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Influence of gradient corrections on the bulk and surface properties of TiO_2 and SnO_2

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First-principles calculations based on density-functional theory and the pseudopotential method have been used to investigate the influence of gradient corrections to the standard local-density-approximation technique on the equilibrium structure and energetics of rutile TiO_2 and SnO_2 perfect crystals and their (110) surfaces. We find that gradient corrections increase the calculated lattice parameters by roughly 3%, as has been found for other types of material. Gradient corrections give only very minor changes to the equilibrium surface structure, but reduce the surface energies by about 30%.

I. INTRODUCTION

Most first-principles calculations on condensed matter are based on density-functional theory.[1–5] This theory is formally exact, but in practice an approximation has to be made to the exchange-correlation energy, and the vast majority of calculations employ the local-density approximation (LDA). The basic assumption is that the exchange-correlation energy per electron at any point in the system is related to the electron density at that point in the same way as in a uniform electron gas, and density gradients are ignored. Some theoretical justification can be given for this,[6–8] and in practice the LDA works well in a wide range of situations. However, its accuracy is not always satisfactory, particularly when energy differences associated with changes of bonding are needed, as in, e.g., molecular dissociation or the adsorption of molecules at surfaces. Attempts to improve the situation by adding lowest-order corrections in powers of the density gradient are not successful, but important progress has been made recently by requiring that the dependence of the energy on the gradients satisfies certain physical requirements. This has led to various forms of generalized gradient corrections (GGC).[9–13]

In the past few years, there has been a large amount of work on the influence of different GGC schemes on the total energies of atoms and molecules,[9–11,14–17] the equilibrium structure and cohesive energies of covalent crystals,[18–22] the ground state of iron,[23,24] and the energetics of molecular adsorption on metal surfaces.[25–27] However, as far as we are aware, there has been little work on the effect of GGC on the properties of partially ionic materials such as the oxides TiO_2 and SnO_2 treated here. The surface properties of materials such as these are extremely important because of their application as gas sensors and catalysts. We have recently reported a detailed study of the bulk and surface properties of SnO_2,[28,29] and we have initiated work on the interaction of molecules with the surfaces of both TiO_2 and SnO_2.[30] An understanding of GGC is of considerable importance in this general area. The goal of the present paper is to study the effect on the bulk and surface properties of TiO_2 and SnO_2 of the two widely used GGC schemes due to Perdew and Wang[10,11] and Becke and Perdew.[10,12]

II. TECHNIQUES

The calculations are performed using the pseudopotential method,[4,5] so that only the valence electrons are represented explicitly, the valence-core interaction being represented by nonlocal norm-conserving pseudopotentials, which are generated by first-principles calculations on isolated atoms. Pe-

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TABLE I. Comparison of theoretical and experimental values of lattice parameters a and c and the internal coordinate u of SnO_2 and TiO_2. The theoretical values are calculated using the Ceperley-Alder form of LDA, and the Perdew-Wang (PW) and Becke-Perdew (BP) forms of GGC. Experimental values are from Ref. 40.

		a (Å)		c (Å)		c/a	u
SnO_2	LDA	4.645	(-1.9%)	3.060	(-4.0%)	0.659	0.307
	PW	4.868	(2.8%)	3.183	(0.0%)	0.654	0.307
	BP	4.809	(1.5%)	3.159	(-0.8%)	0.657	0.307
	Expt.	4.737		3.186		0.673	0.307
TiO_2	LDA	4.625	(0.7%)	2.911	(-1.6%)	0.629	0.305
	PW	4.781	(4.1%)	3.072	(3.9%)	0.643	0.305
	BP	4.747	(3.3%)	3.039	(2.7%)	0.640	0.305
	Expt.	4.594		2.958		0.644	0.305

riodic boundary conditions are used, with the occupied electronic orbitals expanded in a plane-wave basis. The expansion includes all plane waves whose kinetic energy $\hbar^2k^2/2m$ (k the wave vector, m the electronic mass) is less than a chosen cutoff energy $E_{\rm cut}$. The inclusion of gradient corrections within the pseudopotential plane-wave technique has recently been discussed in detail by White and Bird,[31] who show that a robust and accurate calculation of the GGC exchange-correlation energy and potential can be achieved by summation on exactly the same real-space grid as would be used for the LDA. This technique has been used in the present work.

The first-principles pseudopotentials in Kleinman-Bylander representation[32] were generated using the optimization scheme of Lin *et al.*[33] in order to reduce the required value of the plane-wave cutoff $E_{\rm cut}$. The pseudopotentials used in the GGC calculations were constructed consistently by including gradient corrections in the generation scheme. The Sn pseudopotential was generated using the $5s^25p^2$ configuration for s- and p-wave components, and the $5s^15p^{0.5}5d^{0.5}$ configuration for the d wave. The core radii were equal to 2.1, 2.1, and 2.5 a.u. for the s, p, and d components, respectively. The Ti pseudopotential was generated using the $4s^{1.85}3d^2$ configuration for s and d waves and the $4s^14p^{0.5}3d^{0.5}$ configuration for the p wave, with core radii of 2.2, 1.5, and 2.4 a.u. for s, p, and d waves, respectively. The oxygen pseudopotential used in our LDA calculations was generated using the $2s^22p^4$ configuration for the s and p waves and the $2s^22p^{2.5}3d^{0.5}$ configuration for the d wave, with a single core radius of 1.65 a.u. For the gradient-corrected oxygen pseudopotential, we have used the single configuration $2s^22p^{3.5}3d^{0.45}$ and the same core radius. The use of a core radius of 1.65 a.u. means that there is an appreciable overlap of the oxygen and metal core spheres in the SnO_2 and TiO_2 crystals, and in principle this could cause inaccuracies. However, direct comparisons of the present results with our earlier work on SnO_2,[29] which employed an oxygen pseudopotential with the smaller core radius of 1.25 a.u., show that any errors due to core overlap are very small. The calculations have been done using a plane-wave cutoff $E_{\rm cut}$ of 600 eV for SnO_2 and 1000 eV for TiO_2. Our tests show that with these cutoffs the energy per unit cell is converged to within 0.2 eV, the convergence with respect to $E_{\rm cut}$ not being noticeably influenced by the inclusion of gradient corrections, even though the gradient corrected pseudopotentials are less smooth and regular than the LDA ones.[18,34]

The calculations were performed using the CETEP code[35] (the parallel version of the serial CASTEP code[5]) running on the 64-node Intel iPSC/860 machine at Daresbury Laboratory. The code uses the band-by-band conjugate-gradient technique to minimize the total energy with respect to plane-wave coefficients. The LDA calculations were performed using the Ceperley-Alder exchange-correlation function.[36]

For the ground-state calculations Brillouin-zone sampling is performed using the lowest-order Monkhorst-Pack set of k points,[37] as in our earlier work on SnO_2.[28] Electronic densities of states (DOS) associated with the ground state were calculated using the tetrahedron method,[38,39] with k-point sampling corresponding to 750 tetrahedra in the whole Brillouin zone.

III. RESULTS AND DISCUSSION

A. Perfect SnO_2 and TiO_2 crystals

The 6-atom rutile unit cell of SnO_2 and TiO_2 is characterized by the two lattice parameters a and c and the internal parameter u: the positions of the four oxygens are $(\pm u, \pm u, 0)$, $(\frac{1}{2}\pm u, \frac{1}{2}\mp u, \frac{1}{2})$. The equilibrium structure has then been determined by relaxation with respect to the lattice parameters a and c and the internal parameter u. The equilibrium values of these parameters both with and without gradient corrections are given in Table I.

As usually happens, there is a tendency for the LDA to underestimate the lattice parameter. This is especially noticeable for SnO_2, where there may also be an effect due to our treatment of the 4d shell as part of the core. The inclusion of gradient corrections tends to increase the lattice parameters, as has already been found for semiconducting and metallic systems.[18,21,22] The increase is 4% or more for the Perdew-Wang GGC, and leads to results for a and c that are appreciably greater than experimental values. For the Becke-Perdew GGC, the increase is roughly 3%. Both the c/a ratio and the u parameter are almost unaffected, and this suggests that the gradient corrections have the effect of an isotropic negative pressure, as pointed out by Seifert *et al.*[22]

TABLE II. Comparison of calculated bond length modifications on SnO_2 (110) and TiO_2 (110) with respect to the bulk values for LDA and the Perdew-Wang (PW) and Becke-Perdew (BP) forms of GGC exchange correlation.

	SnO_2			TiO_2		
	LDA	PW	BP	LDA	PW	BP
O_{IV} - M_{II}	-4.5%	-4.9%	-4.2%	-5.6%	-5.5%	-5.6%
O_I - M_I	-3.7%	-4.0%	-3.8%	-4.9%	-5.5%	-5.5%
O_{II} - M_{II}	-1.2%	-1.2%	-1.2%	-0.9%	-1.2%	-1.2%
O_{III} - M_I	4.3%	4.3%	4.8%	4.6%	4.7%	4.5%
O_{II} - M_I	2.7%	2.9%	2.9%	2.3%	2.8%	2.8%

We have calculated the electronic DOS for the SnO_2 perfect crystal using both LDA and the two GGC schemes, but the changes caused by GGC are very small and we do not show the results here.

B. The SnO_2 and TiO_2 (110) surfaces

Our calculations on the stoichiometric (110) surface of both materials have been done with the usual repeating slab geometry. The rutile structure can be regarded as consisting of (110) planes of atoms containing both metal (M) and oxygen (O) atoms, separated by planes containing oxygen alone, so that the sequence of planes is O-M_2O_2-O-O-M_2O_2-O etc. The entire crystal can then be built up of symmetrical 3-plane O-M_2O_2-O units. The slabs we use contain three of these units, and our repeating cell contains 18 atoms (6M and 12 O). The perfect (110) surface consists of rows of bridging oxygens lying above a metal-oxygen layer. The vacuum separating the slabs has been taken wide enough to ensure that interactions between neighboring slabs are small. The width we use corresponds to two O-M_2O_2-O units, and is such that planes of bridging oxygens on the surfaces facing each other across the vacuum are separated by about 6.8 Å.

The surface structure has been determined by relaxing the entire system to equilibrium, and the calculations have been done with and without gradient corrections. As in our previous work on SnO_2 (110),[29] and the work of Ramamoorthy, King-Smith, and Vanderbilt on TiO_2 (110),[41] we find displacements of the surface atoms of order 0.1 Å, with fivefold and sixfold coordinated metal atoms (M_{II} and M_I) moving respectively into and out of the surface, in-plane oxygens (O_{II}) moving out and bridging oxygens (O_I) moving very little. The changes of the bond lengths between the surface atoms, including sub-bridging oxygens (O_{III}) and the uppermost oxygens (O_{IV}) of the following O-M_2O_2-O unit, for LDA and gradient corrected calculations are given in Table II. From these results, it is clear that gradient corrections have only a minor effect on the relaxed equilibrium structure. As we have already noted for the perfect crystal case, modifications of atomic structure with respect to LDA results are more pronounced in the Perdew-Wang scheme.

We have calculated the surface formation energy in the standard way, by subtracting from the slab total energy (18 atoms) three times the energy of a 6-atom perfect crystal unit cell and dividing by the total surface area. We report in Table III the relaxed surface energies of SnO_2 (110) and TiO_2 (110) calculated with the LDA and with the Perdew-Wang (PW) and Becke-Perdew (BP) versions of GGC. We note that our LDA result for SnO_2 is close to the value of 1.50 J m^{-2} reported earlier,[29] and that our LDA result for TiO_2 is close to the value of 1.06 J m^{-2} reported by Ramamoorthy, King-Smith, and Vanderbilt.[41] The results of Table III show that for both GGC schemes the surface energies are lowered by $\sim$ 30% with respect to the LDA values, and that the differences between the two GGC schemes are very small. The decrease of surface energy by GGC is consistent with the general tendency of gradient corrections to remove the systematic overestimation of electronic binding energy in the LDA.

The electronic DOS of the SnO_2 (110) surface using the LDA and the two GGC schemes are compared in Fig. 1. In order to separate out effects of electronic structure, all the

TABLE III. Relaxed surface energies of SnO_2 and TiO_2 (units of J m^{-2}) calculated using the LDA and the Perdew-Wang (PW) and Becke-Perdew (BP) forms of GGC.

	LDA	PW	BP
SnO_2	1.66	1.13	1.16
TiO_2	1.14	0.82	0.84

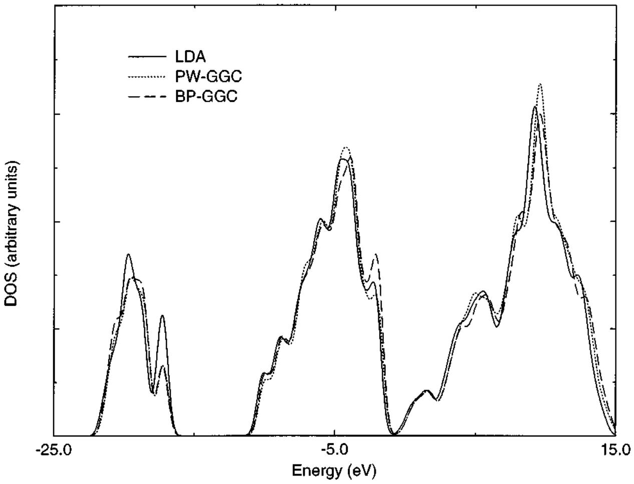

FIG. 1. The electronic DOS of the SnO_2 (110) surface for LDA (solid line), PW-GGC (dotted line) and BP-GGC (dashed line). The calculations are made at the equilibrium lattice parameters of the BP scheme. For presentation purposes, we have broadened the calculated DOS by Gaussians of width 0.5 eV.

calculations are done at the equilibrium lattice parameters and the relaxed positions produced by the BP scheme. Overall, the differences between the three sets of results are small. However, there are significant differences at the top of the valence band and at the top of the O$(2s)$ band. As we found in our previous work[28] there are peaks at the top of both bands due to surface states, these states being concentrated on the bridging oxygens. The effect of GGC is to reduce the intensity of the peak at the top of O$(2s)$ band. The effect on the intensity of the valence band peak is less systematic, since BP increases it but PW decreases it. The reason that these effects are interesting is that there appears to be no experimental evidence for the surface-state peak at the top of the valence band, so that the LDA predictions seems not to be consistent with experiment. The present results suggest the possibility that this inconsistency may be due to inaccurate treatement of exchange and correlation.

IV. CONCLUSIONS

Our calculations show that gradient corrections increase the lattice parameters of TiO_2 and SnO_2 by ~4% for the Perdew-Wang scheme and ~3% for the Becke-Perdew scheme. These effects are similar to those reported previously for metals and semiconductors. For the surfaces we examined, gradient corrections have very little effect on the relaxed surface structure, but the surface energies are substantially reduced – by ~ 30% in both the Perdew-Wang and the Becke-Perdew schemes. The effects of gradient corrections on the electronic DOS of SnO_2 (110) surface are very small, except at the top of the O$(2s)$ and O$(2p)$ bands. The changes we find at the top of the O$(2p)$ band may be relevant to apparent inconsistencies between calculated and experimental results for the surface DOS in this region.

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