The Electronic and Superconducting Properties of Oxygen-Ordered MgB$_2$ compounds of the form Mg$_2$B$_3$O$_x$

Juan C. Idrobo  
Department of Physics, University of California-Davis,  
Davis, One Shields Ave, Davis CA, 95616, USA.

Serdar Öğüt  
Department of Physics, University of Illinois at Chicago,  
845 West Taylor Street (M/C 273), Chicago, IL 60607

Taner Yıldırım  
NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 USA

Robert F. Klie  
Brookhaven National Laboratory, Upton, New York 11973

Nigel D. Browning  
Dept. of Chemical Engineering and Material Science,  
University of California-Davis, One Shields Ave, Davis CA, 95616, USA and  
National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA  
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Possible candidates for the Mg$_2$B$_3$O$_x$ nanostructures observed in bulk of polycrystalline MgB$_2$ have been studied using a combination of Z-contrast imaging, electron energy loss spectroscopy (EELS) and first-principles calculations. The electronic structures, phonon modes, and electron phonon coupling parameters are calculated for two oxygen-ordered MgB$_2$ compounds of composition Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$, and compared with those of MgB$_2$. We find that the density of states for both Mg$_2$B$_3$O$_x$ structures show very good agreement with EELS, indicating that they are excellent candidates to explain the observed coherent oxygen precipitates. Incorporation of oxygen reduces the transition temperature and gives calculated $T_C$ values of 18.3 K and 1.6 K for Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$, respectively.

The discovery of superconductivity in MgB$_2$ with a transition temperature of 40 K has attracted the attention of the scientific community for two main reasons: the technological applications of this material and the new insights that such a simple structure could bring to superconductivity theory. Efforts to improve the superconductivity properties of MgB$_2$ have included doping with elements such as Y, Zr, C, Al, Cu and Ag, but the results varied for different groups. A simple explanation for this behavior is that the transport properties of MgB$_2$ have a strong dependence on the sample preparation conditions, which makes it hard to obtain unambiguous results even for undoped samples. In fact, there have been reports from different groups showing that MgB$_2$ samples are not a single phase material, but rather a rich collection of different phases including MgB$_2$, MgO, B$_y$O$_x$, Mg$_2$B$_y$, Mg$_x$B$_3$O$_y$. Oxygen, unlike some other elements, is present in MgB$_2$ as an unintentional impurity due to its high reactivity with MgB$_2$. Typically, oxygen rich precipitates form in the bulk of MgB$_2$ where they contribute to the overall transport properties through flux pinning. Moreover, oxygen can segregate at grain boundaries of MgB$_2$ where, unlike the high-$T_C$ materials, it contributes significantly to flux pinning, increasing the overall $J_C$ as the grain size decreases. MgB$_2$ has already been used in making wires, tapes, and Josephson junctions, and in order to improve the properties of such devices, the effect that oxygen has on the properties of MgB$_2$ needs to be well understood. Surprisingly, the importance of oxygen in the development of MgB$_2$ devices has been overlooked, and detailed first-principles studies of oxygen ordering and segregation have not yet been performed.

It was previously reported that oxygen impurities can increase the upper critical fields and critical current but lower $T_C$. Liao et al. found that through a slow cooling process, the oxygen in bulk MgB$_2$ can segregate to form nanometer-sized coherent Mg(B,O) in the MgB$_2$ matrix acting as effective flux pinning centers without decreasing $T_C$. Klie et al. previously reported oxygen precipitates in bulk MgB$_2$, where oxygen was incorporated every second boron plane of the MgB$_2$ structure, found by atomic resolution electron energy loss spectroscopy (EELS) studies using a scanning transmission electron microscope. Figure 1 shows an atomic resolution Z-contrast image of one of these oxygen precipitates taken from bulk MgB$_2$ along the [100] orientation. The increase of contrast every second column in Fig. 1 is due to the presence of oxygen. The size of these precipitates was reported to be about 20-100 nm.
Motivated by these experimental observations, in this work we discuss the effects of oxygen-ordering, with different stoichiometries, on the electronic structure and superconductivity properties of MgB$_2$ via first-principles calculations. As possible candidates for the atomic structures of coherent oxygen precipitates in bulk MgB$_2$, we propose two different structures of composition, Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$. We find that incorporation of oxygen in the form of Mg$_2$B$_3$O$_x$ structures decreases the DOS at the Fermi energy and the electron phonon coupling compared with MgB$_2$. From total energy calculations we find that Mg$_2$B$_3$O is less stable compared to Mg$_2$B$_3$O$_2$ but has a higher $T_c$. It is important to notice that our calculations show that oxygen impurities are likely to be present everywhere in MgB$_2$ structures. Therefore, controlling the density and type of these impurities will finally be the limiting factor in improving the transport properties of MgB$_2$.

Our atomic and electronic structure calculations were performed using the ab initio pseudopotential plane wave method [18] within the generalized gradient approximation (GGA) [19], and local density approximation (LDA) for comparison. In order to compare the changes due to oxygen in MgB$_2$, we doubled the unit cell of MgB$_2$ in the c-direction. Brillouin-zone integrations were carried out with $15 \times 15 \times 6$ Monkhorst-Pack grids for Mg$_2$B$_4$ and Mg$_2$B$_3$O$_x$. An energy cutoff of 400 eV was used for all the calculations. The lattice volumes, shapes, and all atoms were allowed to relax for the new structures using a force criterion of $10^{-2}$ eV/Å. The zone-center phonons and electron phonon couplings were calculated using density functional perturbation theory [20].

The relaxed geometries for structures with partial substitution of boron atoms with one and two oxygen atoms, Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$, as well as Mg$_2$B$_4$, are shown in Fig. 2. Other oxygen concentrations were tried as well (i.e. Mg$_2$B$_3$O$_3$, where one additional oxygen was inserted in the boron plane), but these resulted in a significant distortion of the MgB$_2$-like symmetry and did not reproduce features observed in the coherent oxygen precipitates. We found that the incorporation of oxygen changes the well-defined B-B planes by the formation of BO$_x$ units in the Mg$_2$B$_3$O$_x$ structures. Both Mg$_2$B$_3$O$_x$ structures belong to the space group P3m1 ($C_{3v}^3$, No. 156). The relevant structural parameters for the three structures considered are shown in Table I. Introduction of oxygen considerably increases the distance between neighboring Mg planes, but decreases the distance between the other Mg planes, which are above and below the boron layer left intact. As a result, the lattice stretches in the c-direction compared to Mg$_2$B$_4$. Such behavior was reported by Eom et al. where thin films rich in oxygen showed a higher c lattice parameter suggesting that boron can be substituted by oxygen [10]. The calculated ratios of the distances between the Mg-BO$_x$--Mg and Mg-BB-Mg layers are 1.22 and 1.49 for the theoretical Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$ structures, respectively, while the estimate from the experimental image is 1.14 ± 0.05. The overestimated theoretical values for the ratios compared with the experimental can be explained in two different ways: (i) pressure effects from the surrounding bulk into the precipitate, which shrinks the lattice parameter in the c-direction, and (ii) the concentration of oxygen in the BO$_x$ planes is slightly lower than the ones calculated here, where $x < 1$.

We also investigated the phase stability of the Mg$_2$B$_3$O$_x$ compounds relative to atomic constituents and bulk MgB$_2$. Both Mg$_2$B$_3$O$_x$ structures are stable against phase separation into their atomic constituents. However, the magnitudes of the binding energies per atom for Mg$_2$B$_3$O are found to be 0.16 eV and 0.63 eV smaller compared to that of MgB$_2$ calculated using atomic oxy-
TABLE I: Summary of properties for MgB$_2$, Mg$_2$B$_4$, Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$ crystal structures. The Mg$_2$B$_3$O$_x$ structures belong to the space group P3$_1$ (C$_{6h}$, No. 156). Lattice parameters are in Å, $N(E_F)$ in states/eV, frequencies ($\omega$) in meV. The parenthesis next to the frequencies indicates degeneracy of those modes. $T_C$ is given in K. The lattice parameters are shown for GGA (LDA) approximations. The phonon modes, electron phonon coupling, and the critical temperatures were all calculated using the values from the GGA calculations.

| MgB$_2$ | Mg$_2$B$_4$ | Mg$_2$B$_3$O | Mg$_2$B$_3$O$_2$ |
|--------|-------------|--------------|-----------------|
| a=3.086$^a$ | a=3.046(3.086) | a=3.067(3.016) | a=3.143(3.016) |
| c=3.524$^a$ | c=7.054(7.048) | c=7.701(7.545) | c=8.633(8.231) |
| $N(E_F)$=0.69$^b$ | $N(E_F)$=1.35(1.38) | $N(E_F)$=0.85(0.87) | $N(E_F)$=1.05(1.99) |

| $\omega_p/\omega_\lambda$ | $\lambda_p/\lambda_\lambda$ | $\omega_p/\omega_\lambda$ | $\lambda_p/\lambda_\lambda$ |
|--------------------------|--------------------------|--------------------------|--------------------------|
| 87.1(1)B$_{15g}$ | - | 26.3(2) | 0.027 |
| 74.5(2)E$_{2g}$ | 907 | 27.0(2) | 0.029 |
| 49.8(1)A$_{2u}$ | - | 39.0(1) | 0.010 |
| 40.7(1)E$_{1u}$ | - | 39.7(2) | 0.010 |
| 49.3(1)A$_{2u}$ | 0.51 | 53.0(1) | 0.005 |
| 68.0(2) | 0.46 | 72.1(2) | 0.506 |
| 79.2(1) | 0.03 | 90.4(1) | 0.002 |
| 86.3(1)B$_{15g}$ | 0 | 161.8(1) | 0.088 |
| $\omega_{log} = 74.5$ | $\omega_{log} = 64.5$ | $\omega_{log} = 65.6$ | $\omega_{log} = 48.9$ |
| $T_C = 39.4$ | $T_C = 40.73$ | $T_C = 18.31$ | $T_C = 1.62$ |

$a$Taken from Ref. [2]  
$b$Values for $N(E_F)$, $\omega$, $\lambda$, and $T_C$ (with $\mu^* = 0.15$) are taken from Ref. [20]

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Figure 3 shows the calculated unoccupied boron DOS for the theoretical Mg$_2$B$_3$O$_x$ nanostructures compared with the experimental boron K-edge spectra taken from the B-B plane (darker columns in Fig. 1) and BO$_x$ plane (brighter columns in Fig. 1) respectively. Each experimental spectrum is the sum of seven individual spectra with an acquisition time of 1 sec. and an energy resolution of 1.2 eV. The spectra have been summed up to increase the signal to noise ratio, and background subtracted and corrected for multiple-scattering contributions [1]. To obtain a better comparison between theory and molecular oxygen, respectively. On the other hand, the magnitudes of the binding energies per atom for Mg$_2$B$_3$O$_2$ are 0.11 eV higher, and 0.71 eV lower compared to that of MgB$_2$ calculated using atomic oxygen, and molecular oxygen, respectively. These calculations suggest that (i) the theoretical Mg$_2$B$_3$O$_x$ structures are not stable against phase separation into MgB$_2$ and molecular oxygen, and (ii) Mg$_2$B$_3$O$_2$ is stable with respect to phase separation into MgB$_2$ and atomic oxygen. This does not, however, mean that these structures have to be ruled out as possible candidates for coherent oxygen precipitates, since they can still exist as metastable phases in bulk MgB$_2$.

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![Graph](image-url)
and experiment, we have calculated the boron \( p_{xy} \) and \( p_z \) states. We then took into account the scattering momentum transfer dependence of the electron microscope optical conditions and crystal orientation to weigh the boron \( p_{xy} \) and \( p_z \) states according to the experimental setup \[21\]. Analysis of the spectra for energies in the range of 15-20 eV above the Fermi level was not performed, since multiple scattering and lifetime broadening limit the resolution of the spectra, which makes comparison between experiment and theory uncertain in that regime \[21\]. The theoretical spectra was obtained in the \( Z \) approximation, which has worked well for bulk MgB\(_2\) \[21\], have been convoluted for an energy resolution of 1.2 eV and 0.4 eV (shown for comparison purposes only).

Figure 3(a) shows the experimental and theoretical spectra for the B-B plane, where both structures, Mg\(_2\)B\(_3\)O and Mg\(_2\)B\(_3\)O\(_2\) (energy resolution of 1.2 eV), have good agreement with experiment. The pre-peak of the boron K-edge at 189 eV in the experiment is well reproduced in both theoretical structures. A peak at 192 eV, which is present in both theoretical spectra, is not resolved in the experimental spectra. This is possibly due to the low signal to noise ratio of the experimental spectra. Figure 3(b) shows the spectra for the BO\(_x\) plane, where the enhancement of the peak at 195 eV, which was previously attributed to oxygen \[11\] \[22\], is very well predicted by both theoretical structures. This peak has a lower intensity for the B-B plane spectra (Fig. 3(a)). Finally, the pre-peak in the BO\(_x\) plane experimental spectra shows an enhancement in intensity compared with the B-B plane experimental spectra. Here, both theoretical spectra present a remarkable agreement with the experiment, especially the Mg\(_2\)B\(_3\)O structure where the difference in intensity of the pre-peak between the B-B plane and the BO\(_x\) plane spectra is more pronounced. Additionally, monochromated spectra (energy resolution of 0.3 eV) from bulk MgB\(_2\) and a region containing oxygen are shown in Fig. 3(a) and Fig. 3(b), respectively. Notice that the pre-peak is completely resolved for Fig. 3(a) and Fig. 3(b). Furthermore, the monochromated spectrum (Fig. 3(b)) presents an enhancement due to oxygen of the peak at 195 eV.

To investigate the effect of oxygen incorporation by partial boron substitution on the superconducting properties of MgB\(_2\), we first calculated the phonon modes and electron phonon coupling parameters for Mg\(_2\)B\(_3\), Mg\(_2\)B\(_3\)O, and Mg\(_2\)B\(_3\)O\(_2\). The results are shown in Table \[\]\[\]. In order to obtain the transition temperatures \( T_C \) of the theoretical Mg\(_2\)B\(_3\)O\(_2\) nanostructures we used the McMillian expression \[22\]

\[
T_C = \frac{\omega_{\text{log}}}{1.2} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\mu^*\lambda)} \right),
\]

where \(\omega_{\text{log}}\) is the logarithmic average frequency, \(\lambda\) is the total electron phonon coupling defined as \(\lambda = \sum_{p \in \Gamma} \lambda_p\), with \(\lambda_p\) being the electron phonon coupling for each mode at \(\Gamma\), and \(\mu^*\) represents the Coulomb repulsion interaction. We used the value of \(\mu^* = 0.19\). In the case of MgB\(_2\), the Eliashberg function has a sharp peak around the \(E_{2g}\) mode \[24\]; therefore, it is sufficient to take the \(E_{2g}\) mode energy as \(\omega_{\text{log}}\) to obtain the transition temperature \(T_C\) \[22\] \[24\]. In fact, using only this mode, not only \(T_C\) but also the isotope effect and pressure dependence of \(T_C\) can be successfully explained \[27\]. However, for the Mg\(_2\)B\(_3\)O nanostructures, the \(E_{2g}\) mode is no longer well defined and \(\omega_{\text{log}}\) has to be averaged throughout all the phonon modes. We approximated \(\omega_{\text{log}}\) as

\[
\omega_{\text{log}} \approx \exp \left( \frac{1}{n} \sum_{p \in \Gamma} \log(\omega_p) \lambda_p \right),
\]

and only calculated the phonons at the zone center \(\Gamma\). We obtained transition temperatures \(T_C\) of 40.73 K, 18.31 K, and 1.62 K for Mg\(_2\)B\(_4\), Mg\(_2\)B\(_3\)O, and Mg\(_2\)B\(_3\)O\(_2\), respectively.

In conclusion, we have proposed two different structures, Mg\(_2\)B\(_3\)O and Mg\(_2\)B\(_3\)O\(_2\) as possible candidates for the Mg\(_2\)B\(_3\)O\(_2\) nanostructures observed experimentally in bulk MgB\(_2\) \[1\]. Both structures present an increase of the lattice parameter with respect to Mg\(_2\)B\(_4\), where the Mg\(_2\)B\(_3\)O structure is closer to the experimental value. The experimental spectra for the B-B plane and BO\(_x\) plane are well explained by the Mg\(_2\)B\(_3\)O and Mg\(_2\)B\(_3\)O\(_2\) structures. Both structures are good candidates for coherent oxygen precipitates, although their superconductivity properties differ. Mg\(_2\)B\(_3\)O\(_2\) precipitates would behave as a pinning center for temperatures higher than 2 K, while Mg\(_2\)B\(_3\)O precipitates would start to behave as a pinning center for temperatures higher than 18 K. Our results show that oxygen impurities are likely to be present everywhere in MgB\(_2\), highlighting the importance of oxygen as an agent in the creation of flux pinning centers and as a factor of improvement upon the critical current density \(J_c\).

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* Electronic address: jidrobo@lbl.gov

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