Inertness and degradation of (0001) surface of Bi2Se3 topological insulator

V. A. Golyashov, K. A. Kokh, S. V. Makarenko, K. N. Romanyuk, I. P. Prosvirin et al.

Related Articles

Additional information on J. Appl. Phys.

Inertness and degradation of (0001) surface of Bi$_2$Se$_3$ topological insulator

V. A. Golyashov,[1] K. A. Kokh,[2] S. V. Makarenko,[3] K. N. Romanyuk,[1,3] I. P. Prosvirin,[4] A. V. Kalinkin,[4] O. E. Tereshchenko,[1,3] A. S. Kozhukhov,[3] D. V. Sheglov,[3] S. V. Eremeev,[5,6] S. D. Borisova,[5,6] and E. V. Chulkov[7,8]

[1]*Novosibirsk State University, Novosibirsk 630090, Russian Federation*
[2]*Institute of Geology and Mineralogy, SB RAS, Novosibirsk 630090, Russian Federation*
[3]*Rzhanov Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russian Federation*
[4]*Boreskov Institute of Catalysis, SB RAS, Novosibirsk 630090, Russian Federation*
[5]*Institute of Strength Physics and Materials Science, 634021 Tomsk, Russia*
[6]*Tomsk State University, 634050 Tomsk, Russia*
[7]*Donostia International Physics Center (DIPC), 20018 San Sebastián/Donostia, Basque Country, Spain*
[8]*Departamento de Física de Materiales UPV/EHU, Centro de Física de Materiales CFM-MPC and Centro Mixto CSIC-UPV/EHU, 20080 San Sebastián/Donostia, Basque Country, Spain*

Inertness of the cleaved (0001) surface of the Bi$_2$Se$_3$ single crystal, grown by modified Bridgman method, to oxidation has been demonstrated by X-ray photoelectron spectroscopy, scanning tunneling microscopy, and by *ab initio* DFT calculations. No intrinsic bismuth and selenium oxides are formed on the low-defect, atomically flat Bi$_2$Se$_3$(0001)-(1 × 1) surface after a long-time air exposure. The inertness of Bi$_2$Se$_3$(0001) to O$_2$ and NO$_2$, as well as bismuth-oxygen bonding formation under molecular adsorption in the Se vacancy was supported by DFT calculations. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4767458]

I. INTRODUCTION

In recent years, extensive studies of V-VI compounds including Bi$_2$Se$_3$ and Bi$_2$Te$_3$ have been made in order to develop efficient materials for higher performance devices based on high speed and spin-polarized carriers with light effective mass.[1] However, for these materials, various problems arise which hinder a prompt practical realization of mass-producible devices. It was shown that the surface electronic properties of the three-dimensional topological insulators (TIs) were affected by the surface adsorption of residual gases,[2] air,[3] CO,[4] H$_2$O,[5] and oxygen.[7,8] In particular, the air exposure over several hours apparently causes the surface oxidation and environmental doping.[6–8] It was demonstrated that oxidation of Bi$_2$Se$_3$ results in a complex band structure because of hybridization of the O-derived states with the substrate states.[9] The formation of intrinsic oxides observed on the (0001) Bi$_2$Se$_3$ and Bi$_2$Te$_3$ surfaces can be responsible for the change of sign in surface conductivity with time[10] and even for deterioration of the topological surface states properties[7] as well as for reduction of the spin current.[9]

On the other hand, the stability and atomic flatness of the surfaces cleaved across weak interlayer bonds in layered structure materials, such as graphite and the transition metal dichalcogenides are well known.[11] From the theoretical point of view, one can expect that the (0001) Bi$_2$Se(Te)$_3$ surfaces should be also stable to oxidation, which is in contradiction with recent results of Refs. 7 and 8. Unfortunately, no detailed analysis of the structural perfection of the studied surfaces was given in Refs. 7 and 8. It is well-known that inertness to oxidation depends on the amount of surface defects (vacancies, substitutional defects, and steps).[12] One can expect that the perfect (0001) V–VI surfaces with low-density of surface defects concentration should be inert to

oxidation because the (0001) surface is stabilized by Se(Te) atoms with covalent bonds oriented into a quintuple layer.

In this work, the properties of the (0001) surface of Bi$_2$Se$_3$ grown by the Bridgman method with the use of a rotating heat field were studied experimentally to find out a relation between the structural perfection, chemical stability, and TI properties of single-crystalline Bi$_2$Se$_3$. The inertness of Bi$_2$Se$_3$(0001) to the oxidation is confirmed by DFT calculations.

II. METHODS

The Bi and Se of 99.999% purity were used for synthesis of polycrystalline Bi$_2$Se$_3$. Suspended components were sealed off in an ampoule which was pumped down to a residual pressure of $\sim 10^{-4}$ Torr. The ampoule was heated in an oven at the rate of 20 °C/h until the temperature became 20 °C higher than the melting point ($T_{melt} = 705$ °C). The oven was switched off in one day. Recrystallization of the obtained ingots was performed using the vertical variant of the Bridgman method with a rotating heat field.[13] The grown crystals consisted of one or several large single crystalline blocks, as shown in Fig. 1(a). As received, fresh surfaces are readily available by cleaving the crystals along its natural cleavage plane. We have found that the surface quality is very sensitive on the cleavage method, in particular, the cleaving with a scotch tape induces a lot of defects while splitting by a cleaver provides nearly a perfect surface. The defects like a half-height quintuple layer induced by scotch cleaved were found in Ref. 14.

The AFM image of the perfectly cleaved surface is shown in Fig. 1(b). The height profile (peak to peak) along the line shown in Fig. 1(b) is given in Fig. 1(d). One can see that the change in the height does not exceed 0.1 nm at 4 μm

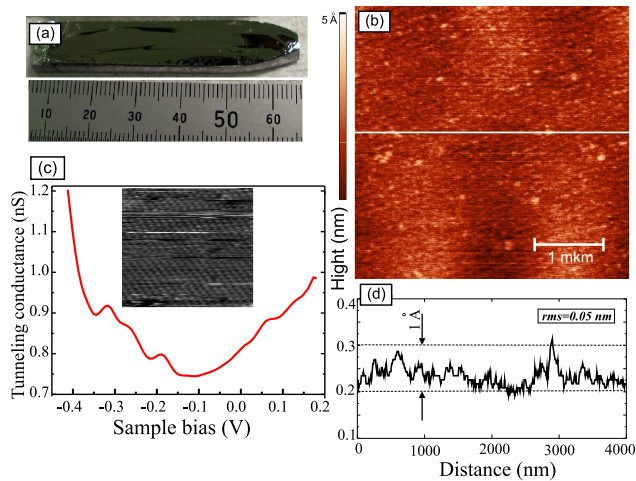**112**, 113702-1

FIG. 1. (a) Cleaved Bi_2Se_3 single crystal, (b) AFM image of $4 \times 4 \, \mu m^2$ surface with profile (d) corresponding to the line drawn in (b) panel, (c) differential conductance spectra and $8 \times 8 \, nm$ topographic map (inset). All measurements were done after two weeks of air exposure.

scale. The *rms* roughness of the surface within the $4 \times 4 \, \mu m^2$ area was 0.05 nm. It is, in fact, the resolution limit of the AFM method. The study of the (0001) surface profile of Bi_2Se_3 within an area of several cm^2 at different points of the sample gives the same picture, which means that the cleaved surface is very flat. Bi_2Se_3 samples were naturally *n*-doped with carrier concentration in the range of (1-9) $\times 10^{18} \, cm^{-3}$, with electron mobility $\mu_n = 3000 \, cm^2/(V \cdot s)$ at $T = 77$ K.

The composition and stoichiometry of the crystals were studied by X-ray photoelectron spectroscopy (XPS) using an SPECS photoelectron spectrometer with a PHOIBOS 150 MCD 9 hemispherical analyzer and a FOCUS 500 X-ray monochromator (emission $AlK\alpha = 1486.74$ eV, 200 W). The binding energy scale was calibrated using the position of the peaks of Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ core levels (932.70 eV). The pressure in the analysis chamber did not exceed 5×10^{-10} Torr. The XPS spectra of elementary Bi and Se were measured to determine the factors of the element sensitivity. The ratios of Bi/Se were found to be very close to 2/3. The surface oxidation was performed by exposure to nitrogen dioxide NO_2 and oxygen O_2 gases obtained through the reaction of lead (II) nitrate $Pb(NO_3)_2$ by decomposition during heating in vacuum: $3Pb(NO_3)_2 \rightarrow Pb_3O_4 \downarrow + 6NO_2 \uparrow + O_2 \uparrow$. Exposure was calculated in Langmuir's ($1L = 1s \times 10^{-6}$ Torr). The morphology and tunneling spectroscopy of the (0001) surface were measured by an Omicron scanning tunneling microscope and by a Solver P 47H atomic force microscope. AFM, STM, and XPS measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Fig. 2 shows the XPS spectra of $4f_{7/2}$ Bi and $3d$ Se lines of Bi_2Se_3 after (a) 1 min exposure to the air during loading into an ultrahigh-vacuum chamber, (b) after the storage of the sample for 30 days in the air, (c) exposure of the freshly cleaved surface to $NO_2 + O_2$ gas, and (d) after Ar^+-ion treatment followed by $NO_2 + O_2$ exposure. It can be seen in

Fig. 2 that there are no chemically shifted components in the XPS spectra of the Bi_2Se_3 surface after fast loading and after one month of air exposure, as well. The absence of oxygen on the surface is confirmed by the fact that there is no O1s line in XPS spectra. Thus, the exposure of the $Bi_2Se_3(0001)$ surface to the air during 30 days did not lead to the formation of oxide components in the spectra. Therefore, the cleaved (0001) surfaces of single-crystalline Bi_2Se_3 are inert to oxidation and preserve the ideal surface properties within months. This contradicts the results of Refs. 7 and 8, where the formation of Bi, Te, and Se oxides was observed during the first minutes of surface exposure to the air. The discrepancy with our results can be explained by a different crystalline perfection of the initial surfaces. The fact that Bi oxidation was observed prior to Se oxidation in Ref. 7 is in favor of this hypothesis. Since the outer layer in an ideal crystal is terminated by selenium atoms, oxidation of bismuth atoms is possible only at defects (selenium vacancies, bismuth substitution of upper selenium atoms). In this case, bismuth dangling bonds, that exist on the surface, can interact with oxygen.

To check this hypothesis, we first studied the interaction of nitrogen dioxide and oxygen with the freshly cleaved atomically flat (0001) surface of Bi_2Se_3 and, second, after ion bombardment which is known to induce surface damage. Fig. 2(c) shows the spectra of $4f_{7/2}$ Bi and $3d$ Se lines after the exposure of freshly cleaved surface to $NO_2 + O_2$ gases at the dose of 5 kL. Exposure to the oxidants up to 5 kL did not lead to the appearance of the O1s signal, as well as the chemically shifted components[7,16] in the Bi and Se within the sensitivity of XPS. It gives estimation of the sticking coefficient less than 10^{-6}. Only after Ar^+ bombardment and following $NO_2 + O_2$ exposure, the chemically shifted component in $4f_{7/2}$ Bi line was observed (Fig. 2(d)). While $NO_2 + O_2$ increases exposure, BiO_x peak keeps growing, corresponding to the increase of bismuth oxide. The absence of SeO_x for the samples with a relatively short time exposure to oxidants may come from the stronger tendency of oxygen to react with Bi, and close electronegativity of Se to oxygen.
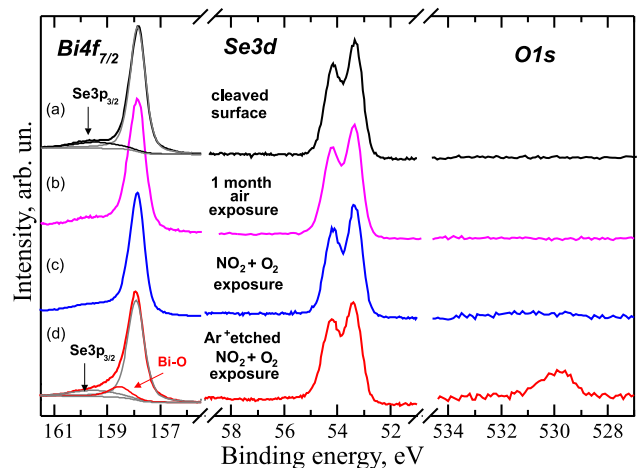

FIG. 2. XPS spectra of the Bi $4f_{7/2}$, Se $3d$, and O 1s peaks for the Bi_2Se_3 (0001) surface (a) after 1 min exposure to air, (b) after the storage of the sample in air for 30 days, (c) exposure of freshly cleaved surface to NO_2, D = 5 kL and (d) after Ar-treatment followed by NO_2 exposure, D = 3 kL.

The stability of the $Bi_2Se_3(0001)$ surface to oxidation in the air was also confirmed by STM measurements. Fig. 1(c) shows the differential tunneling conductance, which reflects the local density of states (DOS) and the corresponding STM image of the (0001) atomic-resolved surface, which were measured after two weeks of Bi_2Se_3 exposure to the air. The image exhibits the two-dimensional hexagonal lattice of the Se-terminated unreconstructed (1×1)-(0001) surfaces. The streak lines visible in the STM image were produced by abrupt increased of tunneling current caused by the physisorbed molecules attached to the tip. The STM studies confirm that (1) the surface is atomically flat, and (2) the density of defects on the cleaved surface of single-crystalline bismuth selenide is low. The differential tunneling conductance shows that the local density of states has a V-shaped STS spectrum with a minimum at ~ -0.1 V relative to the Fermi energy, which corresponds to the Dirac point. A finite offset at -0.1 V is only twice higher than those measured at 5 K.[17] The measured DOS shape is typical for freshly cleaved surfaces of Bi_2Se_3 (Refs. 14 and 15) that gives the evidence that the TI properties of surface state are preserved after a long exposure to the air.

Regarding the concentrations and mobilities, the standard Hall method measurements show that these characteristics are stable within 5% for several months. This result is in contradiction with the observed degradation of the bulk properties in thin Bi_2Se_3 films affected by environmental factors for several days.[6]

In order to clarify the details of interaction of NO_2 and O_2 with the Bi_2Se_3 surface, we have performed *ab initio* DFT calculations. We considered the adsorption of O_2 and NO_2 molecules within a slab model of a 3×3 surface supercell of Bi_2Se_3. We use the Vienna *ab initio* simulation package (VASP)[18,19] with the generalized gradient approximation (GGA)[20] to the exchange correlation potential and the projector augmented wave (PAW)[21,22] basis sets to solve the resulting Kohn-Sham system. The Bader analysis was implemented to estimate a charge transfer in the adsorbed systems.

First, three adsorption sites for the O_2 on the surface were examined: fcc and hcp hollow sites, as well as on-top position. It was revealed that the O_2 interacts rather weak with the surface in any position (Figs. 3(a)–3(c)). In the hollow sites, the equilibrium distance between O_2 and closest Se atom is 3.14 Å and 3.30 Å in fcc and hcp positions, respectively, and, thus, negligible charge transfer ($\sim 0.1e$)

from the surface to the molecule and a small increase of the molecule bond length ($\sim 1.1\%$ in the fcc site and 0.8% in the hcp site), as compared to O-O distance in the free molecule, were found. In the on-top site, where the molecule is situated at 3.44 Å above the surface Se atom, its interaction with the substrate is not much different from the previous cases. Thus, on the ideal surface, molecular oxygen very slightly interacts with the surface Se atoms.

The situation becomes significantly different for the oxygen molecule adsorbed in the Se vacancy site (Fig. 3(d)). In this case, the molecule binds to the second layer bismuth atoms. It leads to a huge charge transfer to the molecule, $\sim 2e$ and to an increase in O-O bond length by 23.7%. In this case, at moderate temperature, dissociation of the molecule can occur. The fact that the oxidation is not observed in our experiment is an indication of the absence of surface vacancies on the cleaved surface.

Next, we have considered nitrogen dioxide adsorption. It is known that NO_2 dissociation is much more facile than O_2 dissociation because NO_2 is coordinatively flexible, and O_2 is not. For this reason, NO_2 is more reactive than O_2 and is often used in the oxidation processes, including NO_2-assisted molecular-beam epitaxy.[23] As in the case of adsorption of oxygen molecule, the deposited NO_2 is located far from the surface. A slightly preferred configuration of the molecule in the position, where one of the oxygen atoms is closer to the selenium atom than the second O (Fig. 4(a)). In this case, the shortest O-Se distance is of 2.94 Å. Like in the previous case, negligible charge transfer ($\sim 0.1e$) from the closest Se to NO_2 and small increase of the N-O bond length ($\sim 1\%$) were found. When the selenium vacancies are present on the surface, which is realized after Ar^+ etching, the second layer Bi adsorption positions become the most preferred for the adsorption. In Fig. 4(b), the relaxed geometry for NO_2 molecule, initially situated above Se vacant site, is shown. As clearly seen in the figure, the molecule plunges into the vacancy resulting in one of the oxygens bound to the bismuth atom. This binding is determined by the charge transfer of $0.41\,e$ from bismuth to oxygen. The equilibrium Bi-O distance of 2.44 Å is comparable to the sum of Wigner-Seitz radii of bismuth and oxygen (2.45 Å). At the same time, the distance between the bonded oxygen and N increases by 63% under adsorption. This leads to the fact that the rest NO becomes almost a free nitrogen mono-oxide molecule. Thus, the N-O bond length of 1.17 Å is the same
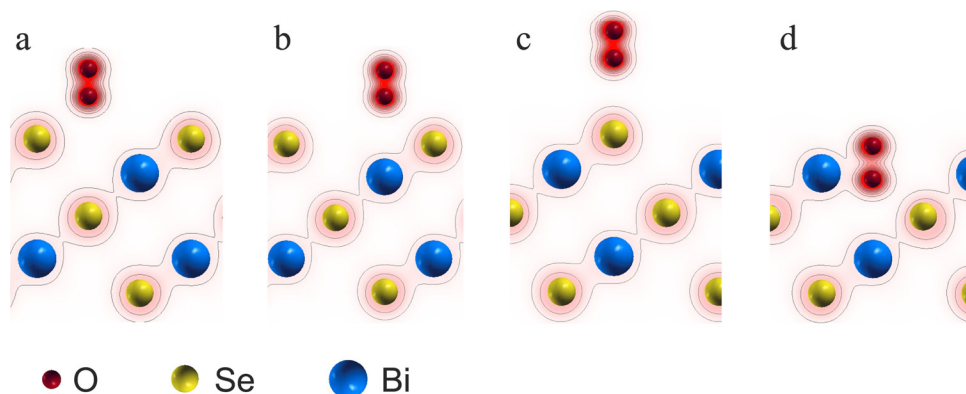

FIG. 3. The total valence charge density distribution in $(11\bar{2}0)$ plane for O_2 adsorbed in (a) fcc, (b) hcp, (c) on-top positions, and (d) in vacancy position on the Bi_2Se_3 surface.
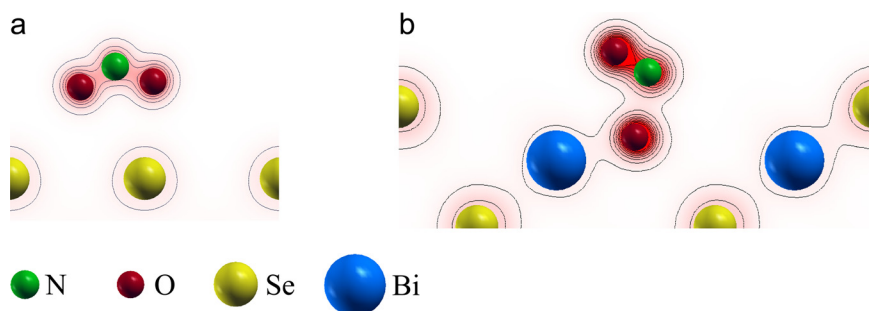
● O   ● Se   ● Bi

FIG. 4. The total valence charge density distribution for NO_2 adsorbed on the ideal surface (a) and in the Se vacancy (b).

● N   ● O   ● Se   ● Bi

as for the calculated free NO molecule (1.15 Å is an experimental bond length for NO) and the net valence charge of the rest NO, $10.96e$, is close to the value for the neutral NO molecule. It is necessary to note that Se vacancies, i.e., bismuth adsorption sites can also be the effective traps for atomic oxygen. The energy gain for the oxygen atom to be adsorbed in Se vacancy is 2.81 eV as compared to the on-top Se atom adsorption. On the whole, the DFT results fully corroborate the bismuth oxide formation after Ar^+ etching.

IV. CONCLUSION

In summary, we have shown that the (0001) surfaces of the Bi_2Se_3, grown by the modified Bridgman method, have inert properties, which are generic for layered materials with high-perfection surfaces. The stability of the (0001) TI surface can be explained by the fact that the surface selenium atoms at the ideally terminated (0001) surface have closed electronic shells with bonds oriented into the quintuple layer and have no dangling bonds. The measured results have shown that the TI surface state of the perfectly cleaved (0001) surface of the bulk topological insulator stays intact during a long-term storage in the atmosphere. The inertness of $Bi_2Se_3(0001)$ surface to molecular oxygen and nitrogen dioxide was supported by DFT calculations which show absence of the binding of O_2 and NO_2 with the surface in the lack of Se vacancies.

[1]R. F. Service, Science **323**, 1000 (2009).
[2]M. Bianchi, D. Guan, S. Bao, J. Mi, B. B. Iversen, P. D. C. King, and Ph. Hofmann, Nature Commun. **1**, 128 (2010).
[3]C. Chen, S. He, H. Weng, W. Zhang, L. Zhao, H. Liu, X. Jia, D. Mou, S. Liu, J. He, Y. Peng, Y. Feng, Z. Xie, G. Liu, X. Dong, J. Zhang, X. Wang, Q. Peng, Z. Wang, S. Zhang, F. Yang, C. Chen, Z. Xu, X. Dai, Z. Fang, and X. J. Zhou, PNAS **109**, 3694 (2012).
[4]M. Bianchi, R. C. Hatch, J. Mi, B. B. Iversen, and Ph. Hofmann, Phys. Rev. Lett. **107**, 086802 (2011).
[5]H. M. Benia, C. Lin, K. Kern, and C. R. Ast, Phys. Rev. Lett. **107**, 177602 (2011).
[6]M. Brahlek, Y. S. Kim, N. Bansal, E. Edrey, and S. Oh, Appl. Phys. Lett. **99**, 012109 (2011).
[7]D. Kong, J. J. Cha, K. Lai, H. Peng, J. G. Analytis, S. Meister, Y. Chen, H.-J. Zhang, I. R. Fisher, Z.-X. Shen, and Y. Cui, ACS Nano **5**(6), 4698 (2011).
[8]H. Bando, K. Koizumi, Y. Oikawa, K. Daikohara, V. A. Kulbachinskii, and H. Ozaki, J. Phys. Condens. Matter **12**, 5607 (2000).
[9]X. Wang, G. Bian, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **108**, 096404 (2012).
[10]A. A. Taskin, Z. Ren, S. Sasaki, K. Segawa, and Y. Ando, Phys. Rev. Lett. **107**, 016801 (2011).
[11]X. L. Wu, P. Zhou, and C. M. Lieber, Phys. Rev. Lett. **61**, 2604 (1988).
[12]B. M. Goltsman, V. A. Kudinov, and I. A. Smirnov, *Thermoelectrical Semiconductors Material Based on* Bi_2Te_3 (Nauka, Moscow, 1972).
[13]K. A. Kokh, B. G. Nenashev, A. E. Kokh, and G. Yu. Shvedenkov, J. Cryst. Growth **275**, e2129 (2005).
[14]S. Urazhdin, D. Bilc, S. D. Mahanti, and S. H. Tessmer, Phys. Rev. B **69**, 085313 (2004).
[15]S. Kim, M. Ye, K. Kuroda, Y. Yamada, E. E. Krasovskii, E. V. Chulkov, K. Miyamoto, M. Nakatake, T. Okuda, Y. Ueda, K. Shimada, H. Namatame, M. Taniguchi, and A. Kimura, Phys. Rev. Lett. **107**, 056803 (2011).
[16]J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, in *Handbook of X-ray Photoelectron Spectroscopy*, edited by J. Chastain (Perkin-Elmer Corporation, Physical Electronics Division, 1992).
[17]T. Hanaguri, K. Igarashi, M. Kawamura, H. Takagi, and T. Sasagawa, Phys. Rev. B **82**, 081305(R) (2010).
[18]G. Kresse and J. Hafner, Phys. Rev. B **48**, 13115 (1993).
[19]G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[20]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[21]P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[22]G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[23]T. Fujii, F. M. F. de Groot, G. A. Sawatzky, F. C. Voogt, and T. Hibma, and K. Okada, Phys. Rev. B **59**, 3195 (1999).