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Density-functional-theory calculations of electronic band structure of single-crystal and single-layer WS_2

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Electronic band structures of single-crystal and single-layer WS_2 are investigated by first-principles calculations based on local-density-functional theory using a plane-wave basis with ultrasoft pseudopotentials. The band structure calculated for the single crystal corresponds very well with experimental data and recent calculations using an augmented-spherical wave basis [A. Klein *et al.*, Phys. Rev. B **64**, 205416 (2001)]. The calculations for the single layer show that compared to the bulk case no significant structural relaxations of the atomic positions occur. This result is confirmed by the good agreement of our calculated band structures for the single layer with the data from angle-resolved photoemission measurements.

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I. INTRODUCTION

The electronic structure of semiconducting layered chalcogenides has been studied for decades both theoretically and experimentally because of their interesting quasi-two-dimensional crystallographic structure (see, e.g., Refs. 1–7 and references therein). Strong covalent chemical bonds are present inside the layers while the interactions between the layers are very weak and usually called van der Waals-like. There is strong dispersion of the energy bands parallel to the layers. Despite the weak interlayer interactions there is also a significant dispersion perpendicular to the layers. The interlayer interactions across the so-called van der Waals gap are particularly important for interface formation. Since single crystals are available for many layered materials, they are ideal model systems to study the electronic interactions at this class of interfaces. These interactions not only control the electronic characteristics, but may also affect the growth properties.[8]

Recently, it was shown that thin films of layered metal chalcogenides deposited onto graphite substrates by van der Waals epitaxy[8] are electronically nearly decoupled from the substrate as a result of different electronic structures and lattice constants.[7–10] The electronic structure of such films is therefore similar to that of free-standing films. Because of the absence of interlayer interactions, single-layer films can be clearly distinguished spectroscopically.[9] The possibility for their preparation offers an ideal opportunity to study the details of van der Waals interlayer interactions. The remaining influence of the substrate, however, needs to be worked out, which can be done, e.g., by a comparison of the experimental results with electronic structure calculations.

In the previous work angle-resolved ultraviolet photoelectron spectroscopy data of single-crystal and single-layer WS_2 have been described and compared to band-structure calculations based on scalar relativistic density-functional theory using an augmented spherical wave-basis set (ASW).[7] A good agreement between experiment and theory was observed for the single crystal. The experimentally determined band structures for the single layer, however, showed significant deviations from the theoretical results. Since the ASW calculation assumed the same atomic position for bulk and single layers, it was finally suggested that atomic relaxations within the single layer might be the reason for this mismatch between experiment and theory.[7]

In the present work we have revisited the problem in order to answer the question of whether structural relaxations of atomic positions or lattice parameters affect the band structure of single-layer WS_2 determined from epitaxial films on graphite substrate. In contrast to previous work, the present calculations were performed using a plane-wave method as described in Sec. II. This approach is computationally efficient yet accurate, and therefore allows for full structural relaxation of the supercell.

II. METHOD OF CALCULATION

Total energy and electronic structure calculations were carried out in the framework of the density functional theory (DFT) Ref. 11 using the code CASTEP.[12,13] Nonrelativistic ultrasoft pseudopotentials were employed, and exchange and correlation terms were described within the local density approximation (LDA).[14]

The number of k points was varied from 8 to 25, and a kinetic-energy cutoff of 220 eV has been used for the plane waves in order to achieve best convergence. During the calculation full relaxation of the lattice parameters a and c as well as of the internal coordinate z, which determines the intralayer sulfur plane distance, were allowed. The structural relaxation was stopped when the energy gain per atom was less than 2×10^{-5} eV/atom, root-mean-square (rms) displacements were smaller than 10^{-3} Å, and rms forces were smaller than 0.05 eV/Å.

III. RESULTS

The $2H$ polytype of crystalline WS_2 has the hexagonal space group $P6_3/mmc$. Lattice constants were experimentally determined by Schutte *et al.*[15] Starting with structural parameters close to the experimental values, we relaxed the external cell parameters first and allowed internal coordinates to adjust in a subsequent calculation with fixed cell geometry until zero internal stress was achieved. Table I

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TABLE I. Calculated structural parameters of WS_2 compared to experimental data by Schutte et al. (Ref. 15). Given are the lattice constants a and c and the internal coordinate z, which determines the intralayer sulfur plane distance.

	Single crystal	Single layer	Ref. 15
a(Å)	3.171	3.167	3.153
c(Å)	12.359	-	12.323
z	3.095	3.086	3.142

shows the lattice parameters a and c as well as the intralayer sulfur plane distance z after full relaxation. The calculations give slightly larger lattice constants compared to the data from x-ray diffraction. This is in contrast to the known tendency of the LDA to underestimate the lattice parameter. Additional calculations showed, however, that the electronic structure was not significantly affected by these small changes of the structural parameters.

The agreement of the c-axis parameter with the experimental number as well as the width of the energy bands in the z direction imply that the interlayer interaction is not of van der Waals type, since dipole-dipole interactions are missing in this type of DFT calculation.

Calculations of the single layer were performed in a supercell geometry where all atoms from the second layer in the unit cell were removed. Increasing the lattice constant c by a factor of 2 ensured an electronic decoupling of the mirror cells. In a first calculation the intralayer lattice parameters of the single layer were kept at calculated values of the single crystal. Then relaxation of the intralayer sulfur plane distance z and of the lattice parameters a was allowed, but only minor changes could be observed (see Table I). Hence the atomic positions in the single layer are essentially identical to those of the single crystal. The absence of significant relaxation in our calculation further implies that the electronic structure of the single layer is not affected by atomic relaxations.

In Fig. 1 the electronic valence band structures of single-crystal (dotted line) and single-layer (full line) WS_2 as calculated by the present plane-wave pseudopotential method are shown for comparison. The given band structures correspond to the lattice parameters given in Table I. In the ALH plane, which is the top plane of the Brillouin zone [see Fig. 1(a)], where the bulk bands are doubly degenerated, the single crystal and single layer band structures are almost identical. Some differences in band crossing due to different hybridization as a result of different symmetry groups are observed.[7] The largest binding-energy difference is observed for the topmost valence band at A, which is derived mainly from the W $5d_{z^2}$ orbitals. In the central ΓMK plane of the Brillouin zone the bulk bands are split due to the interlayer interactions. Also, in this plane the agreement between bulk and layer band structures is very close and the interlayer splittings are easily identified.

The experimentally determined band structure of single layer WS_2 has been presented previously.[7,10] In Fig. 2 it is compared to the present band-structure calculation along the symmetry directions ΓM and ΓK. The valence-band width and in particular the topmost valence bands are closely reproduced by the calculation. Furthermore, the calculated valence band maximum is at the K point of the Brillouin zone, in agreement with experiment. The splitting of the experimental topmost energy bands at K is due to spin-orbit splitting, which is not included in the calculation.

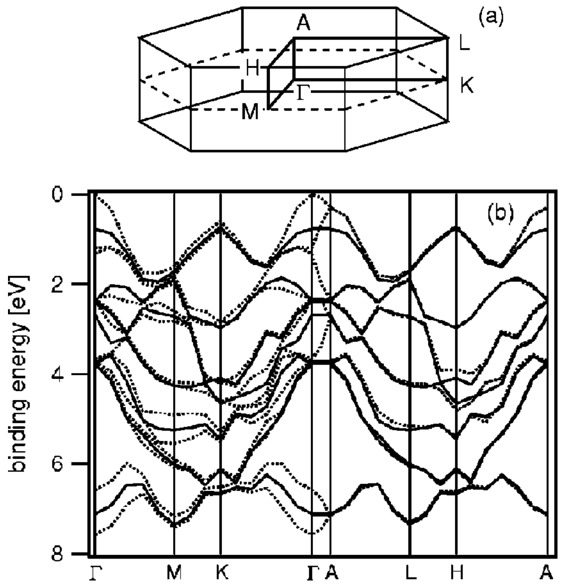

FIG. 1. (a) The hexagonal Brillouin zone of WS_2. (b) Comparison between calculated electronic band structures of single crystal (dotted lines) and single layer (full lines) WS_2. Unoccupied bands and S 3s bands are not shown for clarity.

IV. DISCUSSION

There is a good agreement between the results obtained from non-relativistic local density functional theory calculations using ultrasoft pseudopotentials with a plane-wave basis set and the experimental band structure for single layer WS_2, as shown in Fig. 2. This is also true for the single-crystal band structures. The agreement between the experi-

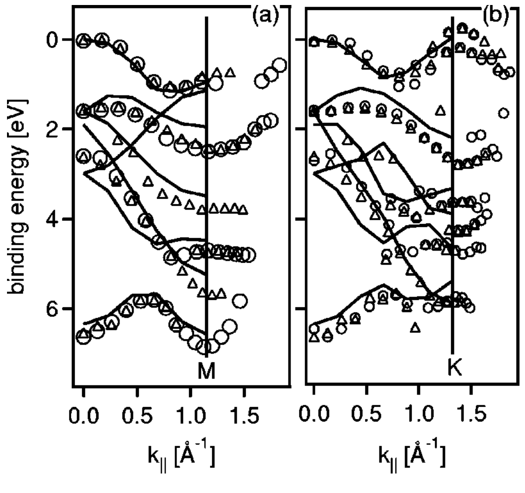

FIG. 2. Comparison of calculated and experimental band structures for single layer WS_2 along ΓM (a) and ΓK (b). The experimental data are described in detail in Ref. 7.

mentally determined band structures of single-layer and single-crystal WS_2 (Refs. 7 and 10) is reproduced by the present calculations (see Fig. 1).

Although the lattice parameters were allowed to relax, no significant changes were determined. Hence the intralayer atomic positions are not strongly affected by the presence or absence of interlayer interactions. This result is important as it justifies a comparison of calculated band structures with those determined from single-layer films deposited on graphite substrates by van der Waals epitaxy. It should be noted, at this point, that relativistic corrections as well as electronic excitations could potentially affect the good quantitative agreement of theory and calculation.

Although such corrections might somehow affect the good agreement between experiment and calculation, there are fundamental differences between the present results and those obtained from calculations based on the ASW approach.[7] Using the ASW method a difference between calculated bulk and layer band structures is observed: the electronic states derived from orbitals perpendicular to the layers (p_z and d_{z^2}) have consistently lower binding energies for the single layer (see Fig. 5 in Ref. 7). As the experimental bulk and layer band structures are very close,[7,10] this shift is not reproduced in the experimental band structures. Assuming a relaxation of the atomic positions in the single layer as a result of missing interlayer interactions was the most reasonable explanation for the discrepancies between experiment and theory. The present calculations in contrast do not show a comparable difference between single layer and single crystal band structure (see Fig. 1). With the present calculations it is thus not necessary to assume a relaxation of the single-layer atomic positions to explain the band structures of single crystal and single layer WS_2 determined by experiment. Whether the restriction on spherical symmetries or another reason leads to the mismatch between experiment and ASW calculation for the single layer needs to be investigated.

V. SUMMARY AND CONCLUSIONS

We have presented band-structure calculations for single-crystal and single-layer WS_2 using a plane-wave method with ultrasoft pseudopotentials. Both, the calculated bulk and layer energy bands agree very well with experimental results. The single-layer band structure was calculated allowing for full structural relaxation of the atomic positions. Only negligible differences in atomic positions of the relaxed single layer compared to the relaxed single crystal were observed. According to the experimental results the calculated energy bands show only small differences between bulk and layer geometries, contrasting with previous ASW calculations. We conclude that intralayer atomic positions of WS_2 are not affected by the presence or absence of interlayer interactions. This proves that an experimental setup, where the WS_2 layer is deposited on a graphite substrate, is an appropriate model system for a free standing film.

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