On the existence of solid solutions based on magnesium diboride

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Dense samples of pure magnesium boride and of the compositions $Mg_{(1-x)}A_xB_2$ (A = Na, K, Ca, Sr, Ba, Sn, Ti; 0.05 < x < 0.15) were prepared by sintering and using high temperature—high pressure treatment. The lattice parameters of most of the doped MgB₂ samples vary only slightly as compared to those of the pure MgB₂ irrespective of the sample preparation procedure, high temperature—high pressure treatment conditions, and the amount of dopant, thus indicating the absence of extended solid solution regions. The superconducting transition temperatures of all the samples did not exceed the value characteristic of MgB₂ (39±1 K). The results obtained for the dense MgB₂ samples using the Andreev reflection and tunneling spectroscopies confirm the two-gap nature of superconductivity in magnesium diboride and point to analogy between the superconductivity mechanisms in this compound and in cuprates.

Key words: magnesium, borides, alkali metals, solid solutions, doping, superconductivity.

The discovery¹ of superconductivity in magnesium diboride, MgB₂, a compound with simple composition and structure (hexagonal lattice; AlB₂ structure type), was as unexpected and unpredictable as the discovery of cuprate-based superconductors. Magnesium diboride has been known for more than six decades² and over forty years it has been used as a catalyst of the transformation of hexagonal boron nitride into its cubic modification.³ The superconducting transition temperature, T_c , of MgB₂ (39 K) lies at boundary between the highest T_c values for the classical Bardeen-Cooper-Schrieffer (BCS) superconductors⁴ and the lowest T_c values for copper-oxide ceramics.⁵ Magnesium diboride also possesses some properties typical of both the true BCS superconductors and cuprates. Taken altogether, these findings make the problem of determining the nature and mechanism of superconductivity in magnesium diboride topical.

For instance, studies^{6–12} of the effect of pressure on the superconducting transition temperature of MgB₂ revealed that the action of hydrostatic pressure on the sample always causes a decrease in T_c , which is typical of the BCS superconductors. Large boron isotope effect¹³ clearly indicates that the superconductivity in MgB₂ is due to phonon-mediated pairing of charge carriers.

At the same time the discovery of cuprate-like physical properties of this compound¹⁴ gives an impetus to search for methods of increasing T_c by modifying its structure and composition using experimental techniques developed for copper oxide based superconductors. Indeed, it was shown¹⁵⁻¹⁹ that, similarly to cuprates, the transition temperature of MgB₂ should be most sensitive to changes in both the electronic configuration of charge carriers and the crystal lattice parameters. In other words, the nature and number of chemical elements whose atoms replace the magnesium or boron atoms can strongly affect the $T_{\rm c}$ value. FLMTO (Full Linearized Muffin-Tin Orbital) calculations²⁰ revealed that Be impurity in the boron sublattice (as well as Li, Na, and Cu impurities in the Mg sublattice) and the formation of both types of lattice vacancies favor an increase in $T_{\rm c}$. At the same time, the effect of isovalent substitution of Be, Ca, Ba, and Sr for magnesium is still unclear, though an increase in the unit cell volume, which should occur in these cases (except for beryllium), also favors an increase in $T_{\rm c}$.

From the standpoint of crystal chemistry, the existence of hexagonal CaB₂, SrB₂, and BaB₂ (isovalent analogs of superconducting MgB₂) is thought to be impossible²¹ despite indirect data¹⁶ indicating that CaB₂ can be synthesized. However, analysis of the experimental data available thus far shows that replacement of magnesium atoms by those of other elements or doping responsible for the appearance of lattice defects either cause a decrease in T_c (Al, C, Fe, Co, Ni, Mn) or have virtually no effect on this parameter (Si, Zn and Li).²² Here, we will

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not dwell on consideration of such evident reasons for the decrease in T_c^{23-25} as the effect of impurities, low density of diboride samples, and nonstoichiometry of sample compositions. Two experimental studies^{26,27} on the doping of magnesium diboride with Zn atoms revealed a decrease in T_c upon doping, the reduction magnitude being not in proportion to the Zn concentration. The lattice parameters of the doped MgB₂ increase linearly with an increase in the doping level.

By and large, despite negative results of the experiments on replacement of magnesium atoms by other metal atoms we cannot say that the potentialities of the methods of heterovalent and isovalent substitution are exhausted. Probably, in doing so researchers are on the right track.

In this work we report on the synthesis, X-ray phase analysis, and electrophysical studies of dense magnesium diboride and mixed $Mg_{(1-x)}A_xB_2$ (A = Na, K, Ca, Sr, Ba, Sn, Ti; 0.05 < $x \le 0.15$) samples.

Results and Discussion

A widely used method for the preparation of MgB_2 at atmospheric pressure is based on the reaction between magnesium powder and amorphous or crystalline boron at temperatures above 920 K in closed tantalum or molybdenum tubes.^{28–31} Polycrystalline magnesium diboride samples thus obtained have a highly porous structure and are therefore unsuitable for performing well-reproducible physical and electrophysical experiments. Preparation of more dense samples by substantially increasing the sintering temperature is precluded by relatively low thermal stability of MgB₂.^{32–33} In this case it is more appropriate to apply high temperature—high pressure treatment;^{34–38} however, the process can be accompanied by formation of secondary phases, namely, MgB₆ and MgB₁₂, because the higher the temperature, the higher the formation probability of these phases.³²

In this work the procedure for preparation of highly ordered, pure, and dense samples of both stoichiometric and doped MgB_2 was divided into some stages. The necessary amounts of magnesium, boron, and a metal dopant were specified prior to sintering stage (stages), while compaction and additional homogenization of the samples were performed under conditions of high temperature—high pressure treatment of ceramics.

The sintering conditions, T_c values, and lattice parameters of the Mg_(1-x)A_xB₂ samples are listed in Table 1, while a number of X-ray diffraction patterns are presented in Fig. 1. As can be seen in Table 1, the lattice parameters of all the MgB₂ samples coincide, within the limits of experimental error, with the published data³⁹ irrespective of the sample preparation procedure. The lattice param



Fig. 1. X-Ray diffraction patterns of MgB_2 doped with Ca (*a*), Sr (*b*), and Ba (*a*). Shown are the MgB_2 (indicated "*hkl*"), CaB₆ (asterisked; sample No. 10), SrB₆ (symbolized "o"; sample No. 13), and BaB₆ lines (symbolized "#"; sample No. 16).

Run	Mixture composition	Sintering conditions			$T_{\rm c}/{\rm K}$	MgB ₂ lattice parameters	
		P/kbar	T/K	t/min		a	с
1	а					3.0864	3.5215
2	$Mg + B_2$		970	480	39	3.084 ^b	3.521 ^b
3	$Mg + B_2$		1020	60	39		
4	$Mg + B_2$		1320	120	40	3.085(1)	3.520(1)
5	MgB ₂	40	970	3	39	3.085	3.521
6	MgB ₂	40	1020	5	40.5	3.086	3.522
7	MgB ₂	40	1470	5	40	3.086	3.525
8	MgB ₂	80	1470	5	38.5	3.086	3.526
9	$Mg_{0.95} + Ca_{0.05} + B_2$		1270	180	40	3.088(2)	3.525(3)
10	$Mg_{0,9} + Ca_{0,1} + B_2$		1270	180		3.085	3.523
11	$Mg_{0.85} + Ca_{0.15} + B_2$		1270	180	40	3.088	3.524
12	$Mg_{0.95} + Sr_{0.05} + B_2$		1270	180	39	3.087(2)	3.523(2)
13	$Mg_{0.9} + Sr_{0.1} + B_2$		1270	180		3.085	3.523
14	$Mg_{0.85} + Sr_{0.15} + B_2$		1270	180	40	3.089	3.523
15	$Mg_{0.95} + Ba_{0.05} + B_2$		1270	180	39	3.085	3.522
16	$Mg_{0.9} + Ba_{0.1} + B_2$		1270	180		3.086	3.521
17	$Mg_{0.85} + Ba_{0.15} + B_2$		1270	180	40	3.088(2)	3.523(2)
18	$Mg_{0.95} + Ca_{0.05} + B_2$	40	1470	5	40	3.085	3.523
19	$Mg_{0.95} + Ca_{0.05} + B_2$	80	1470	5	39.5	3.088(3)	3.524(2)
20	$Mg_{0,9} + Ca_{0,1} + B_2$	40	1470	3	39	3.084	3.524
21	$Mg_{0.95} + Sr_{0.05} + B_2$	40	1470	5	40	3.083	3.521
22	$Mg_{0.9} + Sr_{0.1} + B_2$	40	1470	3		3.082	3.522
23	$Mg_{0.95} + Ba_{0.05} + B_2$	40	1470	5	39	3.084	3.521
24	$Mg_{0.9} + Ba_{0.1} + B_2$	40	1470	3		3.085	3.519
25	$Mg_{0.95} + Na_{0.05} + B_2$		1270	180	40	3.085	3.520
26	$Mg_{0.9} + Na_{0.1} + B_2$		1270	180	40	3.085	3.520
27	$Mg_{0.95} + Na_{0.05} + B_2$	40	1470	5	40	3.086	3.518
28	$Mg_{0.95} + Sn_{0.05} + B_2$	40	1470	3		3.085	3.522
29	$Mg_{0.95} + Sn_{0.05} + B_2$	80	1470	5		3.084	3.519
30	$Mg_{0.95} + Ti_{0.05} + B_2$		1270	210	40	3.084	3.519
31	$Mg_{0.9} + Ti_{0.1} + B_2$		1270	210		3.084	3.519

Table 1. Sintering conditions and properties of pure MgB_2 and doped magnesium diboride samples

^a JCPDS No. 38-1369.39

^b The lattice parameters were determined with an accuracy of $\pm (0.001 - 0.003)$ Å.

eters of most of the mixed samples prepared by sintering also vary only slightly and remain very close to those of the pure magnesium diboride. This indicates a low solubility of impurities under sintering conditions.

Figure 1 shows that replacement of Mg by isovalent Ca, Sr, and Ba or doping magnesium diboride with these elements result in two-phase mixtures. The major phase is MgB₂, while the secondary phases are apparently hexaborides CaB₆, SrB₆ or BaB₆ with face-centered cubic lattices (space group *Fm3m*). Data on the existence of BaB₂⁴⁰ and CaB₂¹⁶ were not confirmed. Analyses of the samples doped with other elements (Sn, Ti, Na) also revealed the presence of MgB₂ and some impurity phases.

Sequential increases in the temperature (>1470 K), pressure (>50 kbar), and duration (>5 min) of high temperature—high pressure treatment cause a progressing decomposition of magnesium diboride according to the reaction $3 \text{ MgB}_2 = 2 \text{ Mg} + \text{MgB}_6$ and a corresponding

increase in the reflection intensities of the hexaboride phases MB₆ (M = Ca, Sr, Ba, Mg) and magnesium metal in the X-ray diffraction patterns. The process is accompanied by gradual decrease in the T_c values of the samples and by broadening of the transition temperature interval. Because of this, all other boride ceramic samples were prepared by high temperature—high pressure treatment at temperatures at most 1470 K, a pressure of 40 kbar, and a treatment duration of at most 5 min.

Figures 2–4 present the magnetic susceptibility vs. temperature plots for a number of pure and doped magnesium boride samples prepared under different sintering conditions and high temperature—high pressure treatment regimes. The superconducting transition temperatures of all the samples did not exceed the value characteristic of MgB₂ (39±1 K), while a marked decrease in T_c was usually observed only for the heavily doped (>0.15 at.%) samples.



Fig. 2. Magnetic susceptibility *vs.* temperature plots for pure magnesium diboride prepared at a pressure of 0 (1), 40 (2), and 80 kbar (3) (sample Nos. 4, 6, and 8, respectively).



Fig. 3. Magnetic susceptibility *vs.* temperature plots for Ca-doped magnesium diboride prepared at a pressure of 0 (1), 40 (2), and 80 kbar (3) (sample Nos. 11, 18, and 19, respectively).



Fig. 4. Magnetic susceptibility *vs.* temperature plots for magnesium diboride doped with 0.05 at.% of Na (1), Ca (2), Sr (3), and Ba (4) after high temperature—high pressure treatment (40 kbar, 1470 °C) (sample Nos. 27, 18, 21, and 23, respectively).

High temperature-high pressure treatment of the samples at a pressure of 40 kbar and at temperatures below 970 K for at least 3 min causes narrowing of the transition temperature interval, which is consistent with the available data on the positive effect of the sample density on the electrophysical characteristics. These results were obtained for both the pure and calcium-doped diboride samples (see Figs. 2 and 3, respectively). At the same time, the electrophysical properties of the samples obtained after high temperature-high pressure treatment at 80 kbar approach those of the less dense samples prepared by sintering (see Figs. 2 and 3). Thus, the best results were obtained for the ceramic samples sintered at a pressure of 40 kbar. Substantial compaction of ceramics achieved by high temperature-high pressure treatment under optimum conditions and the addition of alkali-earth metals or sodium to the starting materials (nearly 0.05 at.%) stabilize magnesium diboride, thus making it more stable toward external conditions. Because of this, the transition to the superconducting state becomes much more sharp and narrow and the corresponding electrophysical characteristics of differently doped samples approach one another (see Fig. 4).

According to calculations,^{41,42} two weakly interacting superconducting condensates (σ -band and π -band) coexist in MgB₂ at temperatures below T_c . The relatively high T_c value (nearly 39 K) is due to quasi-two-dimensional σ -bands, the superconductivity in which arises from strong electron—phonon interaction. Calculations for the superconducting gap corresponding to these bands gave $\Delta_L \approx 7-8$ meV ($T \rightarrow 0$). For the three-dimensional charge carriers in the π -bands (weak superconductivity), the gap, Δ_S , is about 2 to 3 meV. Both gaps simultaneously vanish (close) at $T = T_c$ due to intrinsic proximity effect. These theoretical results were confirmed in our experiments.

Using the MgB₂ samples prepared at P = 40 kbar, T =1020 K, and t = 5 min. (run 6, see Table 1), we measured the current-vs.-voltage curves in the temperature range 4.2 K $\leq T \leq T_c$ for more than 150 point contacts obtained by break junction technique. The gap structures corresponding to both the large two-dimensional $\Delta_L~(\sigma\text{-band})$ and small three-dimensional Δ_{S} (π -band) superconducting gaps in the normalized conductance spectra of the MgB_2 junctions are shown in Fig. 5. The subharmonic gap structure in the conductance spectrum of the Andreev junction (Fig. 6, curve 2) exhibits a number of dips whose positions coincide with those of the features of the point contact obtained using the same sample by mechanically adjusting the junction (Fig. 6, curve 1'). Our variabletemperature study of the behavior of both superconducting gaps showed that the large gap, Δ_L , decreases obeying a BCS type dependence as the temperature increases. However, the $2\Delta_{\rm I}/kT_{\rm c}$ ratio is as high as nearly 5 to 6, being typical of superconducting cuprates and much higher than the BCS theoretical value (3.5). We found that the



Fig. 5. Conductance spectra of S-I-S-I-... tunnel junctions in MgB₂ at 4.2 K normalized to point contact: five-junction stack (1), five-junction stack (2), two-junction stack (3), and single junction (4). All spectra exhibit two-gap structures with $\Delta_L = 8 \text{ meV}$ and $\Delta_S = 1.7 \text{ meV}$ (sample No. 6).

characteristic values of the large superconducting gap, Δ_L , lie between 7 and 11 meV, which is apparently determined by the method employed to obtain point contacts at helium temperatures (this prevents the surface from poisoning with oxygen and other substances). The smaller Δ_L gaps correlate with the lower T_c values; therefore, the $2\Delta_L/kT_c$ ratio remains nearly constant for different gaps. Measurements for the small gap, Δ_S , gave 1 to 3 meV at T = 4.2 K. At $T > T_c/2$, the temperature dependence $\Delta_S(T)$ is typical of induced superconductivity.

The characteristic voltages, $V_c = I_c R_n$, of the Josephson junctions studied in this work lie between 3.0 and 6.0 meV, which is in good agreement with the predictions made using the two-gap model.⁴³

The results obtained confirmed correctness of the assumption of two-gap superconductivity in MgB₂.⁴⁴ In carrying out this work we have repeatedly observed the spectra of S-I-S-I-... (internal Josephson effect, see curve *1* in Fig. 5) and S-n-S-n-... junctions (effect of intrinsic multiple Andreev reflections, see curve *2* in Fig. 5). The lastmentioned phenomenon is due to the layered structure of MgB₂ and, along with the value of the $2\Delta_I/kT_c$ ratio



Fig. 6. Current-*vs.*-voltage curve (1) and conductance spectrum (1') of a S-I-S-I... tunnel junction and the conductance spectrum of the Andreev S-n-S-n junction (2). Positions of the dips in the subharmonic gap structure in the conductance spectrum of the Andreev junction (2) coincide with positions of the features of the point contact (1') obtained using the same sample by mechanically adjusting the junction. $\Delta_{\rm L} = 8\pm0.5$ meV and $\Delta_{\rm S} = 1.9$ meV, T = 4.2 K.

 $(2\Delta_{\rm L}/kT_{\rm c} \approx 5-6)$, points to analogy between the nature of superconductivity in this compound and in cuprates.

Experimental

Starting materials were sintered from elemental Mg and B and dopants (when necessary). Magnesium flakes or powder (both of 99.8% purity) were used. Amorphous boron of reagent purity (99.7% purity) was pre-heated in dynamic vacuum at 600-650 K over a period of 1 to 1.5 h. A tube (8 mm in diameter and 80 mm long) made of "12X18H10T" stainless steel was filled with the reaction mixture in a dry box under nitrogen, welded at both ends, and sintered at T = 1170 - 1200 K and P = 1 atm. for periods between 3 and 6 h. In the second stage (in some cases this stage was omitted) the tube was opened in the dry box, the samples were ground in an agate mortar, the powders were pressed in pellets at some excess pressure, and then sintered again under the first-stage conditions. The third stage involved a high temperature-high pressure treatment of the samples at P = 3 - 8 GPa and T = 1070 - 1870 K in high-pressure chambers of the recessed anvils type. For comparison, a number of samples were obtained from elemental magnesium and boron by high

temperature—high pressure treatment under conditions of the third stage of the multistage process. The results obtained for these samples were the same as those reported for the samples prepared using the first method.

In all stages the number of phases and the phase compositions were monitored by X-ray phase analysis (XRD) (URD-6 instrument and a Guinier chamber) (CuK α radiation, with Si as internal reference). According to quantitative XRD data, the MgO content in the finished samples was at most 0.5% by mass. Magnesium oxide was detected only in the samples synthesized using magnesium flakes as the starting material.

The superconducting properties were studied by dynamic magnetic susceptibility (in rel. u.) measurements (inductance measurements) in an alternating magnetic field (1 Oe, 27 Hz) in the temperature range from 15 to 290 K. An original setup using an APD Cryogenics closed-cycle cryostat was designed at the Inorganic Chemistry Chair, Department of Chemistry, M. V. Lomonosov Moscow State University.

Tunnel junctions for investigating the current-vs.-voltage curves of MgB₂ polycrystals were produced by cracking the samples at helium temperatures. The junctions were measured using the Josephson, tunneling, and Andreev reflection spectroscopies. The break junctions were driven into different measurement regimes by mechanically adjusting the point contacts at liquid helium temperatures. This allowed obtaining both the S-I-S (superconductor—insulator—superconductor) and S-n-S (superconductor—normal metal—superconductor) junctions using the same sample and permitted comparison of the results obtained by different methods. The experimental data were found to be self-consistent and well reproducible.

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