First-principles investigation of BaFe$_2$As$_2$(001)

G. Profeta,$^{1}$ C. Franchini,$^{2}$ K. A. I. L. W. Gamalath,$^{3}$ and A. Continenza$^{4}$

$^{1}$SPIN-CNR, Dipartimento di Fisica, Università degli Studi di L’Aquila, Via Vetoio 10 L’Aquila, Italy
$^{2}$Faculty of Physics, Center for Computational Materials Science, Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria
$^{3}$Department of Physics, University of Colombo, Colombo 03, Sri Lanka
$^{4}$CNISM, Dipartimento di Fisica, Università degli Studi di L’Aquila, Via Vetoio 10 L’Aquila, Italy

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The structural, electronic, and magnetic properties of several different terminations of the BaFe$_2$As$_2$(001) surface are investigated by means of first-principles calculations. Analysis of the surface stability as a function of the chemical potentials reveals that the three possible terminations (As, full and half Ba coverage) can all be stabilized in different chemical-potential ranges. We determine the most stable structure in each case and study its magnetic and electronic properties. A study of the scanning tunnel microscope maps and work functions provides helpful insights for the interpretation of the still debated experimental findings.

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I. INTRODUCTION

The new class of Fe-based compounds have recently boost$^{1,2}$ even further the already high interest in superconductivity and in its intriguing interplay with the structural and magnetic degrees of freedom.$^{2}$ The Fe-pnictide family, in fact, provides a large variety of different materials where pressure, magnetism, and doping directly$^{2,4,5}$ tune the material properties leading to phases where antiferromagnetism and superconductivity often coexist or compete.

In addition, the layered-like structure which characterizes these materials poses several different questions on the role played by the layer stacking sequence and the mutual interactions between different layers. To this end, a few papers recently appeared reporting results on the BaFe$_2$As$_2$ surface structure probed by means of scanning tunnel microscope (STM) and low-energy electron diffraction (LEED) experiments. However, the nature and morphology of the topmost surface layer and its properties are still quite debated issues. While a general agreement is found regarding the in-plane $p(1 \times 1)$ (001) surface unit cell with the bulk orthorhombic structure, no consensus has been reached regarding the specific type of the termination (FeAs according to Refs. 6–8 or Ba 50% according to Refs. 9 and 10). Starting from surface morphological characterization, all the experimental studies find large surface areas compatible with a square ($\sqrt{2} \times \sqrt{2}$)R45° in plane cell (referred to the tetragonal structure), notwithstanding the well-known orthorhombic structure of this compound at low temperature. Moreover, although few surface calculations$^{11,12}$ of the FeAs pnictide already appeared, no detailed calculations of the relative stability of the different possible surface terminations nor a comprehensive study of the surface electronic and magnetic features have been so far presented. Eschrig et al.$^{11}$ in particular, presented a study of the cleavage behavior in LaOFeAs while some ab initio results for specific surface structures were presented supporting the experimental results discussed in Refs. 6 and 10. Finally, a recent report$^{12}$ describes the ($\sqrt{2} \times \sqrt{2}$)R45° and the (1 × 2) arrangements for Ba-terminated (Ba-t) and As-terminated (As-t) systems.

The aim of the present paper is to investigate the properties of different surface terminations through a detailed analysis of (i) the magnetic and structural properties, (ii) the relative stability of the various surface terminations as a function of the chemical potential (i.e., surface phase diagram), and (iii) the termination-dependent changes in the work functions. Our results show that the surface termination depends on the chemical potential of the Ba atom and that at different values, different terminations can be stabilized. A study of the calculated STM reveals features that will help identification of the surface termination while the evaluation of the work function is found to establish a quick and easy criterion to characterize the sample surface. We believe that our computational study can supply useful insights for the correct interpretation of the available experimental results and, most importantly, will stimulate surface measurements on pressure ranges not yet explored.

II. COMPUTATIONAL DETAILS

The calculations were performed using the VASP package$^{13,14}$ within the generalized gradient approximation (GGA) (Ref. 15) to density-functional theory (DFT), projector augmented wave pseudopotentials$^{16}$ were used for all the atomic species involved. The energy cutoff was set at 300 eV, test performed on larger cutoffs (up to 450) showed that local relaxations nor total-energy differences were affected within numerical accuracy. Integration of the irreducible Brillouin zone was performed considering shells up to (6,6,1) an (8,8,1) $k$ points in the Monkhorst and Pack$^{17}$ scheme. Larger $k$-point sampling did not give appreciable differences in the relaxed structures nor in the total-energy differences.

All surface simulations were performed in the repeated slab technique, taking two bulk unit cells along the $z$-axis direction and modeling different in-plane cells in order to simulate different possible reconstructions and magnetic alignments (as sketched in Fig. 1). More specifically, we have considered two Ba-t surfaces at both full [1 monolayer (ML)] and half (0.5 ML) coverages and one As-t surface. In addition to the as-cleaved 0.5 ML Ba-terminated surface we have also considered a second 0.5 ML Ba-terminated reconstruction, constructed by alternatively removing (110) rows...
of Ba atoms from the fully Ba-covered surface, resulting in a (2×1)-like periodicity [see Fig. 1(c)]. We have also tested other (2×1) geometries constructed by a suitable arrangement of Ba dimers (not shown), which turned out to be unstable against structural relaxations [i.e., after a full geometrical relaxation the Ba dimers dissociate, and the initial structure is converted into the standard Ba-terminated (1×1) structure]. For all models we have adopted a two-dimensional a × b [p(1×1)] unit cell with lattice parameters set to the corresponding antiferromagnetic (AFM) experimental values (a=5.614 Å and b=5.574 Å), which are found to be almost identical to the GGA-optimized bulk values (the relative difference between the experimental and calculated values is 1.7% and 0.4% for a and b, respectively). We remind that the lattice parameter a can be expressed in terms of the tetragonal lattice constant a0 as a=a0√2. Then, keeping fixed the in-plane lattice parameters to the experimental values for the magnetic phase, we relaxed all the atomic internal positions in the slab according to the ab initio forces, up to 0.01 eV/Å. In addition to the well-known stripe-like AFM alignment, we considered also the so-called checkerboard AFM ordering.

The considered slab is symmetric along the z-axis direction resulting in two symmetry equivalent surfaces. This setup rules out any possible spurious effect coming from a charge imbalance between the top and bottom surfaces. A vacuum layer of more than 14 Å separates two successive slabs (about 25 Å thick) containing five Ba and four Fe-As layers. The overall simulation cell is large enough to recover bulk conditions (in terms of bond-length distances and atom-projected density of states) in the inner layers.

III. SURFACE ENERGIES AND STABILITY

First of all we investigate the surface free energies of the different possible terminations examined. The surface energy per surface area (A) can be calculated as following:

\[
\sigma = \frac{1}{A} \left[ G - \sum_i n_i \mu_i \right].
\]

where \(G\) being the Gibbs free energy of the solid with the surface and \(n_i\) and \(\mu_i\) the number and the chemical potential of the atoms composing the slab. The surface is in equilibrium with the bulk phase, thus the following condition holds for the bulk BaFe2As2 Gibbs potential \(g_{\text{BaFe2As2}}\):

\[
\mu_{\text{Ba}} + 2 \times \mu_{\text{Fe}} + 2 \mu_{\text{As}} = g_{\text{BaFe2As2}}.
\]

Since our interest is on the low-temperature phases of the surfaces, we consider that the contributions coming from vibrations and entropy terms are the same and therefore can be neglected. Thus, we can replace the free energies with the respective total energies. We therefore obtain

\[
\sigma = \frac{1}{A} \left[ E_{\text{slab}} - n_{\text{bulk}} E_{\text{BaFe2As2}} + \sum_i n_i \mu_i \right],
\]

where \(E_{\text{slab}}\) is the calculated total energy of the slab with the definite surface termination, \(n_{\text{bulk}}\) is the number of BaFe2As2 cells contained in the slab, and \(n_i\) and \(\mu_i\) are the number of the remaining atoms and their corresponding chemical potential, respectively. In our particular case, the previous equation can be casted in a much simpler form considering that the atoms present in the slab and exceeding (lacking) the commensurate bulk stoichiometry are only the Ba atoms in the case of fully covered Ba-terminated (As-terminated) case. In this respect, the slabs with only one Ba on the surface layers (the 0.5 ML Ba-t) are perfectly stoichiometric and therefore their surface energies are not dependent on any chemical potential. With this in mind, we can calculate the surface energy for the 0.5 ML Ba-t case as

\[
\sigma_{0.5 \text{ ML Ba-t}} = \frac{1}{A} \left[ E_{\text{slab}} - n_{\text{bulk}} E_{\text{BaFe2As2}} \right]
\]

whereas the surface energies for the full As-t and Ba-termination read

\[
\sigma_{\text{As-t}} = \frac{1}{A} \left[ E_{\text{slab}} - (n_{\text{bulk}} E_{\text{BaFe2As2}} + 2 \mu_{\text{Ba}}) \right],
\]

\[
\sigma_{\text{Ba-t}} = \frac{1}{A} \left[ E_{\text{slab}} - (n_{\text{bulk}} E_{\text{BaFe2As2}} - 2 \mu_{\text{Ba}}) \right].
\]

Now, we observe that an appropriate estimate of the range of variation in \(\mu_{\text{Ba}}\) can be obtained by assuming that gas phase of Ba does not condensate on the sample (upper limit) whereas the lower limit is the heat of formation of BaFe2As2. By introducing the formation energy of bulk BaFe2As2 with respect to its constituents in their bulk equilibrium phase \(\Delta H_f = E_{\text{BaFe2As2, bulk}} - \mu_{\text{Ba}} - 2 \mu_{\text{Fe}} - 2 \mu_{\text{As}}\) and the chemical potential \(\mu_{\text{Ba}}\) of bcc-bulk Ba (which we take as reference energy) we finally obtain the following relation:
Here, the upper limit holds in the Ba-rich case (decomposition into bcc-Ba bulk) while the lower one states the equilibrium condition with bulk BaFe$_2$As$_2$. Our results are shown in Fig. 2 for the different systems considered and for values of the Ba chemical potential ranging in the limits set above. The curves reported are obtained for the most stable AFM state which, for all the cases studied, is found to be the stripe phase. The energy differences with the other possible AFM alignment (checkerboard phase) are on the order of 50 meV/cell depending on the surface considered. Interestingly, we found that in the allowed chemical-potential range, there are three surfaces thermodynamically stable. From the results shown in Fig. 2 we find that the surface at full Ba coverage is energetically stable at rather large Ba concentrations (i.e., when $\mu_{\text{Ba}}$ is about 1 eV smaller than the Ba-bcc cohesive energy). The stoichiometric surface, that is the one with only one Ba on the topmost layer, becomes energetically favored at intermediate range of $\mu_{\text{Ba}}$. At rather low Ba concentrations the As-terminated becomes the most stable as also found in some experiments reporting ordered As-terminated surface with disordered Ba adatoms. It is interesting to observe that the 0.5 ML Ba coverage preferred is the one which is compatible with the $p(1 \times 1)$ geometry rather than the one with the $2a_0 \times a_0$ one: we remind that in the former case, the surface Ba atoms form stripes parallel to the Fe AFM stripes while in the latter case the Ba are aligned on rows forming 45° with the Fe stripes. The coexistence of three different phases in a rather limited range of Ba chemical potential can in part give a rationale for the difficulties to obtain a clean and ordered single surface phase. Considering that the Ba chemical potential can be related to the partial Ba pressure, we infer that the precise calibration of the Ba pressure in a surface experiment could be exploited to tune the formation of the desired reconstruction.

In line with bulk calculations for these compounds, we find that the paramagnetic phase of the considered surfaces (calculated in the tetragonal cell) are constantly less energetically favored with respect to the orthorhombic magnetic phases: in these cases the slab total energies are more than 0.6 eV larger (0.68 and 0.87 eV for the 1 ML Ba-t and 0.5 ML Ba-t, respectively) than the corresponding orthorhombic AFM phases. Therefore, surface effects do not change the magnetic order of the Fe layers.

### IV. STRUCTURAL PROPERTIES

Since the magnetic properties in these compounds are strongly dependent on the structural details and in particular on the Fe-As distance, we report the structural properties of the surface structures considered, obtained fully relaxing all the internal atomic positions till the ab initio forces were lower than 0.01 eV/Å. The results obtained for some of the most relevant atomic (plane) distances in the fully relaxed structures are reported in Table I and compared with the corresponding values calculated for the bulk compound at the same experimental in-plane lattice constants. As reference, we note that the bulk experimental values close to the bulk calculated values, reported on Table I, and give the Ba-As bond length ($d_{\text{Ba-As}}$) slightly smaller than the calculated value (3.37 Å to be compared with 3.39 Å), and the Fe-As bond length slightly larger (2.39 Å to be compared with 2.37 Å). The small inconsistency is of course related to the DFT-optimized $z_{\text{As}}$ value. We observe that the bulk values are well recovered (within 0.01 Å) in the inner layers of the slabs and this gives us confidence on the slab thickness considered. We find a general inward relaxation of the surface layer along the direction perpendicular to the surface ($z$ axis) in both Ba-terminated surfaces; the contraction is pretty large (about 0.4 Å) for the surface with only one Ba/cell on the topmost

<table>
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<th>0.5 ML Ba-t</th>
<th>1 ML Ba-t</th>
<th>As-t</th>
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layer resulting in shorter Ba-As interlayer distance (quickly recovered in the layer just below the surface). In fact, while the Fe-As interlayer distance is practically unchanged (or even larger in the case of the Ba-terminated surfaces), most of the contraction is related to the topmost Ba layer coming closer to the underneath As layer. Increasing further the Ba coverage relaxation effects decrease due to the lower charge transfer for each Ba atom. In addition, in the 0.5 ML Ba we find a buckling of the under-surface As atoms (about 0.05 Å), related to the missing topmost Ba atom, which rapidly disappears in the inner layers. This is the reason why two different values are reported in the table for the Fe-As bond length and interlayer distance. Surprisingly, we observed that structural data interpolated from experiments give reasonable agreement when compared with calculations for the 0.5 ML Ba-terminated surface. However, while the bare As-terminated surface shows smaller vertical interlayer distances at the surface, experiment reports an expansion. We must underline that in Ref. 6 LEED reveals a \(p(1 \times 1)\) tetragonal unit cell rather than the orthorhombic one as seen by STM in the same work. In addition, more recent experiments on the Co-doped compound report that STM images for the cleaved (001) surface are consistent with a Ba-terminated surface at half Ba coverage. All these evidences suggest that Ba atoms are mobile at the experimental temperature.

V. ELECTRONIC PROPERTIES

The electronic and magnetic properties are investigated in terms of atom-projected density of states. A summary is reported in Fig. 3. Important changes in the density of states are evident, as expected, for the full ML Ba termination. The extra Ba atoms on the surface induce additional states at the Fermi level, strongly hybridized with Fe \(d\) states; moreover, they do not simply induce a rigid 

![Graph](image_url)

FIG. 3. Atom-projected density of states for some of the surfaces considered: [panel (a)] 1 ML Ba-t and [panel (b)] 0.5 ML Ba-t. As a convention, the majority (minority) states are plotted as positive (negative) values; the shaded regions show the atom-projected density of states in the bulk compound.

magnetic moment. These changes affect the magnetic properties of the topmost layers: the calculated magnetic moments reported in Table I show an enhancement of the Fe magnetic moments at the surface layer for all the Ba-terminated surfaces while a much smaller magnetic moment is found on the As-terminated surface (about 0.4 \(\mu_B\)). The lower magnetic moment at the surface is related to the shift toward lower binding energy experienced by the Fe minority states confirming the link between structural (Fe-As distance) and magnetic properties.

![Graph](image_url)

Figure 5 presents the band structure of the most stable surface in the intermediate chemical-potential regime, the 0.5 ML Ba-t surface in the orthorhombic cell. As already evident from the DOS, surface-induced states fall in the projected bulk band structure (gray-shaded regions). However, the presence of additional surface states in the projected band gap around the \(\Gamma\) point, induces states at about 0.25 eV at \(\Gamma\) not present in the bulk band structure. The presence of surface-induced states (within the projected bulk band gaps) must be considered for the interpretation of photoemission experiments.

VI. STM MAPS AND WORK FUNCTIONS

Scanning tunneling microscopy represents the main experimental tool for the determination of the surface termina-
The low charge-density regime only.

Therefore in the following we will focus our discussion and the surface morphology remains essentially unparable with experimental images, they represent important features that can be summarized as follows:

(i) The 0.5 ML Ba-t surface presents rather feeble features, which correspond to the signals arising from the topmost Ba atoms. The weakness can be explained as due to the rather low Ba density of s states in the explored voltage range (EF ± 0.2 eV). The main visible difference between the occupied and unoccupied profiles is manifested by the

FIG. 4. Contribution to the total density of states coming from the Fe atomic site at the surface of the As-t slab resolved in t2g and e_g components with the corresponding quantities in bulk BaFe2As2 (shaded regions). Positive (negative) values refer to majority (minority) spin states.

A bias voltage of ±0.2 V was applied and the contours of constant integrated charge density were calculated at low charge density (1 × 10^5 electrons/Å^3), following loosely the standard experimental conditions. In order to detect possible changes in the surface profile as a function of the tunneling current high charge-density maps (1 × 10^5 electrons/Å^3) were also simulated. We observe a general increase in the surface corrugation for higher charge density whereas the contrast and the surface morphology remains essentially unaffected. Therefore in the following we will focus our discussion on the low charge-density regime only (Fig. 6).

Analysis of the calculated STM maps reveals several features that can be summarized as follows: (i) the As-terminated surface does not show strong variations in the topography going from positive (empty states) to negative (occupied states). However, quite sensible changes are observed in the corrugation which is significantly smaller at negative voltage (1.17 Å) with respect to the corresponding positive voltage value (1.78 Å). Atomic resolution reveals that the As-t STM consists of a regular network of bright spots, attributable to the As atoms with appreciable dispersion along the As-Fe-As bonds.

(ii) The 0.5 ML Ba-t surface presents rather feeble features, which correspond to the signals arising from the topmost Ba atoms. The weakness can be explained as due to the rather low Ba density of s states in the explored voltage range (EF ± 0.2 eV). The main visible difference between the occupied and unoccupied profiles is manifested by the

FIG. 5. Electronic band structure for the 0.5 ML Ba surface in the orthorhombic cell. The gray-shaded regions are the bulk electronic states projected on the z axis while the black lines refer to surface states. The Brillouin zone of the tetragonal (larger square—solid lines) and orthorhombic cell (smaller square—dashed lines) are indicated in the right panel together with the irreducible wedge of the latter cell (dotted line).

Ba-t 0.5 ML

FIG. 6. (Color online) Constant current topograph (isosurface at constant charge density 10^-5 electrons/Å^3) of the various terminations considered at both positive (+0.2 V) and negative (-0.2 V) bias voltage. The insets indicate the calculated corrugation. Color coding: bright (dark) spots refer to protrusions (depressions).
films have been recently obtained and studied\textsuperscript{26} with transi-
tedoping at the Fermi level. In addition, potassium-doped thin
internal pressure effects, namely, lattice softening, and hole
critical temperatures.

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BaFe\textsubscript{2}As\textsubscript{2} experiment in which an As-t surface is covered with 0.5 ML
that, fixing the K and Ba chemical potentials to their respec-
tive positive voltage whereas at negative voltage they form par-
allel stripes along y separated by a wider dark region (this
also explains the higher corrugation found for the filled states
image).

(iii) The 1 ML Ba-t surface is very different. Here, elec-
tronic effects dominate over the structural ones in fact the
bright protrusions do not correspond to the topmost Ba spe-
cies but rather to the subsurface As and Fe atoms. The flow-
erlike As-Fe hybridization maintains roughly the same shape
and intensity at both positive and negative voltages. We re-
mind that the Ba-t 1 ML surface, which we find to be favor-
able at Ba-rich condition, has not been detected or recog-
nized so far in any experimental study. The reason for this
could be the extremely small corrugation (0.02–0.04 Å)
which is probably beyond the limit of STM accuracy.

Work-function measurements in metals have always been
used to discriminate between different surfaces and even dif-
ferent surface orientations of the same compound. In order
to provide such information, we calculated the work function
of the three terminations examined: this can be achieved by
evaluating the difference between the electrostatic potential
in the middle of the vacuum region and the Fermi level of the
slab.

As expected, the As-t surface presents the higher work
function (5.0 eV). Partial coverage with alkaline earth metal
(0.5 ML Ba-t surface) strongly reduces the work function
down to 1.4 eV, due to the dipole layer forming at the surface.
Full coverage with Ba atoms (1 ML Ba) increases again
the work function up to 2.8 eV, close to the barium bulk
work function [2.52–2.7 (Ref. 22)]. This is a common feature
observed in the work-function behavior as a function of al-
kalidepsorbate,\textsuperscript{25} mainly due to adsorbate-adsorbate interac-
tion and depolarization effects.

These results show that \textit{ab initio} calculations predict large
work-function variations depending on surface termination
(from 1.4 to 5.0 eV): presence of different Ba adsorbate lay-
ers should therefore be easily detected by means of local
work-function measurements, via STM experiments.

VII. SURFACE DOPING: 0.5 ML K COVERAGE

In this section, we perform a step forward, predicting the
electronic properties of a potassium-doped As surface. As
well known, KFe\textsubscript{2}As\textsubscript{2} compound is stable in the same crystal
structure of the Ba analog and is a superconductor even if
with very low critical temperature.\textsuperscript{24} Optimal K doping in
BaFe\textsubscript{2}As\textsubscript{2} (concentrations in the range 40–50 \%) has been
used\textsuperscript{25} to make BaFe\textsubscript{2}As\textsubscript{2} superconductor with rather large
critical temperatures (up to $T_c = 38$ K) since it provides both
internal pressure effects, namely, lattice softening, and hole
doping at the Fermi level. In addition, potassium-doped thin
films have been recently obtained and studied\textsuperscript{26} with transi-
tion temperatures up to 36 K. We consider here only an ideal
experiment in which an As-t surface is covered with 0.5 ML
potassium coverage with K atoms replacing Ba in Fig. 1
panel (b).

A quick check on the energetics of the surface reveals
that, fixing the K and Ba chemical potentials to their respec-
tive bulk stable phases (bcc-Ba and bcc-K) the K-covered
surface is, as expected, not energetically favored over the
native Ba-covered surface (about 2.0 eV). However, the
deposition process is not an equilibrium process and the sur-
face could be stabilized. The atomic relaxations are rather
similar to the 0.5 Ba ML and mainly driven by the different
atomic size: the surface K-Ba interlayer distance is 6.23 Å
(cf. 6.11 Å in the Ba analog), related to a larger K-As sur-
fance distance 1.67 Å (versus 1.55 Å) and followed by a
slightly smaller Fe-As interlayer distance 1.33 Å (1.37 Å in
the Ba analog). Figure 7 shows the atom-projected density
of states compared with the corresponding one in bulk
BaFe\textsubscript{2}As\textsubscript{2}. As in the 0.5 ML Ba, no surface states at the
Fermi level are induced by K; when comparing with the
similar surface at 0.5 ML Ba-t, we find that the main effect
of K coverage is an upward and practically rigid shift (about
$\sim0.5$ eV) of the states from the Fe-As-Fe surface layer to-
der lower binding energies, confirming a rigid electron
doping as far as the surface remains at 0.5 ML coverage. The
density of states at the Fermi level is larger with respect to
the Ba covered mainly due to the contribution of the minority
surface $t_{2g}$-like states that are now not completely filled.
It is interesting to observe that the missing electron, when con-
sidering a rough electron counting with respect to the Ba
case, comes almost entirely from the empty surface minority
$t_{2g}$-like states. In fact, integration of the minority surface
Fe $d$ states from the Fermi level up to the $d$ pseudogap gives
something more than 0.2 electrons/atom which, considering
that there are 4 Fe/layers, adds up to more than 0.8 electron.
However, when considering the total majority and minority
occupation, the effect on the magnetic moment is not rel-
evanten: the magnetic moment on the surface Fe sites is
1.86 $\mu_B$ similar to the corresponding value in the 0.5 ML
Ba. This shows that local doping can be easily achieved in
this systems and, at the same time, that the added states will
localize around the Fe atoms rather than being just “free
states” as also observed with cobalt doping on Fe sites.

VIII. SUMMARY AND CONCLUSIONS

To summarize, our first-principles study on the possible
surface terminations of BaFe\textsubscript{2}As\textsubscript{2} shows that the three ter-
nations considered, 0.5 ML Ba-t, 1 ML Ba-t, and As-t, can be
stabilized in specific ranges of the Ba chemical potential: in
the Ba-poor limit the As-t is found to be the most favorable reconstruction until −2.2 eV where the 0.5 ML Ba-t surface becomes the energetically most stable termination. At the other limit, beyond −0.9 eV, DFT favors the 1 ML Ba-t surface. Local relaxations affect only the atomic layers close to the surface and vanish already on the layer underneath, showing that the surface presence is not dramatically changing the compound bulk properties. Differences in the electronic properties for the different terminations with respect to bulk are analyzed and understood in terms of “effective” potential at the surface. A detailed study of the STM maps and work functions reveals helpful insights which could guide the interpretation of the experimentally observed STM images and stimulate further experiments in pressure ranges different from those explored until now. Finally, a study of the 0.5 ML K-covered As-terminated surface shows that surface local hole doping is possible.

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