

***Ab initio* lattice dynamics and thermodynamics of RuO₂(110) surfaces**Klaus-Peter Bohnen,^{1,*} Rolf Heid,¹ and Omar de la Peña Seaman^{1,2}¹*Forschungszentrum Karlsruhe, Institut für Festkörperphysik, P.O. Box 3640, D-76021 Karlsruhe, Germany*²*Department of Applied Physics, CINVESTAV-Mérida, A.P. 73 Cordemex Mérida, Yucatán 97310, Mexico*

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Using *ab initio* density-functional perturbation theory the lattice dynamics of the RuO₂(110) O-bridge terminated surface has been extensively studied. Excellent agreement with high-resolution electron-energy-loss spectroscopy measurements was obtained. It was found that the (1×1) surface is unstable over a wide range of reciprocal-lattice vectors. This suggests that substrate and/or defect influence play a more important role for the stability of the (1×1) structure than thought so far, with important consequences for catalysis. A stable (1×2) reconstruction was found which allowed a reliable determination of the vibrational contribution to the surface-free energy. Comparing these results with estimates based on a very simple Einstein model the *ab initio* results can be reproduced only by assuming an *ad hoc* 50% decrease of the Einstein mode frequency at the surface. This clearly demonstrates the need for an *ab initio* treatment of the vibrational surface-free energy to obtain reliable phase diagrams for catalysis.

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Over the past few years substantial progress has been made in our understanding of simple catalytic processes. Especially the CO oxidation has received a lot of attention together with transition-metal oxides (TMOs) as catalysts. Among these RuO₂(110) has been studied as a prototype system experimentally^{1,2} as well as theoretically. Density-functional calculations (DFTs) have been applied with great success to determine the structure and energetics of the various surface terminations (O-bridge, O-cus, Ru).^{3,4} Temperature and pressure effects which are essential for catalytic processes are taken into account in the framework of “*ab initio* thermodynamics.”³ This requires in principle the knowledge of free energies and/or free enthalpies of all particles involved in the reaction. To make contact with DFT calculations temperature (T) and pressure effects (P) of the substrate catalyst are neglected. The only (T, P) effects are thus taken into account via the gas phase components. While this approximation seems to be justified for the pressure range one is normally interested in, neglecting temperature effects of the catalyst seems more questionable. Justification is normally based on estimations using simple model phonon spectra (mostly Einstein model) and parameter variation to simulate surface effects.³ The ambiguity inherent in this approach is reflected in the fact that not even the sign of the vibrational surface-free-energy contribution can be predicted. This clearly indicates the need for a more rigorous treatment. The method of choice is the *ab initio* density-functional perturbation theory for calculation of lattice dynamics. As a parameter-free method it allows to determine the phononic contribution to the free energy without the necessity for simplifying assumptions.

Detailed knowledge of the lattice dynamics is not only the prerequisite for any reliable calculation of the vibrational contribution to the surface-free energy, it also allows to check the dynamical stability of the system under study. Since actual catalysts always differ from the model system studied theoretically (e.g., due to defects, film thickness, and support material), it is of crucial importance to verify the dynamical stability of the model system. This can be done

most easily by checking the phonon spectrum for unstable modes.

Despite the importance of having a detailed understanding of the lattice dynamics of TMO's, *ab initio* calculations have been very rare even for the bulk. To our knowledge only RuO₂ bulk has been studied theoretically with *ab initio* lattice-dynamical methods.⁵ No results are available for RuO₂(110) surfaces so far. In this Rapid Communication we present an *ab initio* calculation of the lattice dynamics of the O-bridge terminated RuO₂(110) surface addressing the question of stability and determining the vibrational contribution to the surface-free energy.

Calculations of the structure and the lattice dynamics are performed in the framework of density-functional theory with the mixed-basis pseudopotential method.^{6,7} The linear-response technique has been used for obtaining the vibrational modes.⁸ Well tested pseudopotentials constructed following the description of Vanderbilt⁹ have been used. For Ru the 4*s* and 4*p* semicore states were treated as valence electrons as well as the oxygen 2*s* states. We have restricted our calculations to the RuO₂(110) O-bridge terminated surface which was modeled by an *n*-trilayer ($n=3,4,5$) O-Ru₂O₂-O periodic slab [see Fig. 1(a)] with a vacuum region of 10 Å to decouple neighboring slabs in the supercell geometry.⁴ For dealing with the fairly deep *s*, *p*, and *d* potentials of Ru and the *s* and *p* potentials of O the mixed-basis scheme uses a combination of local functions and plane waves for the representation of the valence states.^{6,7} Supplementary plane waves were taken into account up to a kinetic energy of 22 Ry. For the exchange-correlation functional the local-density approximation (LDA) (Ref. 10) as well as the generalized gradient approximation (GGA) (Ref. 11) have been applied since bulk studies showed substantial differences in the phonon spectrum.⁵

Brillouin-zone (BZ) integrations were performed using a *k*-point mesh of Monkhorst-Pack type¹² in connection with a Gaussian broadening of 0.2 eV. Sufficient convergence of the ground state and the phonon calculations were achieved with a $6 \times 8 \times 1$ *k* mesh. Dynamical matrices were calculated on a

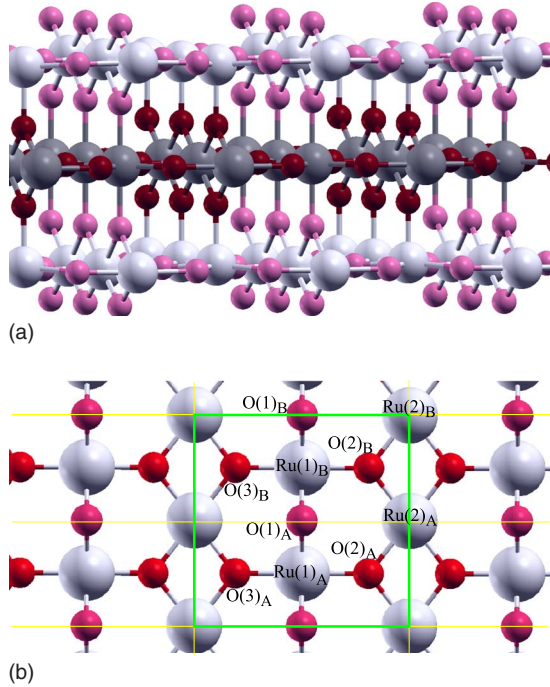


FIG. 1. (Color online) (a) Side and (b) top view of the stoichiometric $\text{RuO}_2(110)$ surface. Small balls represent O atoms and large ones Ru atoms. In (b), the rectangle denotes the (1×2) unit cell, and labels A and B differentiate between inequivalent atoms due to the reconstruction. In the top view, the horizontal x axis corresponds to the direction $[-1, 1, 0]$ and the vertical y axis to $[0, 0, 1]$.

$2 \times 4 \times 1$ grid from which phonon dispersions were obtained by standard Fourier interpolation.^{13,14} Structural relaxation was carried out until all residual forces were less than 10^{-3} Ry/a.u. The bulk structural parameters for RuO_2 have been determined in our earlier publication.⁵ For LDA studies $a=4.4244$ Å, $c/a=0.6944$ and the internal parameter $u=0.3065$, while for the GGA case $a=4.5075$ Å, $c/a=0.6893$, and $u=0.3058$ have been obtained.

Having discussed so far the theoretical treatment we now present the results. Structural results are summarized in Table I with the notation given in Fig. 1(b) for the upper layers. Indices A and B refer to neighboring unit cells in the $[001]$ direction. Deeper layers are labeled according to Ref. 2. Geometries presented are always based on three-trilayer slab calculations. Studies with five-trilayer slabs differed only marginally. For comparison also low-energy electron diffraction (LEED) data² as well as full-potential linearized augmented plane wave (FLAPW)^{3,4} results are given. The differences are mostly due to the different bulk lattice constants while otherwise the relaxation effects are very similar.

Using these optimized structures the phonon dispersion has been calculated as outlined above. High-resolution energy-loss spectroscopy of an as-grown $\text{RuO}_2(110)$ surface found the O-bridge-Ru stretch frequency at the Γ -point at 69 meV.¹⁵ For the (1×1) structure we found this mode at 67 meV with GGA, 75 meV with LDA. In contrast to former calculations, we properly take into account the coupling to all atoms in the slab, which improves the agreement with the experiment. The results show the high sensibility to the ac-

TABLE I. Atomic positions in Å for the (1×1) structure. Components x , y , and z denote directions $[-1, 1, 0]$, $[0, 0, 1]$, and $[1, 1, 0]$, respectively. PPs are our own pseudopotential results.

Atom	LEED ^a	FLAPW-GGA ^{b,c}	PP-GGA	PP-LDA
O(1)-y	1.56	1.56	1.55	1.54
Ru(1)-z	1.16	1.10	1.09	1.07
Ru(2)-x	3.19	3.18	3.19	3.13
Ru(2)-y	1.56	1.56	1.55	1.54
Ru(2)-z	1.34	1.25	1.26	1.23
O(2)-x	2.00	1.97	1.98	1.94
O(2)-z	1.17	1.12	1.12	1.10
O(3)-x	-2.00	-1.97	-1.98	-1.94
O(3)-z	1.17	1.12	1.12	1.10
O(4)-y	1.56	1.56	1.55	1.54
O(4)-z	2.46	2.41	2.41	2.36
O(5)-x	3.19	3.18	3.19	3.13
O(5)-y	1.56	1.56	1.55	1.54
O(5)-z	3.20	3.14	3.14	3.08
Ru(3)-x	3.19	3.18	3.19	3.13
Ru(3)-z	4.41	4.36	4.36	4.28
Ru(4)-y	1.56	1.56	1.55	1.54
Ru(4)-z	4.41	4.36	4.36	4.28
O(6)-x	1.19	1.23	1.23	1.20
O(6)-z	4.41	4.36	4.36	4.28
O(7)-x	-1.19	-1.23	-1.23	-1.20
O(7)-z	4.41	4.36	4.36	4.28

^aReference 2.

^bReference 3.

^cReference 4.

tual geometry as well as the fact that for the surface vibrations GGA seems to give a better description while for the bulk LDA has been shown to be superior.⁵

To be able to clearly separate surface modes and surface resonances from bulk modes, one needs slabs much thicker than those which can be afforded to be treated by *ab initio* methods. This problem was circumvented by using the slab filling method where the *ab initio* force constants for a thin slab are supplemented by bulk force constants (also obtained from *ab initio* calculations) to construct the results for a thick slab. In the following, results for slabs with 32 trilayers are being presented. LDA results are shown in Fig. 2. The most remarkable result is the effect that there are large regions where the system is unstable indicated by the disappearance of certain phonon branches. This happens around the S point, around the Y point as well as along the whole line Y - S . This instability also shows up in GGA calculations, and is thus independent of the exchange and correlation treatment. These results show that the (1×1) -structure is not the lowest energy structure for the clean $\text{RuO}_2(110)$ O-bridge terminated surface but that modulations with wave vectors along the whole Y - S line give rise to structures with lower energy.

To eliminate the possibility that these findings are an artifact of the pseudopotential treatment, we carried out a frozen-phonon calculation with the all-electron WIEN2K

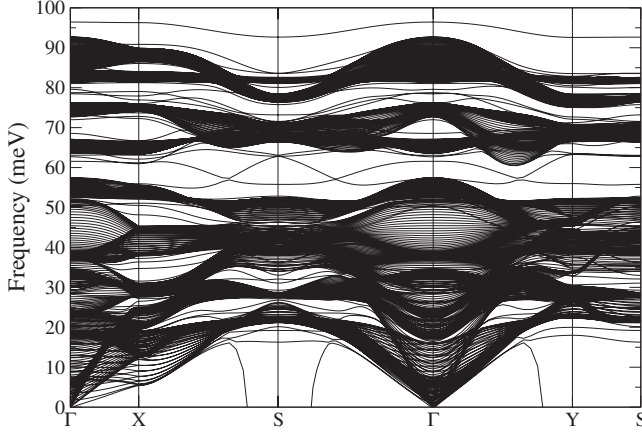


FIG. 2. Phonon dispersion for the (1×1) $\text{RuO}_2(110)$ O-bridge terminated surface along high-symmetry lines as obtained within LDA.

code¹⁶ based on an approximate eigenvector (corresponding to the Y -point instability). Parameters used in this calculation were the same as in Ref. 4. Results confirmed that the modulated structure had the lower energy compared to the Γ -point structure. Unfortunately, from the phonon spectrum we cannot predict which one would be the lowest energy structure. The simplest one would be a (1×2) reconstruction corresponding to the Y -point instability. Such a reconstruction is well established for the $\text{TiO}_2(110)$ surface, which is another system with the rutile structure.¹⁷

We have carried out a structural relaxation for the (1×2) geometry (since these calculations are very involved we have treated from now on only the LDA case) and found indeed a lower energy for a structure which was consistent with the eigenvector of the unstable phonon at Y . Details of the optimized (1×2) structure are given in Table II. Due to the doubling of the unit cell in the y direction there are now

two inequivalent atoms A and B for each species. For notation see Fig. 1(b). The biggest effect is a buckling of 0.1 \AA of the O-bridge atoms along the (001) direction with resulting buckling and pairing of Ru and O atoms in deeper layers. These effects decay however very quickly thus only the pairing of the Ru atoms in the second layers is a distortion in deeper layers beyond 0.01 \AA . The energy gain between the (1×2) and the (1×1) structure is very small indicating that structural modifications due to defects and/or due to the presence of a support material can influence the stability. This is consistent with the experimental difficulty to grow $\text{RuO}_2(110)$ films. So far only very thin films have been grown on $\text{Ru}(0001)$ with a thickness between 1 and 2 nm.¹

For the optimized (1×2) structure we have again calculated the phonon spectrum. The O-bridge-Ru stretch frequency now lies at 68 meV/ 78 meV within LDA. The two values for the (1×2) structure arise since we have two inequivalent O-bridge atoms (see Table I). For a slab with 32 trilayers obtained with the slab filling method results are shown in Fig. 3. This is a dynamically stable surface in contrast to the (1×1) . Knowing the full phonon dispersion the vibrational contribution to the free energy of the slab can be calculated in the quasiharmonic approximation according to

$$F_{\text{vib}}^{\text{Slab}}(T) = k_B T \sum_{q\lambda} \ln \left(2 \sinh \frac{\hbar \omega_{q\lambda}}{2k_B T} \right), \quad (1)$$

where the Boltzmann constant k_B , temperature T , and the frequency $\omega_{q\lambda}$ of a phonon of branch λ and momentum q enter. Subtracting the corresponding bulk vibrational free energy the surface vibrational free energy can be obtained. Results in the temperature range from 0 to 1000 K are given in Fig. 4 for the (1×2) structure. For comparison, results obtained with a phonon spectrum based on bulk force constants only as well as neglecting all relaxation effects are shown, too. Between 0 and 1000 K the vibrational free energy varies

TABLE II. Atomic positions in \AA for the (1×2) structure using the same notation as in Table I.

Atom	A	B	Atom	A	B
O(1)-y	1.54	-1.54	O(4)-y	1.54	-1.54
O(1)-z	-0.05	0.05	O(4)-z	2.36	2.37
Ru(1)-y	-0.02	3.09	O(5)-x	3.13	3.13
Ru(1)-z	1.07	1.07	O(5)-y	1.54	-1.54
Ru(2)-x	3.13	3.13	O(5)-z	3.08	3.08
Ru(2)-y	1.54	-1.54	Ru(3)-x	3.13	3.13
Ru(2)-z	1.23	1.23	Ru(3)-y	0.00	3.07
O(2)-x	1.94	1.94	Ru(3)-z	4.28	4.28
O(2)-y	0.00	3.07	Ru(4)-y	1.54	-1.54
O(2)-z	1.10	1.10	Ru(4)-z	4.28	4.28
O(3)-x	-1.94	-1.94	O(6)-x	1.20	1.20
O(3)-y	0.00	3.07	O(6)-y	0.00	3.07
O(3)-z	1.10	1.10	O(6)-z	4.28	4.28
			O(7)-x	-1.20	-1.20
			O(7)-y	0.00	3.07
			O(7)-z	4.28	4.28

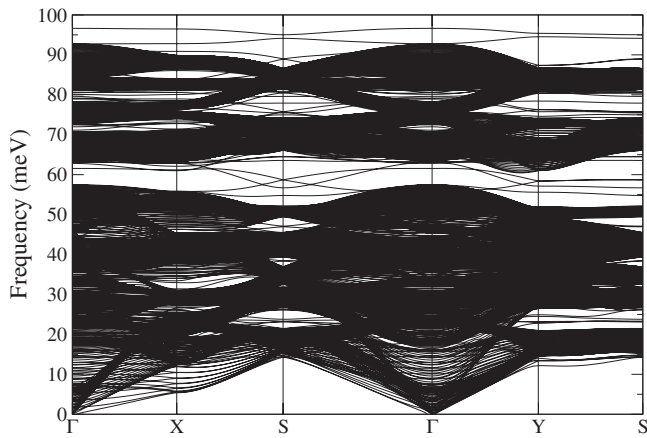


FIG. 3. Phonon dispersion for the reconstructed (1×2) $\text{RuO}_2(110)$ O-bridge terminated surface within LDA.

by roughly 8 meV. The contribution is always negative thus leading to a lowering of the surface-free energy compared to the surface energy.

Comparing these results with the estimation given in Ref. 3 based on a very simple Einstein model we see that the *ab initio* result is close to the upper limit value of this model assuming a 50% decrease in the Einstein mode frequencies at the surface.³ The large *ad hoc* frequency change at the surface necessary to get rough agreement with the *ab initio* results clearly demonstrates the limitations of the Einstein model approach. A reliable estimation of the vibrational surface-free energy is of course of crucial importance for studying surface-phase diagrams as function of T and P . Although the vibrational contribution is usually small, it strongly influences the boundary between energetically very similar phases as can be seen in Ref. 3 as well as in Ref. 18.

In summary, we have presented here an *ab initio* calcula-

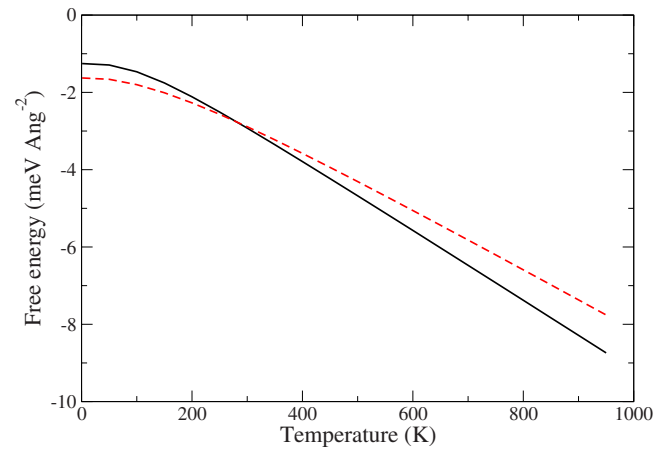


FIG. 4. (Color online) Surface vibrational free energy between $T=0$ K and $T=1000$ K. The full line gives exact results while the broken line was obtained with bulk force constants only.

tion of the phonon spectrum of $\text{RuO}_2(110)$ O-bridge terminated surface. The results show that the clean (1×1) surface is unstable and there is the tendency to reconstruct. The (1×2) structure has been shown to be lower in energy and to be dynamically stable. The surface vibrational contribution of the free energy has been calculated for the reconstructed (1×2) structure by *ab initio* methods and found to be as large as the upper limit considered in studies based on a simple Einstein model. A definite sign for this contribution has been obtained and a reliable estimate for the temperature variation could be obtained.

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