a scenario where numerous research teams have been attracted to this new topic like a gold rush, similar to what happened with the oxocuprate superconductors fifteen years ago. Within weeks after the announcement of the discovery, hundreds of publications could be found on preprint servers and a head-to-head race for establishing priorities had started. It is hoped that the lessons from the past will be learned and that not too much research capacity will be wasted and that preliminary results will not be published too hastily. The discovery by Akimitsu and co-workers, however, gives rise to expectations that variants of MgB_2 or further simple materials with even higher critical temperatures will be found which can lead to a better understanding of superconductivity and new potential applications for superconducting materials.

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RNA Interference: A New Way to Analyze Protein Function

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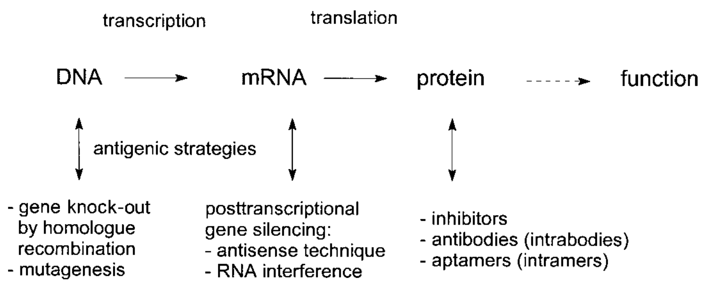
Introduction

Within the last few years a tremendous amount of work has been done to identify the genetic background of different species. Even the human genome has been sequenced. However, the data obtained create a need for additional information that will allow us to understand the determinants of biochemical, biological, and pharmacological processes. In particular, more information is needed to enable us to assign functions to the gene products, mostly proteins, encoded by the genome of a species (functional genomics). Recently, a novel technique has been described which promotes a much faster and simplified analysis of protein function. This technique uses gene-specific double-stranded RNA (dsRNA) to disrupt gene expression at the level of messenger RNA (mRNA) in tissue culture and whole organisms (Scheme 1).[1]

Function of Proteins

Researchers have been looking for methods to study the function of proteins for a long time. In the past various experimental procedures have been used but have often turned out to be very laborious and time consuming. A common method to investigate the function of proteins and other biological molecules is the knock-out experiment.



Scheme 1. Examples of methods for the disruption of protein function.

For this purpose, the phenotype of tissue cultures or organisms that lack a specific protein due to mutations or alterations is analyzed. In humans, inherited diseases were used as models for these knock-out experiments.

One of the most promising new techniques for the study of protein function seems to be the RNA interference (RNAi) method. It is based on the degradation of selected mRNA by administration of double-stranded RNA. RNAi offers strong advantages over other antigenic strategies[2] such as gene knock-out by homologue recombination, antisense oligonucleotides, or ribozymes.[3]

History

RNAi was discovered in 1995 in the nematode *Caenorhabditis elegans*, a model organism for biological experiments,[4] when researchers attempted to use the antisense RNA approach to inactivate the expression of a single gene. *C. elegans* was injected with RNA complementary to a target

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