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Superconductivity of magnesium diboride

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ABSTRACT

Over the past 14 years MgB_2 has gone from a startling discovery to a promising, applied superconductor. In this article we present a brief overview of the synthesis and the basic superconducting properties of this remarkable compound. In particular, the effect of pressure, substitutions and neutron irradiation on superconducting properties are discussed.

Contents

1. Introduction

On March 12, 2001 a large number of condensed matter physicists gathered for a technical session at the American Physical Society March Meeting in Seattle to share their results and thoughts on the newly discovered superconductivity in a simple binary compound, magnesium diboride (MgB_2). For somewhat nostalgic reasons (in memory of so-called "Woodstock of Physics" in 1987, where the discovery and first studies of superconducting cuprates were discussed) this session was quickly dubbed "Woodstock West". As in the case of superconducting cuprates, the discovery of superconductivity in MgB_2 [1] was serendipitous: the compound itself was known [2], and even synthesized in single-crystalline form [3], decades earlier. We can only conjecture that since this material appeared not to fulfill the preconcieved notion of what high temperature superconductivity should look like, the proper experimental test for a possible superconducting ground state was not performed. The specific heat capacity of magnesium diboride was measured and tabulated from ~18 K to ~305 K, through the temperature that now we know to be its T_c, but no feature that could be associated with a transition was reported [4]. All in all, magnesium diboride was waiting almost 50 years for its moment, if not in "the sun", then at least in the cryostat. (As an aside, in a similar way, Ba- and Sr-doped La_2CuO_4 cuprates were synthesized and described [5], but not cooled down below 78 K, almost a decade before the high temperature superconductivity in these materials was discovered [6].) The

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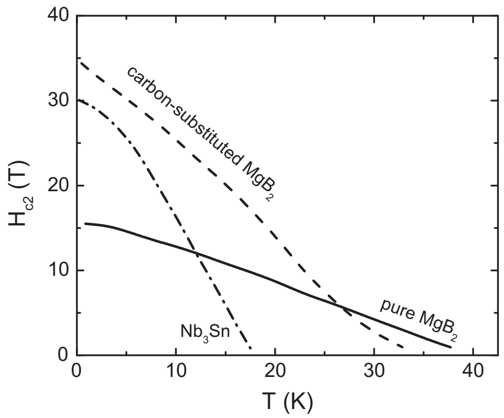

Fig. 1. Temperature-dependent upper critical field of pure and carbon-substituted ($\sim$ 5% of C) MgB_2 in comparison with Nb_3Sn (after Ref. [7]).

discovery of superconductivity with $T_c \sim 40$ K in magnesium diboride caused initial excitement and hopes. Very quickly $H_{c2}(T)$ curves that exceeded those of Nb_3Sn were achieved (Fig. 1) and a "MgB_2 zone of use" around 20 K was delineated. Indeed, in few years the physics of this material was considered understood and applied research efforts took up the arduous task of further improving critical current dencity, J_c, as well as wire development.

In this brief review we summarize, mostly experimental, knowledge about superconductivity in magnesium diboride with more attention to the basic physical properties of bulk samples. MgB_2 films will be mentioned only briefly, for details an interested reader can inquire several general and more specialized reviews [8–13]. An interested reader will be able to find a number of in-depth discussions of specific topics related to superconductivity of magnesium diboride in two special issues of *Physica C* [14,15] and in a number of reviews scattered in different sources [8,16–22], as well as more general, "popular science" reviews [7,23,24].

2. Synthesis

MgB_2 forms in the hexagonal, AlB_2 – type structure (space group: *P6/mmm*) with the lattice parameters $a = 3.0834$ Å and $c = 3.5213$ Å [2]. In this structure the characteristic graphite-like two-dimensional layers formed by boron atoms sandwich the triangular Mg layers forming the structure similar to the intercalated graphite. Number of other metal – diborides are formed in the same structure. Details of chemical bonding in these materials are briefly surveyed by Spear [25].

Bulk polycrystalline MgB_2 can readily synthesized by exposing solid boron to Mg vapor at elevated temperatures [26], that is very close to the approach used in the initial publications on MgB_2 [2,4]. MgB_2 forms as a line compound [27] with possible Mg vacancies of, at most, less than one percent [28]. So to make stoichiometric MgB_2 one needs to mix magnesium and boron in 1 to 2 molar ratio and heat above the melting point of magnesium (650 °C), although often higher temperatures, $\sim$950 °C are used. As MgB_2 is the most magnesium rich of all stable Mg–B binary phases [27], to ensure complete reaction, it is possible to use excess of magnesium. This approach provides a form preserving method of turning boron objects (filaments, films, tapes) into MgB_2 objects with similar morphologies [29–32]. The properties of resultant MgB_2 (resistivity, T_c, upper critical field, etc.) can vary depending upon presence of impurities, in particular in boron [33].

Despite serious efforts of several groups there was no obvious success in growing MgB_2 single crystals of significant size (larger than few μm) at ambient pressure. The only viable technique for single crystal growth is high pressure synthesis. Crystals with dimensions up to $1.5 \times 1 \times 0.1\ \mathrm{mm}^3$ and mass in excess of 200 μg can be grown under high pressure. The Mg–B phase diagram under pressure of 45 kbar [34] contains a eutectic at Mg:B $\approx$20:80 with a temperature slightly above 550 °C. This phase diagram presents the possibility of MgB_2 single crystal growth from solution at temperatures up to $\sim$2200 °C. Since in real experiments [35,36] the synthesis is performed in a BN container which reacts with the melt at high temperatures (and pressures), the reaction in the ternary Mg–B–N system should be considered. Synchrotron studies of the MgB_2 formation under pressure was reported in Ref. [37], overviews of the MgB_2 single crystal growth under pressure were given in several publications [35,36].

There were a number of attempts at partial replacement of Mg and B in MgB_2 by different elements. To judge the veracity of such claims, a set of three criteria known as "Bob's rules" was suggested [38]: (1) second phases should not grow systematically in proportion with increasing dopant concentration; (2) a shift of the lattice parameters by more than three standard deviations in the series of doped samples should be seen; and (3) properties of the superconductor should change on doping. The applicability of these criteria is not limited to substitution in MgB_2, but, in our opinion, should be considered in any study that involves chemical substitution. Of the attempts of substitution in MgB_2, only three are generally accepted as successful at this point: $Mg(B_{1-x}C_x)_2$, $Mg_{1-x}Al_xB_2$, and $Mg_{1-x}Mn_xB_2$ [35,36,38,39]. These substitutions were achieved both in polycrystals and in single crystals and all cause a decrease in the superconducting transition temperature. It has to be mentioned that in the case of $Mg_{1-x}Al_xB_2$ a two-phase region was reported for $0.1 < x < 0.25$ [40].

3. Mechanism of superconductivity and electronic structure

Experimentally, the mechanism of superconductivity in MgB_2 was addressed in one of the first publications: rather large difference in T_c values, $\Delta T_c \approx 1$ K, was measured between $Mg^{10}B_2$ and

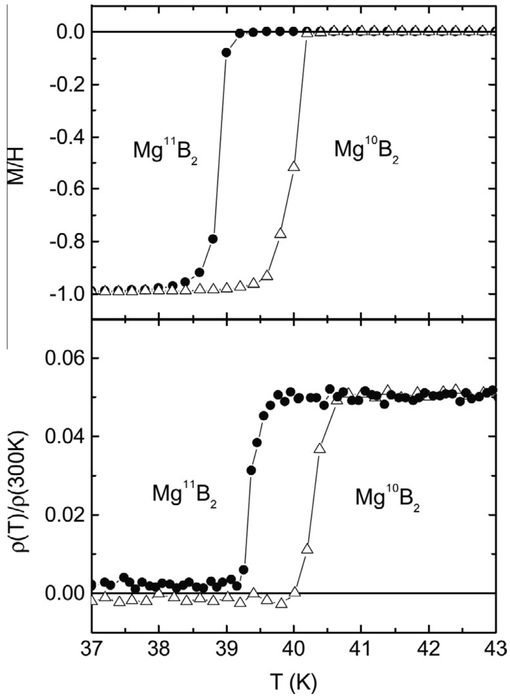

Fig. 2. Boron isotope effect as seen in magnetization (upper panel) and resistance (lower panel) (after Ref. [26]).