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First principles calculation of the energy and structure of two solid surface phases on Ir{100}

Q. Ge^a, D.A. King^{a,*}, N. Marzari^{b,1}, M.C. Payne^b

^a Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, UK ^b Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK

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Abstract

The structure and energetics of the hexagonal reconstruction of $Ir\{100\}$ have been determined with first principles density functional theory calculations based on the local-density approximation with the generalised-gradient correction. The results reproduced the experimentally determined surface buckling and show the presence of some lateral displacement of the reconstructed (1×5) phase with respect to the ideal hexagonal close packed structure. The (1×5) phase is found to be $0.06 \text{ eV}/(1 \times 1 \text{ area})$ more stable than the (1×1) phase. The reconstruction is analysed by examining surface bonding. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

All clean surfaces of $Ir\{100\}$, $Pt\{100\}$ and $Au\{100\}$ reconstruct to give a corrugated hexagonal overlayer on top of the square face-centred-cubic (fcc) substrate. The details and periodicities of these so-called *hex* reconstructions are different in each case; $Ir\{100\}$ forms a relatively simple (1×5) structure, while $Pt\{100\}$ and $Au\{100\}$ display more complex superperiodic patterns [1].

The reconstruction can be removed through the interaction with strongly chemisorbed species on the surface. For example, the adsorption of gases such as CO, NO, H_2 , O_2 and C_2H_4 drives a phase transition for $Pt\{100\}$ from the initial hex phase to the (1×1) phase [2]. A non-linear growth law for this transition [3] has been demonstrated to be a key factor in explaining the oscillatory kinetics observed on $Pt\{100\}$ for the NO+CO [4], $CO + O_2$ [5] and $NO + H_2$ [6] reactions. The lifting of the reconstruction and the ability to prepare a clean metastable (1×1) surface have been used in the first calorimetric measurement of the energy difference between the two surface phases [7,8]. phase The reconstructed hex is about $0.12 \text{ eV}/(1 \times 1 \text{ area})$ more stable than the metastable (1×1) phase. This result contrasts with the result of an ab initio calculation performed using density functional theory together with the local density approximation and the all-electron fullpotential linear muffin tin orbital method [9]. The calculated reconstruction energy for $Pt\{100\}$ is

^{*} Corresponding author. Fax: +44 1223 336362; e-mail: eld8@cam.ac.uk

¹ Present address: Department of Physics and Astronomy, Rutgers University, 136 Frelinghuysen Road, Piscataway, NJ 08855-0849, USA.

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 $-0.03 \pm 0.05 \text{ eV}/(1 \times 1 \text{ area})$, i.e. the *hex* reconstruction is not quite favoured over the bulk-terminated (1 × 1) phase. It should be noted that this calculation for Pt uses structural data from a low energy electron diffraction (LEED) structure for Ir{100}-(1 × 5) [10], and no further atomic relaxation was allowed. This could explain why the theoretical result deviates from experiment; also, entropic effects could play an important role in the stabilisation of the lower symmetry *hex* phase even though the temperature is low.

Two possible top-to-second-layer registries are possible on Ir{100}: in the "two-bridge model" two of the six atoms in the (1×5) unit cell occupy precise bridge positions while in the "centre-top model" one atom takes a precise atop and another a precise hollow site. LEED experiments showed that the "two-bridge model" is favoured [1,10,11]. Since the metastable $Ir\{100\}$ -(1 × 1) and the stable $Ir\{100\}-(1\times 5)$ structures can each be routinely prepared by controlling experimental conditions. the dynamics of the reconstruction process has also been studied with LEED [12]. Owing to the higher density of surface atoms in the final hexagonal-like closed-packed phase than in the initial (1×1) phase, the existence of steps on the surface is inevitable. On the other hand, the average distance between the steps was believed to be of the order of, or larger than, 100 Å, because no beam splitting or broadening caused by steps was observed in the LEED pattern. The activation energy for the (1×1) to (1×5) transition was determined to be 0.88 eV.

There have been some efforts towards understanding the driving mechanism of the reconstruction. The *hex* reconstruction has been modelled in terms of surface tensile stress relief [9], the driving force being attributed to the tensile excess stress of the unreconstructed surfaces [9,13]. The (1×5) reconstruction could remove this surface stress, which originates from the d charge depletion from the surface layer. This point of view was later re-examined by Filippetti and Fiorentini [14]. They argued that, while part of the surface stress presented in the (1×1) phase is relieved by forming a more dense top layer, new stress is also generated in the reconstructed (1×5) phase, owing to mismatch between the surface layer and the substrate. They concluded that "no unique quantity (energy, or stress, e.g.) can be invoked as a general driving force of surface reconstruction for metals".

Experimental measurements of the energy difference between reconstructed and unreconstructed phases, as in the case of $Pt\{100\}$ [7], provide a benchmark and also pose a stimulating challenge to theoretical studies of surface reconstruction. In particular, it is important to assess the ability of state-of-the-art ab initio calculations to reproduce the experimental result, with an improved understanding of the physics underlying the transition. In the present paper we performed total energy calculations for the (1×1) and (1×5) phases of the $Ir\{100\}$ surface. The equilibrium structures and the total energies of the unreconstructed and reconstructed Ir{100} surfaces were calculated. The results show that the calculations do reproduce the experimentally observed structure and the reconstruction energy is then estimated from the difference between the surface energies of the two phases.

2. Calculation

Total energy pseudopotential calculations were performed within the framework of local density functional theory (DFT). We use a basis set consisting of plane waves and periodic boundary conditions to model the surface of a periodically repeated slab in a supercell. Ab initio pseudopotentials in fully separable Kleinman-Bylander form [15] were generated by an improved kineticenergy-filter optimisation scheme [16]. The 5d and 6s states of Ir were treated as valence states. The exchange and correlation are described with either the Ceperly-Alder parameterisation of local-density approximation (LDA) [17], or with the Perdew-Wang form of the generalised gradient approximation (GGA) [18]. Two different implementations were used in finding the ground state of the Kohn-Sham hamiltonian: an all-bands conjugated-gradient direct minimisation, as implemented in the parallel code CETEP [19], and a recently developed extension to metallic systems, called ensemble-DFT [20]. The ensemble-DFT implementation has better converged total energies and especially Hellmann–Feynman forces whenever metals are involved. However, in its present (vector) form of coding, memory requirements prevent its use for the large scale calculations needed for transition metal systems, where parallel computing is needed. In the present study, we performed ensemble-DFT calculations on sparse k-point meshes and reduced plane wave cutoff to obtain relaxed structures that are then refined with CETEP using fine k-point meshes and a proper cutoff energy.

For the energetics calculations we use a plane wave cutoff of 500 eV; LDA yields a lattice constant of 3.814 Å and a bulk modulus of 4.59 Mbar while GGA gives 3.832 Å and 3.76 Mbar, respectively, for the same pseudopotential. These results agree well with the experimental value for the lattice constant (3.834 Å [21]) and for the bulk modulus (3.55 Mbar [22]), giving us confidence in the accuracy of the pseudopotential. The GGA provides slightly better structural results; in general it is expected to be more accurate in the description of the energetics of solid surfaces.

A five-layer slab with inversion symmetry with respect to the centre of the supercell has been used in the study of reconstruction. The Brillouin zone of the (1×5) surface unit cell is sampled with a (10×2) Monkhorst–Pack mesh [23]; time-reversal symmetry reduced these to 10 inequivalent kpoints. In the (1×1) cell, an equivalent sampling is given by a (10×10) mesh, that is reduced by symmetries to 15 special k-points. When calculating surface energy difference, the surface energy of the (1×1) phase and the energy of bulk Ir are calculated using cell and k-point sampling that is equivalent to the (10×2) Monkhorst–Pack mesh in the (1×5) surface unit cell. LDA and GGA calculations were self-consistently performed with their corresponding lattice constants.

3. Results and discussion

3.1. $Ir \{100\} - (1 \times 1)$ relaxation

With a five-layer slab and (1×1) surface unit cell, allowing the outermost layer to relax leads to a contraction in the first interlayer distance,

amounting to ~ 6.5 % of the bulk value. This contraction is somewhat larger than the reported experimental value ($\sim 3.6 \%$ [24]) and the theoretical result (3.8 %) calculated by Filippetti and Fiorentini [14]. We checked our calculation with an increased number of layers and more dense kpoint sample. The results are listed together with the five-layer calculation in Table 1, where all the results are based on the calculation from a (1×1) surface unit cell. All results are well converged with respect to the k-point sampling; the finite-size effects related to the thickness of the slab are also negligible. The slab with five layers of Ir atoms and relaxation limited to the first layer compares well with the results from the seven-layer slab with relaxation in the first two layers. It should be noted from the seven-layer calculation that the change in the second-layer spacing is negligible. This explains why the relaxation results of the outermost layer of the five-layer slab agrees so well with the results from the seven-layer slab.

3.2. Ir $\{100\}$ - (1×5) reconstruction

We first assessed the relative stability of the two possible registries of the (1×5) reconstruction, i.e. the "two-bridge model" and the "centre-top model", on the (1×1) underlying lattice. Our results show that the "centre-top" registry is less stable than the "two-bridge" registry, by $0.07 \text{ eV}/(1 \times 1 \text{ area})$ with LDA. This is consistent with the experimentally determined structure [1,10,11] and also agrees qualitatively with the previous calculation [14].

Furthermore, with a (1×5) surface unit cell and the (10×2) k-points mesh, we calculated the surface energies of the (1×1) phase and the reconstructed (1×5) phase to be 1.59 eV/ $(1 \times 1 \text{ area})$ and 1.60 eV/(1×1 area), respectively, using LDA. The calculated surface energy is slightly higher than the value $(1.57 \text{ eV}/(1 \times 1 \text{ area})))$ calculated with the (1×1) unit cell. Introducing the generalised gradient correction lowers these surface energies to $1.38 \text{ eV}/(1 \times 1 \text{ area})$ and $1.31 \text{ eV}/(1 \times 1 \text{ area})$ area), respectively. The experimental surface polycrystalline reported for energy Ir is $1.38 \text{ eV}/(1 \times 1 \text{ area})$ [25].

The calculated surface energy difference between

Table 1

The LDA relaxed Ir{10}-(1×1) structure and surface energies. The number of k points refer to the irreducible wedge of the (1×1) cell, where (8×8), (10×10) and (12×12) Monkhost–Pack meshes have been used, σ_b and σ are the surface energies of bulk-terminated and relaxed structures, d_{12} , d_{23} and d the first, second and bulk interlayer distances, respectively

No. of layers	No. of k points	$\sigma_{\rm b} \; [{\rm eV}/(1\times 1 \; {\rm area})]$	Relaxed structure			
			$(d_{12} - d)/d$ (%)	$(d_{23} - d)/d$ (%)	$\sigma \text{ [eV/(1 \times 1 \text{ area})]}$	
5	10	1.719	-6.75	n/a	1.605	
	15	1.691	-6.85	n/a	1.574	
7	10	1.719	-6.73	-0.03	1.614	
	15	1.683	-6.77	0.00	1.579	
	21	1.671	-6.56	-0.00	1.583	

the (1×1) phase and the reconstructed (1×5) phase is $-0.01 \text{ eV}/(1 \times 1 \text{ area})$ with LDA, while GGA gives a value of $0.06 \text{ eV}/(1 \times 1 \text{ area})$. Apparently, the (1×5) reconstructed structure is not favoured within the LDA approximation. However our GGA results do give a lower surface energy for the (1×5) reconstructed phase, indicating that the (1×5) phase with the "two-bridge" registry is thermodynamically more stable. The relaxed structure for the (1×5) reconstruction is shown in Fig. 1 and a comparison with the experimentally determined structure is listed in Table 2. As we can see from Table 2, the final relaxed structure for the two-bridge geometry is in *excellent* agreement with the LEED structure. In addition we notice that there are some lateral displacements from the ideal hexagonal closed packing (δ_1, δ_2) .

The reconstructed (1×5) phase is geometrically corrugated and this will effectively increase its surface area in comparison with a flat surface. The "actual" surface area, as measured by connecting the atomic centres in the reconstructed phase, is up to 1% larger than the area projected onto the (1×1) mesh. (The smearing of the charge density at the surface somewhat reduces the surface roughening below that of the atomic geometry.) This will effectively decrease the surface energy of the (1×5) phase. If the increase in surface area due to corrugation is taken into account, the LDA reconstruction energy becomes weakly positive, i.e. favouring the reconstructed phase, and the GGA value is increased from 0.06 to 0.08 eV.

The calculated energy difference between the two phases is small. In fact, the present results

with LDA differ from the result of Filippetti and Fiorentini, who reported a surface energy difference of $0.14 \text{ eV}/(1 \times 1 \text{ area})$ [4]. When a supercell approach is used, extra care needs to be taken in controlling the relative and absolute convergence of the total energies with respect to k-point sampling. By using the same unit supercell and the same sampling to calculate the energy differences between different phases, we are able to reach full k-point convergence much faster than if we had used different cells, or different samplings, for the total energies. In the latter case, in fact, absolute k-point convergence would be required for each phase. Therefore, we used the same surface unit cell with the same k-point set in calculating the surface energies of the (1×1) phase and the reconstructed (1×5) phase and the total energy of a bulk atom, a point perhaps not previously recognised.

Using the calculated surface energy implies that the source of the extra atom to form the (1×5) reconstructed phase is the bulk. In reality, the surface is full of kinks and steps, and these will form the primary source of the Ir atoms for incorporation to form the (1×5) phase. The energy cost to form (1×5) phase from these sources will be lower than that to form it from the bulk. To illustrate this point, we calculated the adsorption energy of Ir on the $Ir\{100\}$ -(1×1) at 0.25 monolayer coverage (i.e. with a (2×2) surface unit cell). We found that incorporating such an Ir adatom (as opposed to a bulk atom) into the surface layer to form a *hex*-like (1×5) structure will lead to an energy gain of 0.80 eV per atom (LDA). The existence of steps and kinks (adatom-



(b) Side view

Fig. 1. Schematic view of $Ir\{100\}-(1 \times 5)$ reconstruction. The side view gives the definition of the parameters.

like) on the surface will effectively increase the reconstruction energy, although not as much as to incorporate an isolated adatom.

3.3. Discussion

When a surface is created, the electrons respond to the loss of atoms above the surface atomic layer, producing a charge redistribution, so that the charge distribution near the surface becomes different from that in the bulk. Much of the bond charge moves from above the surface into the edge of the solid as a result of the missing neighbours for the surface atoms. The charge is then relocated to the area between first-layer atoms and between first- and second-layer atoms. The latter effect can be seen on close examination of data in Fig. 2, showing the logarithmic total valence charge densities for the relaxed $Ir\{100\}-(1 \times 1)$ phase. The backbonds of the surface atoms are strengthened and the bond length becomes shorter; this redistribution of electronic charge leads to a contraction of the distance between the first and second layer. Indeed, the contraction is almost universal for transition metals [26]. This is also what we have found here for the unreconstructed (1×1) phase.

Table 2 Calculated and experimental structure parameters for the "two-bridge model" of (1×5) reconstruction

	d_{12} (Å)	ΔZ_1 (Å)	ΔZ_2 (Å)	δ_1 (Å)	δ_1 (Å)
Present study	1.966	0.467	0.198	0.050	0.025
Ref. [10]	1.975	0.50	0.22	n/a	n/a
Ref. [11]	2.02 ± 0.05	0.48 ± 0.02	0.14 ± 0.02	n/a	n/a
Ref. [1]	2.2 ± 0.1	0.2 ± 0.02	0.06 ± 0.02	n/a	n/a



Fig. 2. Logarithmic total valence charge density of the Ir{100}- (1×1) surface. Cut along $\langle 010 \rangle$ direction.

Competition exists for the electronic charge redistribution between the interlayer space and the space among surface atoms. If the charge mainly goes to the interlayer space, the contraction in the first-layer spacing would be the dominant feature. On the other hand, electronic charge accumulating between the surface atoms will lead to a strong interaction and a tendency to shorten the bond length between the surface to restructure towards a more densely packed structure, if the energy cost in losing registry with the underlying bulk structure is overcome.

The stability of a metal surface against reconstructions which change the density of surface atoms is controlled by three major factors [27]: (a) interatomic interaction to account for the bond length change due to formation of surface; (b) the energy cost associated with adding atoms to or removing atoms from the surface layer; and (c) changes in the bonding between surface atom and substrate. The surface stress does not encompass all of these effects and therefore is insufficient in determining the stability of the surface.

We examined the change in the bonding environment of surface Ir atoms upon reconstruction. On the (1×5) reconstructed phase, the surface atoms are in very different sites with respect to the substrate. In the (1×5) unit cell, two of the six atoms sit precisely in the bridge sites. Two of them are near the fourfold hollow sites and the other two are near the atop sites. The average bond length between surface atoms is about 2% shorter than that for the (1×1) surface, although, among the six pairs, two bonds are stretched slightly (<0.2%). As to the surface-to-substrate bond, the decrease in bond length is to be expected, because the atoms moved from high coordination sites in the (1×1) phase to low coordination sites in the reconstructed (1×5) phase.

4. Summary

The *hex* reconstruction of the Ir{100} surface has been studied with a first principles density functional calculation. The results support the "two-bridge" registry structure as the most stable, and the relaxed structure is in good agreement with the structure determined by LEED I-V analysis. The calculation shows that the reconstructed phase is 0.06 eV/(1 × 1 area) lower in energy than the (1 × 1) phase.

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