A first-principles study of MgB$_2$ (0001) surfaces

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We report self-consistent ab initio calculations of structural and electronic properties for the B- and Mg-terminated MgB$_2$ (0001) surfaces. We employ ultra-soft pseudopotentials and plane wave basis sets within the generalized gradient approximation. The surface relaxations are found to be small for both B- and Mg-terminated surfaces. For the B-terminated surface, both B $\sigma$ and $\pi$ surface bands appear, while only one B $\pi$ surface band exists near the Fermi level for the Mg-terminated surface. The superconductivity of the MgB$_2$ surfaces is discussed. The work function is predicted to be 5.95 eV for the B- and Mg-terminated surfaces respectively. The simulated scanning tunneling microscopy images of the surfaces are not sensitive to the sign and value of the bias voltages, but depend strongly on the tip-sample distance. An image reversal is predicted for the Mg-terminated surface.

The surprising discovery of superconductivity at 39K in MgB$_2$ has attracted great scientific interest. The isotope effect experiments indicate that MgB$_2$ may be a BCS phonon-mediated superconductor, with $T_c$ above the commonly accepted limits for phonon-assisted superconductivity. Band structure calculations show that the Mg donates substantially its 3s electrons to the B layer, and that the Fermi surface is derived mainly from B orbitals with two-dimensional character. The superconductivity is believed to be due to the strong coupling of the holes of the B $\sigma$ bands to the in-plane B phonon lattice vibrations (E$_{2g}$ modes).

Being a simple, low-cost and high-performance binary intermetallic compound, MgB$_2$ is a very promising candidate for superconducting device as well as large-scale applications. Experimentally, scanning tunneling spectroscopy measurements of the surface of superconducting MgB$_2$ have been reported, and the high-quality c-axis-oriented epitaxial MgB$_2$ thin films have been grown successfully on Al$_2$O$_3$ substrates by using a pulsed laser deposition technique. However, there has not been a theoretical study for the MgB$_2$ surfaces so far. In this Letter, we report a first-principles study of MgB$_2$ (0001) surfaces. Both B- and Mg-terminated surfaces are investigated. We show that while the relaxations of the surface layers are small for both surfaces, their electronic structures are quite different.

Our calculations were carried out within the generalized gradient approximation (GGA) using ultrasoft pseudopotentials and plane wave basis sets. A $1 \times 1 \times 1$ supercell geometry was used to model the surfaces in which there are 15 atomic layers and 15 layers of vacuum (hereafter, 15-layer slab model). The plane wave cutoff is 257.2 eV for structural optimizations and 321.5 eV for static electronic structure calculations. Brillouin zone integrations were performed on a grid of $13 \times 13 \times 1$ Monkhorst-Pack special points. During the structural optimizations, we fixed the central 3 atomic layers of Mg atoms and boron honeycomb layers. Our bulk calculations give the lattice constants of $a = 3.067\AA$, $c = 3.515\AA$, which are in good agreement with experimental and other theoretical results. We used this bulk geometry as the initial geometry for the surface optimizations. Table 1 lists the results for the surface relaxations, given in terms of the change $\Delta_{ij}$ of the interlayer distance in percent of the distance in the bulk. From this table, one can see the relaxations for both the B- and Mg-terminated surfaces are rather small (less than 4%). The relaxation affects up to five atomic layers for the B-terminated surface, while it mainly localizes on the first two layers for the Mg-terminated surface. For the B- and Mg-terminated surfaces, an inward relaxation of the top layer by -2.1% and -3.7% and an outward relaxation of the second layer by 2.0% and 1.2% are observed. The energy gains due to the relaxation are 2.31 and 2.38 eV for the B- and Mg-terminated surfaces respectively.

The surface electronic structure of the B- and Mg-terminated MgB$_2$ (0001) surfaces at the optimized geometries is shown in Fig.1 together with the projected band structure (PBS) of the bulk MgB$_2$. From Fig. 1, we can see that for the B-terminated surface, there is only one surface band along each of the bulk bands. The dispersion of these surface bands is very similar to that of the bulk bands, and they can be sorted into the bonding $\sigma$ (sp$_x$sp$_y$) and nonbonding $\pi$ (p$_z$) bands of the surface B atoms accordingly. For the Mg-terminated surface, however, there is only one surface band outside the PBS. This

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band mainly results from the $p_z$ orbitals of B atoms in the second surface layer. The above results can be understood by plotting the charge density distribution. The charge density contour maps for the x-z plane and x-y plane at B layers are shown in Fig. 2. In good agreement with other calculations for the bulk, we found that electrons are transferred from Mg orbitals to B orbitals, but they are not well localized at the B sites, instead they are distributed over the whole crystal. The MgB$_2$ is essentially metallic boron held together by covalent B-B and ionic B-Mg bonding. At the B-terminated surface, both in-plane ($sp_zp_z$) and out-plane ($p_z$) electrons of the surface layer are slightly redistributed due to lack of one nearest neighbor (NN) Mg layer. This kind of electronic redistribution results in the appearance of the $\pi$ surface bands. The total DOS at the Fermi level are exist, but for Mg-terminated surface there is only a $p_\pi$ surface band.

Figure 3 shows the total densities of states (DOS) and layer resolved projected DOS for the B- and Mg-terminated MgB$_2$ surfaces together with those for the bulk. While the total DOS curves are quite similar overall, there are differences in the layer resolved project DOS. The surface-specific features in DOS disappear slowly for the B-terminated surface, while they vanish rapidly for the Mg-terminated surface. For the Mg-terminated surface, those features are mainly localized in the (Mg, B) surface layers. The DOS of the first (Mg, B) sub-surface layers are already virtually identical with those of the bulk. Even in the second (B, Mg) sub-surface layers for the B-terminated surface, however, we still can see those features. The total DOS at the Fermi level ($N(0)$) is calculated to be 0.42 and 0.37 states/(eV×B atom) for the B- and Mg-terminated surfaces respectively. Both are larger than the $N(0)$ of the bulk (0.36 states/(eV×B atom)).

To discuss qualitatively the superconductivity of the MgB$_2$ surfaces, we calculated the layer resolved zone-center $E_{2g}$ (in-plane displacements of borons) phonon frequencies. They are 596 cm$^{-1}$ and 479 cm$^{-1}$ for the first surface B layer of the B- and Mg-terminated surfaces respectively. These values are bigger than that of the bulk-like B layer (476 cm$^{-1}$). From our $N(0)$ and $E_{2g}$ results, we expect that the superconductivity of the MgB$_2$ surfaces is somewhat strengthened. This conclusion is contrary to the conjecture of a weakened surface layer. The conjecture was resulted from that the measured superconducting energy gap is less than the weak-coupling BCS value of 5.9 meV for the bulk $T_c$ of 39 K. However, we notice that the measurement might be done on chemically modified surfaces, not on the ideal surfaces.

We also calculated the work function of the MgB$_2$ surfaces in terms of the difference between the self consistent potential in the vacuum and the fermi level. As listed in Table 1, the B-terminated surface gives a work function of 5.95 eV, while the Mg-terminated surface is 4.25 eV. This result indicates that the electrons on the B-terminated surface are more stable than Mg-terminated surface.

The scanning tunneling microscopy (STM) is a widely used tool in surface research. Here we simulated the STM images for the MgB$_2$ surfaces using the Tersoff and Hamann theory [13]. By assuming an asymptotically spherical tip and taking the limit of small applied bias voltage, the tunneling current was reduced to the local density of states (LDOS) of the surface at the point probed by the tip:

$$I(x, y) \propto \rho(x, y) = \sum_i |\Phi_i(x, y)|^2 \delta(E_i - E_F)$$ (1)

We found while the simulated images are not sensitive to the sign and value of the bias voltages, they depend on strongly the distance between the tip and sample. Fig. 4 shows some simulated images with different tip-sample distances at +0.5 V. From these figures, one can see that at the Mg-terminated surface, the STM images show a "bright-dark" transition. At a short distance, the bright area of the image is corresponding to Mg sites in the surface layer. At a long distance, the bright area is changed to the B sites of the second surface layer. This reversal contrast of the STM images at different tip heights can be understood by Eq.(1). In Eq.(1), the tunneling current is determined by the space and energy windows simultaneously. At the Mg-terminated surface, the energy contributions to the tunneling current mainly come from the B layer while the surface Mg layer gives the most space contributions when the tip is close to the surface.

In summary, we have studied the structural and electronic properties of the B- and Mg-terminated MgB$_2$ (0001) surfaces. The surface relaxations are found to be small. The surface bands are all along the bulk bands. For B-terminated surface, both $p_\sigma$ and $p_\pi$ surface bands are exist, but for Mg-terminated there is only a $p_\pi$ surface band. Compared with the bulk, both the two surfaces are found to increase the total DOS at the Fermi level. The superconductivity of the MgB$_2$ surfaces is found to be somewhat strengthened. The work function is predicted to be 5.95 and 4.25 eV for the B- and Mg-terminated surfaces respectively. The simulated STM images are found to be sensitive to the tip-sample distances. For the Mg-terminated surface we even observed an image reversal for different tip-sample distances.

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FIG. 1. Surface band structure of (a) the B-terminated surface and (b) the Mg-terminated surface. The projected band structure of the bulk MgB$_2$ is shown by shadow areas.

FIG. 2. Charge density contour maps: (a) the x-z plane map of the B-terminated surface, (b) the x-z plane map of the Mg-terminated surface, and (c) the x-y plane maps at the first surface B layers of the B- and Mg-terminated surfaces and at the B layer of the bulk respectively. The contours are in the unit of electrons/Å$^3$.

FIG. 3. Densities of states (DOS) for the surfaces and bulk. (a1)-(a3) are the total DOS of the B-terminated surface, Mg-terminated surface, and bulk. In (a3), we also plot the projected DOS for the B and Mg atomic layers in the bulk. (b1)-(b3) are the layer resolved projected DOS of the first, second and third (B, Mg) layers from the top surface of the B-terminated surface respectively. (b4)-(b6) are the counterparts for the Mg-terminated surface. The bulk DOS was calculated on a 19×19×19 Monkhorst-Pack k-point grid, while the DOS of slab models was obtained on a 19×19×2 k-point grid.

FIG. 4. Simulated STM images of MgB$_2$ (0001) surfaces at +0.5eV: (a) B-terminated surface with the tip-sample distance (d) of 5 Å, (b) B-terminated surface with d=3Å, (c) Mg-terminated surface with d=5Å, and (d) Mg-terminated surface with d=3Å.

|        | $\Delta_{12}$ | $\Delta_{23}$ | $\Delta_{34}$ | $\Delta_{45}$ | $\Delta_{56}$ | $\Phi$ |
|--------|---------------|---------------|---------------|---------------|---------------|-------|
| B-terminated | -2.1%         | 2.0%          | 0.9%          | -1.8%         | 0             | 5.95  |
| Mg-terminated| -3.7%         | 1.2%          | 0.2%          | 0.5%          | -0.3%         | 4.25  |

TABLE I. Relaxation of MgB$_2$ (0001) surfaces (change $\Delta_{i,j}$ of the interlayer distances in percent of the distance in the bulk) and work function ($\Phi$) in eV.
Figure 1 of Li et al.
Figure 3 of Li et al.
Figure 4 of Li et al.