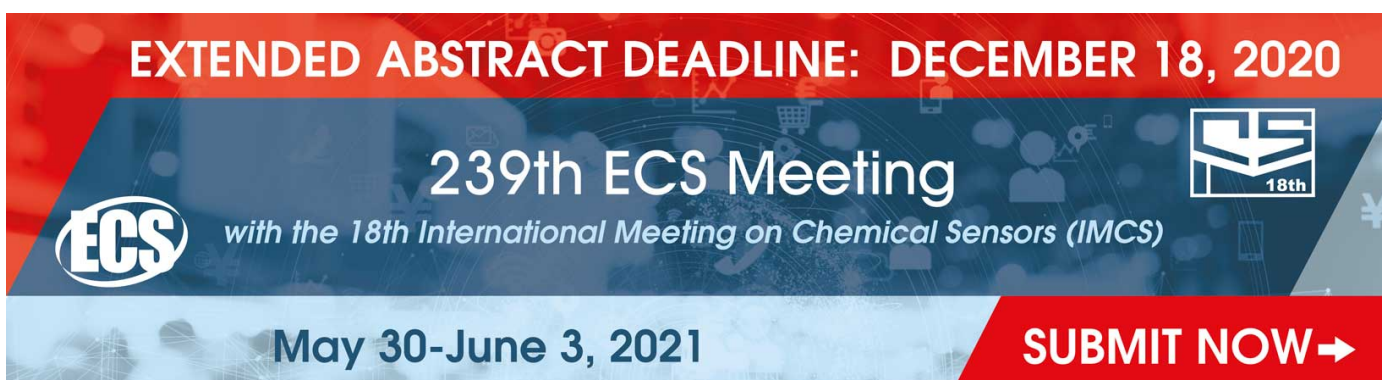


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# Structure and properties of MgB<sub>2</sub> bulks: *ab-initio* simulations compared to experiment

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**Abstract.** Analysis of XRD patterns by Rietveld refinement has been shown that the main phase of superconducting MgB<sub>2</sub>-based bulk materials (with high level of superconducting characteristics) has AlB<sub>2</sub> type structure and near MgB<sub>1.8-1.68</sub>O<sub>0.2-0.32</sub> stoichiometry. The materials demonstrated the critical current densities up to 0.9 – 0.4 MA/cm<sup>2</sup>  $j_c$  (at 0 - 1 T, 20 K); up to 15 T  $B_{c2}$  (at 22.5 K) and  $B_{irr}$  (at 18 K). The *ab-initio* simulation confirmed (1) benefits in binding energy and enthalpy of formation if stoichiometry of the solid solution is near MgB<sub>1.75</sub>O<sub>0.25</sub>; (2) energetic advantage in case if impurity oxygen present only in each second boron plane of MgB<sub>2</sub> cell while the first boron plane of the same cell stays pristine and location of substituted oxygen atoms in the nearby positions. Besides, the results of *ab-initio* modeling allow explanation of the tendency towards segregation of O-impurity in MgB<sub>2</sub> structure during synthesis or sintering, and formation of Mg-B-O inclusions or nanolayers (with MgO type of structure) which effect pinning. Calculated transition temperatures,  $T_c$ , for MgB<sub>1.75</sub>O<sub>0.25</sub> occurred to be 23.3 K, while for MgB<sub>2</sub> it was 21.13 K only. Experimental  $T_c$  of the bulk materials was 35.7-38.2 K.

## 1. Introduction

MgB<sub>2</sub> is oxygen-free superconducting compound with hexagonal AlB<sub>2</sub> type of crystallographic lattice. It contains close packed Mg layers and graphene like B layers alternate along the c axis of the hexagonal unit cell. MgB<sub>2</sub> shows a complex bonding structure consisting of ionic interlayer bonding and covalent/metallic mixed in-plane bonding. Existence of two energy gaps was shown for MgB<sub>2</sub> [1, 2]. The XRD study demonstrates that the MgB<sub>2</sub>-based materials usually contain MgB<sub>2</sub> phase and some



admixture MgO phase even if special atmosphere is used during preparation for avoiding oxidation, see for, example [3, 4], what can be explained by high affinity of Mg towards oxygen. Besides, the presence of other admixture phases such as  $\text{MgB}_4$  (orthorhombic),  $\text{MgH}_2$  and BN, etc. can be observed on XRD patterns [5]. But in  $\text{MgB}_2$ -based materials structures can be as well present dispersed inclusions of higher magnesium borides,  $\text{MgB}_x$ , with  $x > 4$  (as SEM and Auger study witnessed), which cannot be revealed by XRD on the background of  $\text{MgB}_2$  reflexes. The unit cells of higher borides such as  $\text{MgB}_7$  (orthorhombic),  $\text{MgB}_{12}$  (orthorhombic),  $\text{MgB}_{12}$  (trigonal),  $\text{MgB}_{17}$  (trigonal),  $\text{MgB}_{20}$  (trigonal) and  $\text{Mg}_2\text{B}_{25}$  (trigonal) are rather complicated, containing many atoms. The large number of atoms in their unit cells and low symmetries of the cells are resulting in many 'reflecting planes' which essentially reduce the intensities of the XRD reflections, as compared to those of the  $\text{MgB}_2$  (i.e. from a simple hexagonal unit cell). Because of this the dispersed inclusions of the higher magnesium borides can be practically 'invisible' for a traditional XRD analysis [6].

The study of  $\text{MgB}_2$ -based materials structures (bulk, wires, and thin films) by scanning electron microscopy (with quantitative X-ray microprobe analysis) and Auger spectroscopy (with quantitative analysis) showed us presence of oxygen in superconducting materials matrices (in a small amount) and presence of oxygen-enriched dispersed separate inclusions or nanolayers in the matrices. So, no pure MgO (without presence of boron) and no pure  $\text{MgB}_2$  (without presence of oxygen) were experimentally revealed. The SEM and Auger study was performed using a JAMP-9500F which combined SEM SEI, BEI, X-ray and Auger analyzers and allow investigating of non-oxidized surfaces because the construction of the microscope gives possibility to perform etching of  $1 \times 1 \text{ mm}^2$  square surfaces by Ar ions directly in the exploratory chamber and even build depth profiles of distribution of present elements. In contrary to X-ray microprobe analysis which allows to estimate quantity of elements in the volume of material which is not smaller than  $1\text{-}3 \text{ }\mu\text{m}$  in diameter, emanated Auger electrons are collecting from a very small volume ( $10 \text{ nm}$  in diameter and about two lattice parameters in depth) and thus nanoobjects can be properly analysed quantitatively by Auger spectroscopy. Besides, Auger spectroscopy is very sensitive toward light elements and simultaneous presence of B, C, O and N is not the obstacle for correct investigations.

The results of Auger spectroscopy and SEM study [6] of  $\text{MgB}_2$ -based materials with high superconducting performances: highly dense bulks [5-8], wires [9, 10] and thin films [8], would benefit from *ab-initio* modelling of boron atoms substitutions by oxygen atoms to calculate transition superconducting temperature of energetically the most preferable solid solution  $\text{MgB}_{2-x}\text{O}_x$ . The present paper is generalising results of the *ab-initio* modelling. The obtained data can be a basis for interpreting the unusual electronic properties of  $\text{MgB}_2$ -based materials and the development of nano-engineering of these materials with record values of superconducting characteristics.

## 2. Experimental

The microstructure of the materials was characterized by a JAMP-9500F. XRD patterns were obtained by X-ray powder diffraction analyses and Rietveld refinement (using "PHILIPS X'pert" and Dron-3). The critical current densities,  $j_c$ , of the bulks and thin films were estimated from data obtained by an Oxford Instruments 3001 vibrating sample magnetometer (VSM) using the Bean model [11]. Certain inconsistencies which may arise between different measurement techniques [12, 13] do not influence the result and discussion presented in this work. The values of transition temperature,  $T_c$ , the upper critical magnetic field,  $B_{c2}$ , and the irreversibility field,  $B_{irr}$ , were estimated from resistivity measurements (90% and 10% of the resistivity just above the beginning of the transition) using the four probe technique in fields from 0 to 15 T. Transition temperature,  $T_c$ , was experimentally estimated by SQUID magnetometer as well.

The list and characteristics of the materials under the discussion synthesized by the authors are shown in Table 1. The numbers assigned to the samples are used through the paper.

In order to obtain an approximate picture for the electronic structure of  $\text{MgB}_{2-x}\text{O}_x$  compounds we have carried out the *ab-initio* calculations for corresponding  $2 \times 2 \times 2$  and  $2 \times 2 \times 1$  supercells of the initial  $\text{MgB}_2$  unit cell to model various oxygen concentrations of the solid solution. The calculations were

**Table 1.** List and characteristics of film, wires and bulk materials.

No	Material	Initial materials	Preparation*	$T_c$ , K
1	Wire	B (without C) and Mg – Specialty Materials Inc. (SMI)	One filament, 0.83 mm in diameter, Nb surrounding and monel outer sheath	37.5
2	Wire	B (with C) and Mg (SMI)	Magnetron sputtering, 140 nm film thickness	31.6
3	Film	hot pressed MgB <sub>2</sub> target		33.5 ( <i>  ab</i> ) 32.6 ( <i>  c</i> )
4	Bulk	Mg:2B (SMI)	2 GPa, 600 °C, in BN, HP	35.7
5	Bulk	Mg(chips):2B (0.66 wt. % O)	2 GPa, 1050 °C, in BN, HP	-
6	Bulk	Mg(chips):2B (0.66 wt. % O)+10% SiC	2 GPa, 1050 °C, in BN, HP	-
7	Bulk	Mg(chips):2B (1.4 wt. % O)	2 GPa, 900 °C, in BN, HP	38.2
8	Bulk	Mg(chips):2B (1.4 wt. % O)	50 MPa, 1050 °C, in C, SPS	37.5
9	Bulk	Mg(chips):2B (1.4 wt. % O)	30 MPa, 900 °C, in BN, HotP	37.1
10	Bulk	Mg(chips):2B (1.4 wt. % O)	0.1 MPa, 800 °C, in Ar flow	38.1

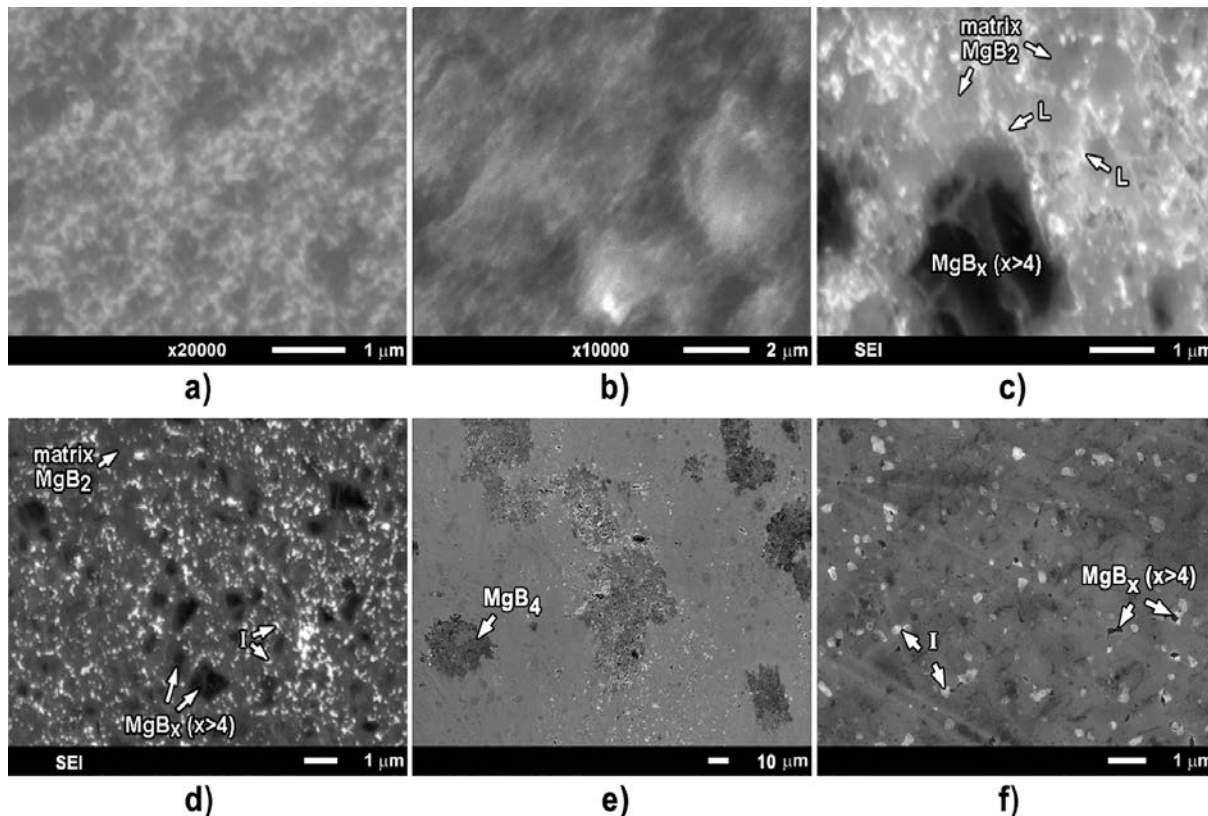
\* HP- high pressure-high temperature conditions; HotP- hot pressed; SPS-spark plasma sintering.

based on the density-functional theory (DFT) and performed by employing the full potential linearized augmented plane waves (FP-LAPW) methods implemented in WIEN2k [14] and Elk [15] implementations) and the full-potential linear muffin-tin orbital (FP-LMTO) implemented in RSPt [16, 17]).

The exchange-correlation potential was taken into account in the local density approximation (LDA) [18] and the generalized gradient approximation (GGA) [19] of DFT. For the used full potential FP-LAPW and FP-LMTO methods any restrictions were not imposed on charge densities or potentials of studied systems that is especially important for anisotropic layered structures. The constructed supercells were based upon the experimental lattice parameters of the hexagonal MgB<sub>2</sub> cell,  $a_0=b_0=0.3086$  nm;  $c_0=0.3524$  nm. For the unit cell  $1\times 1\times 1$ , supercells  $2\times 2\times 1$  and  $2\times 2\times 2$  the lattice parameters  $a$  and  $c$  are considered equal to  $a_0$  and  $c_0$ ,  $2a_0$ , and  $c_0$ ,  $2a_0$  and  $2c_0$ , respectively. In order to determine stable optimized positions of atoms and the related binding energies  $E_b$  in the MgB<sub>2-x</sub>O<sub>x</sub> supercells, we applied the FP-LAPW method [14] within DFT-GGA approximation. The phonon calculations were performed within the Elk code (DFPT) for the optimized structure of MgB<sub>1.75</sub>O<sub>0.25</sub> and the calculations of the superconducting critical temperature were conducted within Eliashberg theory using the formula [20] with the LDA [18] approach. In order to introduce oxygen in the initial MgB<sub>2</sub>, the symmetry was reduced and the supercell  $2\times 2\times 1$  along the *ab*-plane was constructed. The scheme of MgB<sub>2</sub>- $2\times 2\times 2$  supercell and the detailed descriptions of binding energy calculations as well as electronic structure variation of MgB<sub>2</sub> doped with oxygen are given in [21].

### 3. Results and discussions

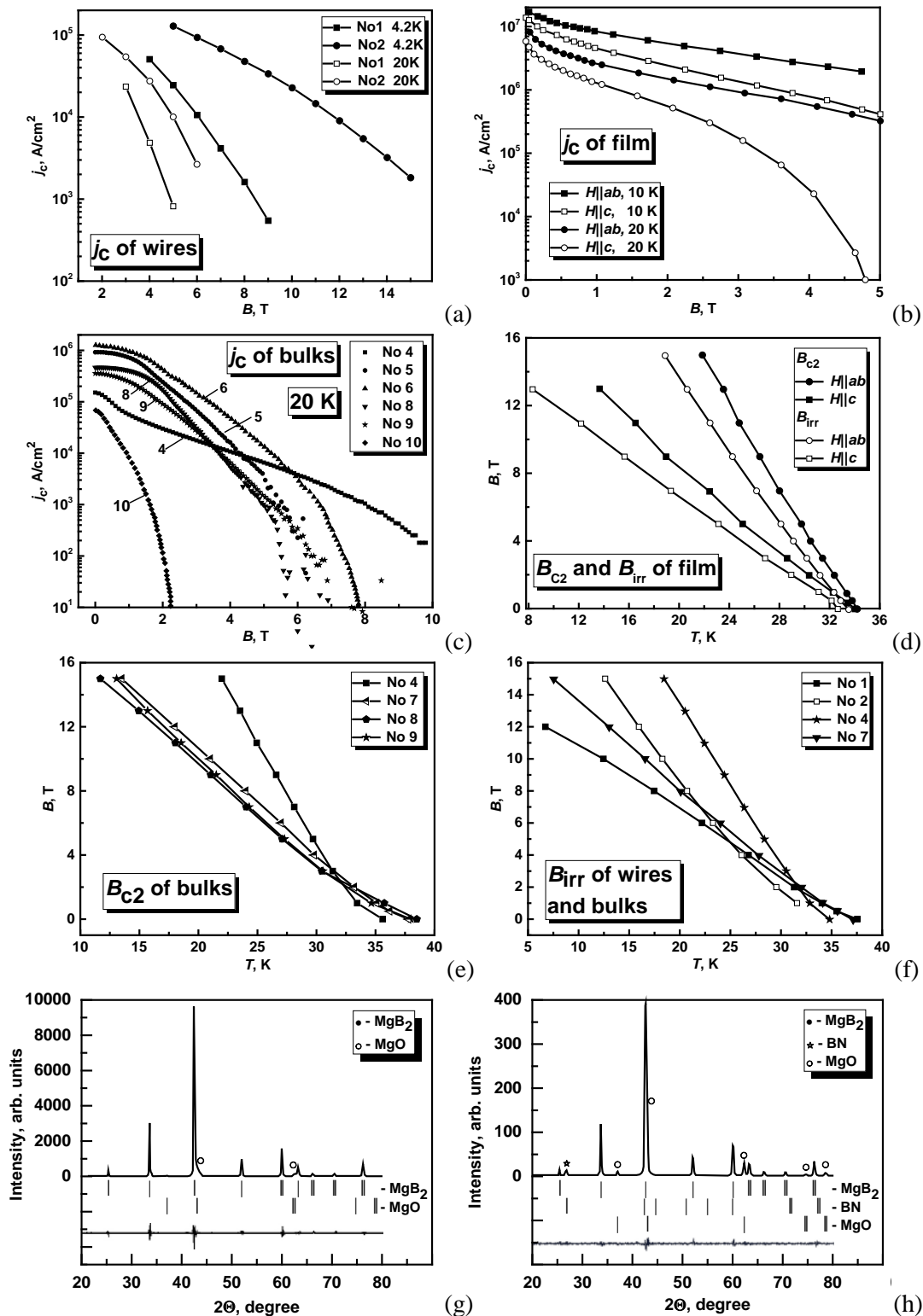
Figure 1 shows the typical microstructures (after etching of their surfaces by Ar ions in the chamber of research microscope) of MgB<sub>2</sub> thin film (figure 1a, No 3 in table 1) wire (figure 1b, No. 1, manufactured by HyperTech from Mg and B without C addition,) and bulks synthesized from Mg:2B (amorphous) mixtures (figures 1c-f): in Ar flow at 800 °C (figure 1c, No10); at 1050 °C and quasihydrostatic 2 GPa pressure (figure 1d, No 5); at 1050 °C under 50 MPa pressure by spark plasma sintering (figure 1e, f, No 8). The differences in colors correlate with variation in concentration of magnesium, boron and admixture oxygen. The big darken gray areas in figure 1e connected with presence of MgB<sub>4</sub> phase (the pressure 50 MPa was not enough to suppress fully Mg evaporation during synthesis at 1050 °C). The materials superconducting characteristics ( $j_c$ ,  $B_{c2}$  and  $B_{in}$ ,  $T_c$ ) and XRD are presented in figure 2. The variation of stoichiometry on nanolevel has been observed (as difference in colors and microprobe quantitative analysis are shown) and the boundaries between areas with different concentration of elements (figure 1) can be responsible for pinning and high critical current density in MgB<sub>2</sub>-based materials (figure 2). The data for the best samples synthesized under



**Figure 1.** Typical microstructures of  $\text{MgB}_2$  film No3 (a), wire No1 (b), and bulks: No 10 (c), No5 (d), No8 (e, f); numbering is according Table 1. All the materials contain B, Mg, admixture O and some small amount of admixture C; the brighter colors at the images correspond to lower concentration of boron and higher concentration of oxygen. By “I” and “L” the O- enriched inclusions and nanolayers, respectively, are marked.

each conditions (high pressure, HP, hot pressure, HotP, spark plasma sintering, SPS, or in Ar flow) are presented here.

Table 2 presents the results of Rietveld refinement of two samples: (1) prepared in protective from oxygenation atmosphere “with purified B” demonstrating  $T_c = 38.9$  K [3] (figure 2g) and (2) synthesized under high pressure, No5 (table 1, figures. 2c, h). The temperature dependences of  $B_{c2}$  and  $B_{irr}$  for the material prepared “with purified B” are given in [3] (at 20 K its  $B_{c2} = 8.8$  T and  $B_{irr} = 7$  T). The results of Rietveld refinement (table 2) show  $\text{MgB}_{1.8}\text{O}_{0.2}$  and  $\text{MgB}_{1.74}\text{O}_{0.26}$  stoichiometries for the main phases present in the analyzed materials. The analysis of ten XRD patterns of  $\text{MgB}_2$  materials with high superconducting performances showed  $\text{MgB}_{1.8-1.68}\text{O}_{0.2-0.32}$  stoichiometries of their main phases. The XRD analysis of the diffraction pattern (figure 2h, table 2) showed the presence of 3 phases: the main phase  $\text{MgB}_2$  and two impurity phases – BN and MgO. The Rietveld refinement revealed the presence of 5.6% on BN, 4.8% of MgO and the rest – 89.6% of  $\text{MgB}_2$ . In the case of the fully ordered  $\text{MgB}_2$  phase with Mg solely occupying  $1a$  (0 0 0) site and B occupying  $2d$  ( $1/3$   $2/3$   $1/2$ ) site the residuals between the calculated and experimental powder patterns were  $R_1 = 2.96\%$ ,  $R_p = 9.77\%$ , and  $R_{wp} = 14.0\%$ . All attempts to refine the isotropic displacement parameters ( $B_{iso}$ ) led to systematically high values for Mg atoms and very low (even negative) for B atoms. For this reason, two other models of the crystal structure were tested. The second model was refined with vacancies in the crystallographic site of Mg atoms. This led to somewhat lower residual  $R_1 = 2.20\%$  with 93.6% occupancy of the  $1a$  site by Mg atoms. The third model was based on the statistical mixture of B and O atoms in  $2d$  crystallographic site. The refinement of the third model revealed the lowest residual among three tested models:  $R_1 = 1.92\%$  and the  $2d$  site occupied by 87% of B atoms and 13% of O



**Figure 2.** (a)-(c) - Dependences of critical current density,  $j_c$ , vs. magnetic field,  $B$ , for: wires (a), thin film (b) and bulks (c); (d) – temperature dependences  $B_{c2}$  and  $B_{irr}$  of thin film (Fig. 2a) at 10 and 20 K in two directions: parallel to the substrate surface ( $H||ab$ ) and perpendicular ( $H||c$ ); (e), (f) – temperature dependences of  $B_{c2}$  and  $B_{irr}$  of bulk and wires; (g), (h) – XRD patterns of MgB<sub>2</sub> bulks made in clean from oxygen conditions (the details are given in [1]) and of No5 (table 1).

**Table 2.** Results of Rietveld refinement.

Sample	MgB <sub>2</sub> (figure 2g), Ref.[3]	MgB <sub>2</sub> (Table 1 No 5, figure 2h)
Space group, structure type	<i>P6/mmm</i> , AlB <sub>2</sub>	
<i>a</i> , <i>c</i> (nm)	0.30848(1), 0.35235(1)	0.30849(4), 0.35227(6)
Mg in 1 <i>a</i>	0, 0, 0	
<i>B</i> <sub>iso</sub> (10 <sup>2</sup> nm <sup>2</sup> )	0.36(5)	0.4(2)
B/O in 2 <i>d</i>	1/3, 2/3, 1/2	
<i>B</i> <sub>iso</sub> (10 <sup>2</sup> nm <sup>2</sup> )	1.11(7)	1.4
Occupancy B/O	1.80(2)/0.20(2)	1.74(2)/0.26(2)
<i>R</i> <sub>1</sub> (%)	1.27	1.92
<i>R</i> <sub>p</sub> (%)	7.60	9.65
<i>R</i> <sub>wp</sub> (%)	11.4	13.9
Additional phases	MgO (1.9%)	BN (5.6 %), MgO (4.8 %)

giving the formula MgB<sub>1.74</sub>O<sub>0.26</sub>. All three models were tested with DFT calculations to compare their heats of formation, and the third model appeared to be the most energetically favorable. The analysis of XRD powder pattern of another bulk sample (figure 2g) showed that the sample contained only 1.9% of MgO impurity phase and the rest was MgB<sub>2</sub>. Rietveld refinement was performed using the fully ordered model of MgB<sub>2</sub> and the model with B and O mixture in 2*d* site. The fully ordered model produced *R*<sub>1</sub>=6.30%, while the model with B and O mixture – *R*<sub>1</sub> = 1.27%. The refined oxygen and boron content in 2*d* site appeared to be very close to the first sample: 90% of B and 10% of O, which led to the formula MgB<sub>1.80</sub>O<sub>0.20</sub>.

For the DFT calculations we used the 2x2x2 supercell to model for the whole extent of dopant content (from 6 to 50 at% of substituting oxygen atoms). By means of FP-LAPW GGA calculations we optimized positions of atoms in the supercell from energetic point of view by method of step-by-step variation of the coordinates of all atoms. The criterion of optimization was taken as 0.001 Ry for energy variations. The results of the binding energies (*E*<sub>b</sub>) calculations for oxygen substitutions were reported in Ref. [21] (see table 4). The analysis of the data has shown that the binding energy for almost all calculated MgB<sub>2-x</sub>O<sub>x</sub> supercells is higher than that of pristine MgB<sub>2</sub>. If we impose restriction to consider the high symmetric cells only, the monotonous increase of binding energy can be noticed, and for MgB<sub>1.5</sub>O<sub>0.5</sub> it reaches *E*<sub>b</sub>=-1.05984 Ry which is about 0.064 Ry higher than that of MgB<sub>2</sub>.

The most energetically beneficial ordering was found to occur for the nearest (paired) oxygen atoms in the (001) type plains. The analysis of these data has shown that in the case of substitution of boron positions for oxygen the binding energy is essentially affected by the superlattice symmetry, the type of ordering of oxygen atoms and the amount of substituting oxygen atoms. In the case of 2×2×2 supercells, boron planes with and without substituting oxygen atoms alternate sequentially. The binding energy can decrease down to *E*<sub>b</sub>=-1.13246 Ry or to *E*<sub>b</sub>=-1.15268 Ry, i.e. below than that for MgB<sub>2</sub>, and the substituting oxygen atoms located in the nearest positions form zigzag chains [21]. Thus the most preferable for the considered supercells is configuration when in the each boron plane (with partly oxygen substitution) the substituting oxygen atoms form zigzag chains and when the each subsequent boron plane contains only boron atoms at near pristine positions. As the calculations have shown [21], in the cases of the most preferable (from the energetic point of view) location of oxygen, when its amount is low, the shift of boron and magnesium atoms from the pristine positions (as compared with the case of ideal MgB<sub>2</sub> without substitutions) was not higher than 0.15 Å. It should be mentioned that results of high resolution TEM studies [22] indicate that oxygen atoms can be present regularly in every second boron plane of MgB<sub>2</sub>. Thus in the practically undisturbed boron planes (from the point of view of binding energy and electron density distribution) there is still a possibility of high *T*<sub>c</sub> superconductivity. Despite the fact that in the case of MgB<sub>1</sub>O<sub>1</sub> chemical composition the formation of zigzag oxygen chains leads to even lower binding energy, *E*<sub>b</sub>=-1.15712 Ry, and the amount of oxygen is so high that zigzag chains can be formed in each boron plane, such distribution in our

opinion will be destructive for superconductivity, because each boron plane would be essentially distorted and the large deviations of Mg and B atoms from their pristine positions would take place. We suppose that such distribution of oxygen (zigzag chains in each boron plane) can be prevailed in the observed Mg-B-O nanolayers “L” or nano-inclusions “I” (figure 1c, d, f). This allows us to explain the tendency towards segregation of impurity O in MgB<sub>2</sub> structure during synthesis or sintering, and formation of Mg-B-O inclusions or nanolayers (with MgO type of structure), which effect pinning. So, seems the synthesis in the Mg-B-O system allows the realization of several phases with AlB<sub>2</sub> type crystal structure. Several (at least two) superconducting phases can be formed during crystallization with the structure of the same material due to the difference in melting temperatures of phases with different O content and the existing tendency for oxygen segregation. This makes it reasonable to perform analysis of such characteristic of MgB<sub>2</sub> as the two-band nature of the superconducting gap [1, 2] and 1.5 superconductivity (disorder of the vortex lattice) [23] in a new way.

In the case of MgB<sub>2-x</sub>O<sub>x</sub> the lowest density of electronic states (DOS) about 0.46 states/eV/f.u. was found for MgB<sub>1.75</sub>O<sub>0.25</sub> if the oxygen atoms are in neighboring positions [8]. If the concentration of oxygen is higher than in MgB<sub>1.5</sub>O<sub>0.5</sub> the MgB<sub>2</sub> structure is destroyed. *Ab-initio* modelling of enthalpy of formation of boron substitution by oxygen in MgB<sub>2</sub> as well shows that this is energetically favourable up to the composition MgB<sub>1.75</sub>O<sub>0.25</sub>. Enthalpy of MgB<sub>2</sub> formation is  $\Delta H_f = -150.6$  meV/atom and that of MgB<sub>1.75</sub>O<sub>0.25</sub> is  $\Delta H_f = -191.4$  meV/atom. The formation of vacancies at the Mg site of both MgB<sub>2</sub> and substituted MgB<sub>1.75</sub>O<sub>0.25</sub> was modelled as well, but has shown that such processes are energetically disadvantageous ( $\Delta H_f$  of Mg<sub>0.875</sub>B<sub>2</sub> and Mg<sub>0.75</sub>B<sub>1.75</sub>O<sub>0.25</sub> are equal to -45.5 and -93.5 meV/atom, respectively) [24].

For MgB<sub>2</sub> and MgB<sub>1.75</sub>O<sub>0.25</sub> the calculations of the superconductive critical temperature ( $T_c$ ) were performed within the framework of Density Functional Perturbation Theory (DFPT). First the calculations were performed on a low k-point mesh (8×8×8) to get the phonon dynamical matrices. After that the calculations of the McMillan-Allen-Dynes critical temperature  $T_c$  were performed on a high k-point mesh (16×16×16). Interesting, that the obtained  $T_c$  for the MgB<sub>2</sub> is 21.13 K, while for the MgB<sub>1.75</sub>O<sub>0.25</sub> it is just a couple of degrees higher 23.3 K. It should be noted that it was hard to achieve the convergence of the phonon calculations for MgB<sub>1.75</sub>O<sub>0.25</sub>, which appeared to be unstable for the constructed supercells.

#### 4. Conclusions

The experimental study and *ab-initio* modeling witnessed about the existence of superconductivity in *P6/mmm*, AlB<sub>2</sub> structural type MgB<sub>1.75</sub>O<sub>0.25</sub>. The level of superconducting characteristics ( $T_c$ ,  $j_c$  in 0-10 T fields,  $B_{irr}$  and  $B_{c2}$ ) of the materials with stoichiometry of the main phase MgB<sub>1.8-1.68</sub>O<sub>0.2-0.32</sub> is the highest reported in literature. DFT calculations showed that B for O substitution in MgB<sub>2</sub> is energetically favorable up to MgB<sub>1.75</sub>O<sub>0.25</sub>. Other variants of substitutions and vacancy formations lead to less stable structure, which is in agreement with the results of Rietveld refinement. The calculated critical temperature  $T_c$  for MgB<sub>1.75</sub>O<sub>0.25</sub> (23.3 K) is just a couple of degrees higher than for pure MgB<sub>2</sub> (21.13 K). The observed experimental  $T_c$  of the bulk MgB<sub>2</sub>-based materials was 35.7-38.2 K. The advantages from location of substituted oxygen atoms in the nearby positions in the same boron plane allow explanation of the tendency towards segregation of impurity O in MgB<sub>2</sub> structure and formation of oxygen enriched areas which can affect pinning and critical current density increase.

#### 5. References

- [1] Bouquet F, Fisher R A, Phillips N E, Hinks D G and Jorgensen D 2001 *Phys. Rev. Lett.* **87** 047001
- [2] Szabó P, Samuely P, Kačmarčík J, Klein T, Marcus J, Fruchart D, Miraglia S, Marcenat C and Jansen A G M 2001 *Physical review letters* **87**(13) 137005
- [3] Jiang J, Senkowicz B J, Larbalestier D C and Hellstrom E E 2006 *Supercond. Sci. Technol. Rapid communication* **19**, L33
- [4] Zhou S, Zhang Y, Pan A V, Dou S X, Chung K C, Kim Y K and Yoo J M 2009 *Supercond. Sci.*



- Technol.* **22**, 045018
- [5] Prikhna T 2016 Structure and properties of bulk MgB<sub>2</sub> *Superconducting Wires: Basics and Applications* ed. R Fluekiger (World Scientific Series in Applications of Superconductivity and Related Phenomena 668 p) chapter 3a pp. 131-157
- [6] Prikhna T A, Eisterer M, Weber H W, Gawalek W, Kovylaev V V, Karpets M V, Basyuk T V and Moshchil V E 2014 *Supercond. Sci. Technol.* **27**(4) 044013–044017
- [7] Prikhna T A, Gawalek W, Savchuk Ya M, Sergienko N V, Moshchil V E, Wendt M, Habisreuther T, Dub S N, Melnikov V S, Kozyrev A V, Schmidt Ch, Dellith J, Litzkendorf D, Nagorny P A, Dittrich U, Sverdun V B, Kovalev L K, Penkin V T, Goldacker W, Rozenberg O A and Noudem J 2008 *Journal of Physics: Conference Series* **97**, 012022
- [8] Prikhna T A, Romaka V V, Shapovalov A, Eisterer M, Sokolovsky V L, Weber H W, Grechnev G E, Boutko V G, Gusev A A, Kozyrev A V, Goldacker W, Podhurska V, Sverdun V.B, Habisreuther T, Schmidt Ch, Kovylaev V V, Shaternik V E, Karpets M V and Shaternik A V 2017 *IEEE Transactions on Applied Superconductivity* **27**, Issue: 4, 6200705 doi: 10.1109/TASC.2016.2638201
- [9] Prikhna T, Eisterer M, Rindfleisch M, Ponomaryov S S, Tomsic M, Romaka V V, Moshchil V, Kozyrev A, Karpets M and Shaternik A 2019 *Journal of Superconductivity and Novel Magnetism* **31**(4) doi.org/10.1007/s10948-019-5062-z
- [10] Prikhna T A, Eisterer M, Rindfleisch M, Kozyrev A V, Shaternik A V, Shaternik V E, Tomsic M, Moshchil V E, Karpets M V, Sverdun V B, Ponomaryov S S, Romaka V V and Seidel P P 2019 *IEEE Transactions on Applied Superconductivity* **29**(5) 1-5. doi: 10.1109/TASC.2019.2907662
- [11] Bean C B 1964 *Rev. Mod. Phys.* **36** 31-36
- [12] Pan A V, Golovchanskiy I A and Fedoseev S A, *Europhys. 2013 Lett.* **103**, 17006
- [13] Golovchanskiy I A, Pan A V, Shcherbakova O V, and Fedoseev S A *J. 2013 Appl. Phys.* **114**, 163910
- [14] <http://www.wien2k.at/>
- [15] <http://elk.sourceforge.net/>
- [16] Wills J M, Alouani M, Andersson P, Delin A, Eriksson O and Grechnev A 2010 Full-Potential Electronic Structure Method” *Energy and Force Calculations with Density Functional and Dynamical Mean Field Theory, Springer Series in Solid-State Sciences, Springer Verlag, Berlin* **167**
- [17] <http://fplmto-rspt.org/>
- [18] Barth von U and Hedin L 1972 *J. Phys. C* **5** 1629
- [19] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77**(18) 3865-3568
- [20] Allen P B and Dynes R C 1975 *Phys. Rev. B.* **12**(5) 905 -922
- [21] Prikhna T A, Shapovalov A P, Grechnev G E, Boutko V G, Gusev A A, Kozyrev A V, Belogolovskiy M A, Moshchil V E, Sverdun V B 2016 *Low Temperature Physics* **42** 380-394 doi: 10.1063/1.4952985
- [22] Klie R F, Idrobo J C, Browning N D, Regan K A, Rogado N S, and Cava R 2001 *J Appl. Phys. Lett.* **79**, 1837
- [23] Moshchalkov V, Menghini M, Nishio T., Chen Q H, Silhanek A V, Dao V H, Chibotaru L F, Zhigadlo N D and Karpinski J 2009 *Phys. Rev. Lett.* **102**, 117001
- [24] Prikhna T, Romaka V, Eisterer M, Shapovalov A, Kozyrev A, Grechnev G, Boutko V, Goldacker W, Habisreuther T, Vakaliuk O, Halbedel B 2017 *IOP Conf. Series: Materials Science and Engineering* 012023. doi:10.1088/1757-899

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