

***Ab initio* modeling of surface structure for SrTiO<sub>3</sub> perovskite crystals**E. Heifets,<sup>1,\*</sup> R. I. Eglitis,<sup>2</sup> E. A. Kotomin,<sup>3,4</sup> J. Maier,<sup>3</sup> and G. Borstel<sup>2</sup><sup>1</sup>*Carnegie Institution of Washington, 5251 Broad Branch Rd., N.W., Washington D.C. 20015*  
and *California Institute of Technology, MS 139-74, Pasadena, California 91125*<sup>2</sup>*Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany*<sup>3</sup>*Max Planck Institut für Festkörperforschung, Heisenbergstrasse, 1, D-70569 Stuttgart, Germany*<sup>4</sup>*Institute for Solid State Physics, University of Latvia, 8 Kengaraga Strasse, Riga LV-1063, Latvia*

(Received 29 May 2001; published 28 November 2001)

We present and discuss the results of calculations of SrTiO<sub>3</sub> (100) surface relaxation and rumpling with two different terminations (SrO and TiO<sub>2</sub>). These are based on *ab initio* Hartree-Fock method with electron correlation corrections and density functional theory calculations with different exchange-correlation functionals, including hybrid exchange techniques. Both approaches use the localized Gaussian-type basis set. All methods agree well on surface energies and on atomic displacements, as well as on considerable increase of covalency effects nearby the surface. More detailed experiments on surface rumpling and relaxation are necessary for further testing theoretical predictions.

DOI: 10.1103/PhysRevB.64.235417

PACS number(s): 68.35.Bs, 68.35.Md, 68.47.Gh

Thin films of ABO<sub>3</sub> perovskite ferroelectrics are important for many high-tech applications including high capacity memory cells, catalysis, optical wave guides, integrated optics applications, substrates for high- $T_c$  cuprate superconductor growth, etc.,<sup>1-4</sup> for which surface structure and quality are of primary importance. In this study, we calculated the relaxed atomic structure of the SrTiO<sub>3</sub> (100) surface for the cubic phase. The SrTiO<sub>3</sub> (100) surface relaxation has been experimentally studied by means of low energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), medium energy ion scattering (MEIS), and surface x-ray diffraction (SXRD) measurements.<sup>5-9</sup> Recently, several *ab initio*<sup>10-16</sup> and shell model (SM) (Refs. 17-20) theoretical studies were published for the (100) surface of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> crystals. In order to check how sensitive surface relaxation properties are to details of the *ab initio* methods used in calculations, i.e., exchange-correlation functionals, pseudopotentials, and localized/plane wave basis set, in this report we performed a detailed comparative study based on a number of different techniques. We employed several methods: HF with different DFT-type *a posteriori* electron correlation corrections to the total energy<sup>21</sup> such as generalized gradient approximation (HFGGA), Perdew-91 (HFPer91), Lee, Yang, Parr (HFLYP) and full-scale DFT calculations based on the Kohn-Sham equation with a number of exchange-correlation functionals, including local density approximation (LDA), generalized gradient approximations (GGA) by Perdew and Wang (PW), Perdew, Burke, and Ernzerhof (PBE), as well as Becke exchange functional with Lee-Yang-Parr correlation functional (BLYP). We also included a comparison with *hybrid* HF-DFT exchange functionals, in which Hartree-Fock exchange was mixed with DFT exchange functionals using Becke's three parameter method, combined with the non-local correlation functionals by Perdew and Wang (B3PW), as those by Lee, Yang, and Parr (B3LYP). For all calculations, we used the CRYSTAL-98 computer code (see Ref. 22, and references therein for all mentioned techniques), in which both (HF/DFT) types of calculations are implemented on equal grounds. Unlike pre-

vious plane-wave calculations, this code uses the localized Gaussian-type basis set. In our simulations we applied the standard basis set recommended for SrTiO<sub>3</sub>.<sup>22</sup> Another advantage of the CRYSTAL-98 code is its treatment of purely two-dimensional slabs, without artificial periodicity in the direction perpendicular to the surface, commonly employed in most other surface calculations (e.g., Refs. 10 and 16).

For optimization of atomic coordinates through minimization of the total energy per unit cell, we wrote a small code that implements conjugated gradients optimization technique<sup>25</sup> with numerical computation of derivatives. Using this code, we optimized the atomic positions in several top layers of a SrTiO<sub>3</sub> slab consisting of seven planes terminated by TiO<sub>2</sub>, or by SrO on both sides of symmetrical a slab.

Before starting the surface calculations, we tested these methods on the bulk properties, the lattice constant  $a_0$  and the bulk modulus  $B$  (Table I). LDA calculations are found to underestimate  $a_0$  by 0.8% and overestimate  $B$  by 20%. The

TABLE I. The optimized lattice constant  $a_0$  and bulk modulus  $B$  for the bulk SrTiO<sub>3</sub> as calculated using DFT and HF approaches. Experimental values:  $a_0$  (extrapolated to 0 K) = 3.89 Å,  $B$  = 179 GPa (Ref. 23). Bulk modulus is calculated using fourth order polynomials, numbers in brackets are results of the fit to the standard Murnaghan equation of the state (Ref. 24).

Method	$a_0$ , Å	$B$ , GPa
DFT: LDA	3.86	215 (210)
BLYP	3.98	165 (157)
PWGGA	3.93	195 (176)
PBE	3.93	195 (171)
Hybrid: B3LYP	3.94	187 (184)
B3PW	3.91	186 (191)
HF: HF	3.93	211 (208)
HF GGA	3.83	253 (245)
HF P91	3.83	252 (245)
HFLYP	3.86	244 (237)

TABLE II. Atomic relaxation of uppermost three layers (in percent of lattice constant) for SrTiO<sub>3</sub> (100) found for the *ab initio* HF and DFT calculations (see text). Positive (negative) values refer to displacements in the direction outwards (inwards) the surface. Note that in DFT calculations only atomic positions in the two outermost planes were optimized. References 10 and 16 refer to LDA-plane wave calculations with Ceperley-Alder exchange-correlation functionals using ultrasoft pseudopotentials and norm-conserving semilocal (Ref. 26) pseudopotentials.

(a) TiO <sub>2</sub> -terminated SrTiO <sub>3</sub> surface													
N	Ion	(Ref. 10)	(Ref. 16)	DFT (Kohn Sham)						Hartree-Fock with <i>a posteriori</i> corrections			
				LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF	HFGGA	HF P91	HFLYP
1.	Ti <sup>4+</sup>	-3.4	-1.79	-2.12	-2.03	-2.19	-2.28	-1.88	-2.31	-2.74	-3.20	-3.19	-3.05
	O <sup>2-</sup>	-1.6	-0.26	-1.11	-0.72	-0.93	-0.90	-0.57	-1.19	-1.38	-2.20	-2.20	-1.87
2.	Sr <sup>2+</sup>	2.5	4.61	2.21	2.38	2.18	2.64	2.75	2.04	1.91	1.81	1.93	1.87
	O <sup>2-</sup>	-0.5	0.77	0.07	0.21	0.01	0.12	0.45	0.0	-0.13	-0.15	-0.17	-0.17
3.	Ti <sup>4+</sup>	-0.7	-0.26							-0.26	-0.28	-0.28	-0.28
	O <sup>2-</sup>	-0.5	0.26							-0.05	-0.13	-0.14	-0.14

(b) SrO-terminated SrTiO <sub>3</sub> surface													
N	Ion	(Ref. 11)	(Ref. 17)	DFT (Kohn Sham)						Hartree-Fock with <i>a posteriori</i> corrections			
				LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF	HFGGA	HF P91	HFLYP
1.	Sr <sup>2+</sup>	-5.7	-6.66	-4.91	-4.28	-4.29	-4.57	-4.60	-4.30	-2.61	-4.16	-4.13	-3.74
	O <sup>2-</sup>	0.1	0.02	0.92	0.64	0.61	0.78	1.00	1.03	1.56	0.41	0.35	0.10
2.	Ti <sup>4+</sup>	1.2	1.79	1.20	1.16	1.25	1.34	1.30	1.20	0.79	0.48	0.48	0.56
	O <sup>2-</sup>	0.0	0.26	0.48	0.86	0.85	0.86	0.67	0.55	0.51	0.23	0.17	0.27
3.	Sr <sup>2+</sup>	-1.2	-1.54							-0.49	-0.69	-0.69	-0.70
	O <sup>2-</sup>	-0.1	0.26							0.01	-0.25	-0.02	-0.14

HF method without any correlation corrections overestimates both  $a_0$  (by 1%) and  $B$  (by 16%). HF with GGA corrections makes  $a_0$  too small (by -1.5%) but  $B$  even larger (by 41%). The hybrid B3PW method gives much better result for  $B$  (a discrepancy by 4%) and by only 1% overestimates  $a_0$ . In other words, it is quite difficult to choose the optimal method reproducing all properties equally well, but the hybrid B3PW method looks the best.

The atomic displacements in the outmost SrTiO<sub>3</sub> planes obtained here using various *ab initio* methods (see Table II) are in qualitative agreement with previous plane wave calculations.<sup>11,16</sup> Both DFT and HF with correlation effects predict Sr displacement on the SrO-terminated surface to be larger than that for Ti atom on the TiO<sub>2</sub>-terminated surface, also in agreement with previous *ab initio* calculations. All theoretical methods predict surface O atom inward relaxation for the TiO<sub>2</sub> termination, in contrast to the SrO termination. Relaxation of atoms in the third plane is already quite small.

Atomic displacements, the effective static charges (obtained using the Mulliken population analysis), and bond populations between nearest metal and oxygen atoms are given in Table III. For the analysis we use the B3PW results. The major effect observed here is strengthening of the Ti-O chemical bond near the surface, which is already pronounced in the bulk. Note that Ti and O effective charges ( $2.3e$  and  $-1.4e$ , respectively) are much smaller than those expected in an ionic model; furthermore the Ti-O bond is considerably populated ( $82me$ ,  $m = \text{milli}$ ). The Ti-O bond population for

the TiO<sub>2</sub>-terminated surface is  $128me$ , which is about 50% larger than the relevant values in the bulk. The Ti-O populations in the direction perpendicular to the surface, i.e., between Ti and O atoms in the first and second, the second and third plane, and lastly, the third and fourth planes ( $124me$ ,  $92me$ , and  $84me$ ) also exceed the bulk value. In contrast, the Sr-O populations are very small and even negative which indicates the repulsion. This effect is also well seen from the Sr effective charges, which is close to the formal ionic charge of  $+2e$ .

Figures 1(a) and 1(c) (total electron densities) confirm the Ti-O covalency effects discussed above, whereas the difference electron density maps [Figs. 1(b) and 1(d)] (calculated with respect to Sr<sup>2+</sup>, Ti<sup>4+</sup>, and O<sup>2-</sup> ions) demonstrate considerable charge density redistribution for both SrTiO<sub>3</sub> surface terminations. These maps show that there is no trace of covalent bonding between Sr and O atoms. The Sr atoms nearest to the surface are polarized. Their electronic density is shifted inwards the bulk on TiO<sub>2</sub>-terminated surface and outwards on the SrO-terminated surface. For both terminations the nearest to the surface Ti-O bond becomes stronger, but the next nearest bond becomes weaker. All these observations, made from the electronic density maps, are entirely consistent with Mulliken charges and bond population analysis in the Table III.

In order to calculate the surface energy, we start with the cleavage energy for unrelaxed SrO- and TiO<sub>2</sub>-terminated sur-

TABLE III. Calculated absolute magnitudes of atomic displacements  $d$  (in Å), the effective atomic charges  $Q$  (in  $e$ ) and bond populations  $P$  between nearest Me-O atoms (in  $me$ ) for the TiO<sub>2</sub> and SrO terminations.

(a) TiO <sub>2</sub> -terminated SrTiO <sub>3</sub> surface							(b) SrO-terminated SrTiO <sub>3</sub> surface								
No.	Ion	DFT		Hartree-Fock		No.	Ion	DFT		Hartree-Fock					
		B3PW	B3LYP	HF	HFGG			B3PW	B3LYP	HF	HFGG				
1.	Ti <sup>4+</sup>	$D$	-0.086	-0.079	-0.107	-0.1245	1	Sr <sup>2+</sup>	$d$	-0.168	-0.168	-0.102	-0.162		
		$Q$	2.165	2.197	2.507	2.502			$Q$	1.829	1.833	1.897	1.894		
		$P$	128	124	146	142			$P$	-4	-2	-20	-20		
	O <sup>2-</sup>	$D$	-0.037	-0.028	-0.054	-0.0856		2	Ti <sup>4+</sup>	$d$	0.024	0.025	0.061	0.016	
		$Q$	-1.241	-1.257	-1.395	-1.400				$Q$	-1.44	-1.459	-1.581	-1.555	
		$P$	-10	-10	-28	-30				$P$	166	160	198	208	
2.	Sr <sup>2+</sup>	$D$	0.085	0.094	0.074	0.0705	2		O <sup>2-</sup>	$d$	0.32	0.033	0.020	0.009	
		$Q$	1.833	1.834	1.890	1.888				$Q$	-1.423	-1.434	-1.517	-1.523	
		$P$	-10	-8	-20	-20				$P$	-10	-8	-20	-20	
	3.	Ti <sup>4+</sup>	$D$			-0.010		-0.011	3	Sr <sup>2+</sup>	$d$			-0.019	-0.027
			$Q$	2.269	2.313	2.553		2.552			$Q$	1.857	1.855	1.907	1.906
			$P$	86	86	114		114			$P$	-10	-8	-22	-22
Bulk		Ti <sup>4+</sup>	$D$			-0.002	-0.005	Bulk		Ti <sup>4+</sup>	$d$			0.0	-0.01
			$Q$	-1.363	-1.376	-1.476	-1.476				$Q$	-1.398	-1.409	-1.508	-1.503
			$P$	-10	-8	-22	-22				$P$	80	80	108	108
	O <sup>2-</sup>	$D$					Bulk		O <sup>2-</sup>	$d$					
		$Q$	2.272	2.325	2.584	2.50				$Q$	2.272	2.325	2.584	2.50	
		$P$	82	74	112	100				$P$	82	74	112	100	
Sr <sup>2+</sup>	$D$					Bulk		O <sup>2-</sup>	$d$						
	$Q$	-1.375	-1.392	-1.497	-1.466				$Q$	-1.375	-1.392	-1.497	-1.466		
	$P$	-10	-8	-20	-28				$P$	-10	-8	-10	-28		
Sr <sup>2+</sup>	$D$						Bulk	Sr <sup>2+</sup>	$d$						
	$Q$	1.852	1.852	1.909	1.898				$Q$	1.852	1.852	1.909	1.898		
	$P$								$P$						

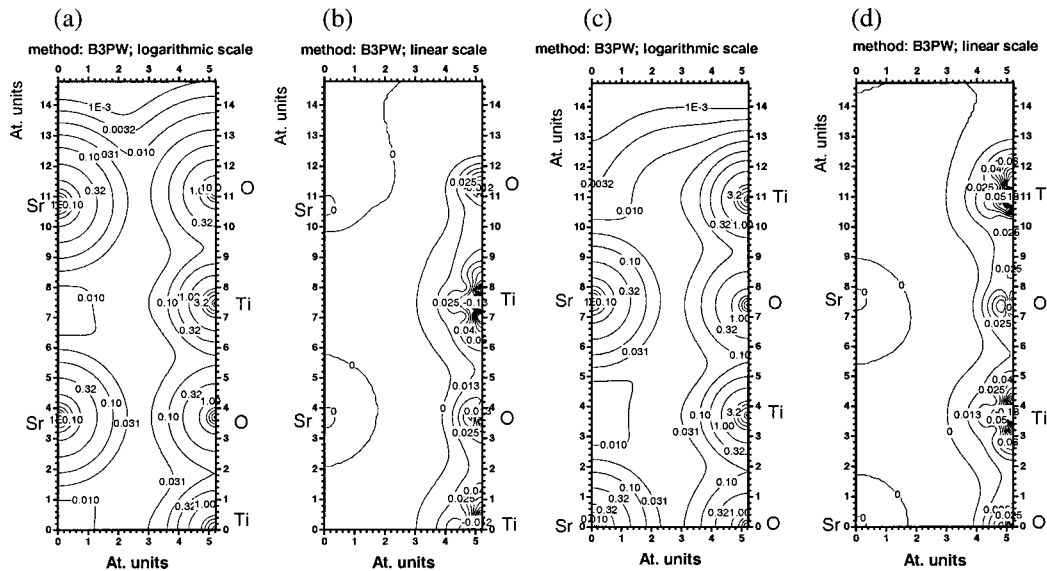


FIG. 1. The total (a and c) and difference (b and d) electron density maps in the cross section perpendicular to the (100) surface with SrO (a,b) and TiO<sub>2</sub> (c,d) terminations.

TABLE IV. Calculated surface energies (in eV per surface cell). Results for Refs. 10 and 16 are averaged over both surfaces.

			DFT (Kohn Sham)						Hartree-Fock with <i>posteriori</i> corrections			
	(Ref. 10)	(Ref. 16)	LDA	B3LYP	B3PW	BLYP	PBE	PWGGA	HF	HFGGA	HF P91	HFLYP
	SrO	1.26	1.21	1.19	1.19	1.18	1.17	1.20	1.16	1.38	1.25	1.26
TiO <sub>2</sub>			1.23	1.24	1.22	1.22	1.25	1.21	1.42	1.28	1.30	1.33

faces. In our calculations the two seven layer SrO- and TiO<sub>2</sub>-terminated slabs represent together seven bulk unit cells. Surfaces with both terminations arise simultaneously under cleavage of the crystal and the relevant cleavage energy is distributed equally between created surfaces. Therefore, we assume that the cleavage energy is the same for both terminations:

$$E_s^{(\text{unrel})} = \frac{1}{4} [E_{\text{slab}}^{(\text{unrel})}(\text{SrO}) + E_{\text{slab}}^{(\text{unrel})}(\text{TiO}_2) - 7E_{\text{bulk}}],$$

where  $E_{\text{slab}}^{(\text{unrel})}(\text{SrO})$  and  $E_{\text{slab}}^{(\text{unrel})}(\text{TiO}_2)$  are unrelaxed SrO- and TiO<sub>2</sub>-terminated slab energies,  $E_{\text{bulk}}$  energy per a bulk unit cell, and a factor of four comes from the fact that we create four surfaces upon cleavage procedure. Next, we can calculate the (negative) relaxation energies for each of SrO and TiO<sub>2</sub> terminations, when both sides of slabs relax:

$$E_{\text{rel}}(A) = \frac{1}{2} [E_{\text{slab}}(A) - E_{\text{slab}}^{(\text{unrel})}(A)],$$

$E_{\text{slab}}(A)$  is a slab energy after relaxation,  $A = \text{SrO}$  or  $\text{TiO}_2$ . Lastly, the surface energy sought for is just a sum of the cleavage and relaxation energies

$$E_s(A) = E_s^{(\text{unrel})} + E_{\text{rel}}(A).$$

The results of calculations for the surface energy of relaxed surfaces  $E_s$  are presented in Table IV. In all calculations the  $E_s$  values for SrO termination are slightly smaller than for the TiO<sub>2</sub> termination. However, the energy difference is small and both surfaces are stable and energetically equally favorable, in agreement with the experimental observation.<sup>5</sup> Note that the surface energy of 1.37 eV/cell, which was calculated for TiO<sub>2</sub>-terminated surface by the SM approach,<sup>20</sup> is also slightly larger than the surface energy for SrO termination (1.33 eV/cell). The *ab initio* LAPW calculations<sup>14</sup> gave similar average surface energies of 1.27 eV/cell.

For both SrO and TiO<sub>2</sub> terminations, surface relaxation is characterized by the surface rumpling ( $s$ ) (the relative displacement of O with respect to a metal atom in the first plane), interplane distances between top metal and the second crystal layers ( $\Delta d_{12}$ ), and between the second and the third crystal layers ( $\Delta d_{23}$ ). Our calculations of the interplane distances are based on the metal ion (Ti or Sr) displacements from unrelaxed planes, which are known to be much stronger electron scatters than O ions.<sup>5</sup>

A comparison of a series of our HF and DFT calculations with the two previous *ab initio* plane-wave studies<sup>10,16</sup> and

TABLE V. Surface rumpling  $s$ , and relative displacements of the three near-surface planes for the Sr- and Ti-terminated SrTiO<sub>3</sub> (100) surfaces (in percent of the bulk lattice parameters).

Method	SrO-terminated			TiO <sub>2</sub> -terminated		
	$s$	$\Delta d_{12}$	$\Delta d_{23}$	$s$	$\Delta d_{12}$	$\Delta d_{23}$
DFT LDA	5.8	-6.1		1.0	-4.3	
BLYP	5.4	-5.9		1.3	-4.9	
PBE	5.6	-5.9		1.3	-4.6	
PWGGA	5.3	-5.5		1.1	-4.4	
B3LYP	4.9	-5.4		1.3	-4.4	
B3PY	4.9	-5.5		1.3	-4.4	
HF	4.2	-3.4	1.3	1.4	-4.7	2.2
HF-GGA	4.6	-4.6	1.2	1.0	-5.0	2.1
HF-P91	4.5	-4.6	1.2	1.0	-5.0	2.1
HF-LYP	3.8	-4.3	1.3	1.2	-4.9	2.2
<i>Ab initio</i> (Ref. 10)	5.8	-6.9	2.4	1.8	-5.9	3.2
<i>Ab initio</i> (Ref. 16)	7.7	-8.6	3.3	1.5	-6.4	4.9
Shell model (Ref. 18)	4.5	-4.8	1.5	1.1	-4.0	1.2
Shell model (Ref. 20)	8.2	-8.6	3.0	1.2	-6.4	4.0
LEED expt. (Ref. 5)	4.1±2	-5±1	2±1	2.1±2	1±1	-1±1
RHEED expt. (Refs. 6,7)	4.1	2.6	1.3	2.6	1.8	1.3

SM calculations<sup>20</sup> is presented in Table V. The agreement is quite good for all applied functionals. All theoretical methods (both quantum mechanical, irrespective on particular exchange-correlation functional and basis set type, and SM) give the same signs for both the rumpling and change of the interplanar distances. They predict much larger rumpling for the SrO surface in comparison to that for the TiO<sub>2</sub> surface, compression of the distance between the first and second planes, and its expansion for the second and third planes.

In general, the results of the LEED experiments<sup>5</sup> agree quite well with our B3PW calculations (except for the compression of the distance between second and third planes in the SrO termination case). It was also found in recent MEIS experiments<sup>8</sup> that on the Ti-terminated SrTiO<sub>3</sub> surface  $s \approx 1.5\%$  which again is in agreement with our results. Note, however, that the LEED and RHEED experiments contradict each other in the sign of the  $\Delta d_{12}$  for SrO-terminated surface. Another problem is that LEED, RHEED, and MEIS experiments argue that the topmost O atoms always move outwards from the surface whereas all calculations predict for the TiO<sub>2</sub> terminated surface that O atoms go *inwards*. The reason for this is not clear and discussed in Refs. 9 and 10. Even more important is a clear contradiction between three abovementioned experiments and recent SXRD (Ref. 9)

where oxygen atoms are predicted to move inwards for *both* surface terminations, reaching 12.5% for the TiO<sub>2</sub> surface. It is obvious that conflicting experimental results should be resolved before further comparison with theoretical calculations.

Summing up, a comparison of *ab initio* HF and DFT calculations employing different exchange-correlation functionals and localized/plane wave basis clearly demonstrates their good agreement for the *rumpling* and the relative displacements of the second and third planes nearby the SrTiO<sub>3</sub> surface. In contrast, four types of electron diffraction experiments used so far clearly contradict each other. Our *ab initio* calculations indicate considerable increase of the Ti-O bond covalency near the surface. This could be important for the electronic structure of surface defects, as well as for adsorption and surface diffusion of atoms and small molecules relevant for catalysis.

This study was partly supported by ONR Grant No. N00014-97-1-0052 (E.H., grant to R. E. Cohen) and by European Center of Excellence in Advanced Material Research and Technology in Riga, Latvia (Contract No. ICA-I-CT-2000-7007 to E.A.K.). Authors are indebted to R. E. Cohen, R. Dovesi, C.R.A. Catlow, F. Cora, R. Resta, R. de Souza, S. Piskunov, and D. Vanderbilt for fruitful discussions.

\*Corresponding author. E-mail address: heifets@wag.caltech.edu

<sup>1</sup>C. Noguera, *Physics and Chemistry at Oxide Surfaces* (Cambridge University Press, New York, 1996).

<sup>2</sup>M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).

<sup>3</sup>O. Auciello, J. F. Scott, and R. Ramesh, *Phys. Today* **July**, 22 (1998).

<sup>4</sup>Proceedings of the Williamsburg Workshop on Fundamental Physics of Ferroelectrics-99 [J. Phys. Chem. Solids **61**, 139-333 (2000)].

<sup>5</sup>N. Bickel, G. Schmidt, K. Heinz, and K. Müller, *Phys. Rev. Lett.* **62**, 2009 (1989).

<sup>6</sup>T. Hikita, T. Hanada, M. Kudo, and M. Kawai, *Surf. Sci.* **287/288**, 377 (1993).

<sup>7</sup>M. Kudo, T. Hikita, T. Hanada, R. Sekine, and M. Kawai, *Surf. Interface Anal.* **22**, 412 (1994).

<sup>8</sup>Y. Kido, T. Nishimura, Y. Hoshido, and H. Mamba, *Nucl. Instrum. Methods Phys. Res. B* **161–163**, 371 (2000).

<sup>9</sup>G. Charlton, S. Brennan, C. A. Muryn, R. McGrath, D. Norman, T. S. Turner, and G. Thornton, *Surf. Sci.* **457**, L376 (2000).

<sup>10</sup>J. Padilla and D. Vanderbilt, *Surf. Sci.* **418**, 64 (1998).

<sup>11</sup>J. Padilla and D. Vanderbilt, *Phys. Rev. B* **56**, 1625 (1997).

<sup>12</sup>B. Meyer, J. Padilla, and D. Vanderbilt, *Faraday Discuss.* **114**, 395 (1999).

<sup>13</sup>F. Cora and C. R. A. Catlow, *Faraday Discuss.* **114**, 421 (1999).

<sup>14</sup>R. E. Cohen, *Ferroelectrics* **194**, 323 (1997).

<sup>15</sup>L. Fu, E. Yashenko, L. Resca, and R. Resta, *Phys. Rev. B* **60**, 2697 (1999).

<sup>16</sup>C. Cheng, K. Kunc, and M. H. Lee, *Phys. Rev. B* **62**, 10 409 (2000).

<sup>17</sup>V. Ravikumar, D. Wolf, and V. P. Dravid, *Phys. Rev. Lett.* **74**, 960 (1995).

<sup>18</sup>J. Prade, U. Schröder, W. Kress, and de F. W. Kulkarni, *J. Phys.: Condens. Matter* **5**, 1 (1993).

<sup>19</sup>S. Tinte, and M. G. Stachiotti, in *Fundamental Physics of Ferroelectrics 2000*, edited by Ronald E. Cohen, AIP Conf. Proc. No. 535 (AIP, Melville, NY, 2000), p. 273.

<sup>20</sup>E. Heifets, E. A. Kotomin, and J. Maier, *Surf. Sci.* **462**, 19 (2000).

<sup>21</sup>M. Causa and A. Zupan, *Chem. Phys. Lett.* **220**, 145 (1994).

<sup>22</sup>V. R. Saunders, R. Dovesi, C. Roetti, M. Causa, N. M. Harrison, R. Orlando, and C. M. Zicovich-Wilson, *CRYSTAL-98 User Manual*, University of Torino, 1999, URL <http://www.ch.unito.it/ifm/teorica/crystal.html>

<sup>23</sup>*Ferroelectrics and Related Substances*, edited by K. H. Hellwege and A. M. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 3 (Springer Verlag, Berlin, 1969).

<sup>24</sup>URL <http://www.treasure-troves.com/physics/MurnaghanEquation.html>

<sup>25</sup>W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN 77*, and 2nd ed. (Cambridge University Press, Cambridge, MA, 1997); URL [http://www.ulib.org/webRoot/Books/Numerical Recipes/](http://www.ulib.org/webRoot/Books/Numerical%20Recipes/)

<sup>26</sup>J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, *Phys. Rev. B* **47**, 4174 (1993).