Chemical Physics Letters 666 (2016) 51–57

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Non-linear modelling of the effects of strain on transition metal surfaces

I.G. Shuttleworth

School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, UK

ARTICLE INFO

Article history:
Received 26 September 2016
In final form 30 October 2016
Available online 1 November 2016

Keywords:
Surface energy
Transition metal
D-band effects
Strain engineering
Non-linear elasticity

ABSTRACT

A sequence of polynomial expressions have been shown to describe the strained surface energy of low-index hexagonal and square transition metal surfaces. Distinguishable functions describe the hexagonal FCC (111) and HCP (0001) surfaces, but a single function describes the FCC (100) and BCC (100) surfaces. A far weaker dependence exists between the strained surface energy and the electronic state of the surface, and the competition between geometric and electronic states across is discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Surface energy is central quantity in the study of metals. The energy arises during cleavage of the bulk metal into two parts [1,2] whereupon the atoms relax from their ideally bulk terminated positions to lower energy sites. The reduction of energy is due to loss of periodicity; surface atoms do not have the same perfectly periodic surroundings that their counterpart atoms in the bulk have, and consequently experience an imbalance in the forces that act on them. This imbalance is relieved by relaxation of the atoms in the surface, and selvedge, regions.

In these circumstances, the underlying bulk atoms remain in equilibrium, and un-stressed and comparison of the surface energies across the d-period show a volcano-type dependence [3]. Contemporary studies [4] of the closely related quantity of surface stress have highlighted the complexity of the field and have reviewed the various models of surface electronic structure that commonly invoked to describe surface relaxation. A central them to these models is the interplay between delocalised sp and localised d orbitals, pioneered by Pettifor [5]. The energetic importance of the d-states has been underlined by the more recent Friedel stress model [6] which has successfully modelled the surface stress across systems where the bulk atoms are unstrained.

Understanding surface energy and stress and their response to changes in the bulk is central to both fundamental surface science and it's applications. Contemporary studies of the surface [7] and bulk [8] hydrogen in strained metallic systems have demonstrated that both the binding position and the electronic state of this catalytically-important element depends sensitively on the development of the surface and bulk energy. A number of approaches have been used to calculate surface energy [9–13]. Simulations based on the jellium model [14] have been applied to systems where the underlying bulk atoms are strained and have proposed a parameterisation of the deformed Wigner-Seitz cell. More recent studies have investigated the energies of hexagonal surfaces [15] using density functional theory (DFT) and have identified correlations between the work function and crystallographic orientations of the surfaces. The requirement for DFT level precision in modelling strained surfaces has been further underlined in studies of Al, Pd, Pt, Au and Ti [16], the low index (111), (110) and (001) faces of $AlCu_3$ [17] and on transition metal carbide films [18].

The current work will be based on density-functional theory (DFT) level simulations and will survey a range of both square and hexagonal transition metal surfaces. To reduce the model the formalism of non-linear elasticity theory will be adopted [19], an approach which has successfully applied to bulk MgO [20]. Elasticity theory describes the response of a system to a finite deformation. The formalism is therefore entirely consistent with the type of investigation performed in the current study where the metallic systems will be strained and the response of the surface will be scrutinised. The theory requires that energy of the system is expanded in a Taylor-series of terms in strain, the first order term then describing the linear response and the higher order terms describing non-linear components.

The current work is divided into three sections: in the first section, an outline of the DFT method and the definition of strain used in the current work is presented. The subsequent section presents the surface energy and non-linear response functions, together with their clear definition and a discussion of the geometric and

---

E-mail address: ian.shuttleworth@ntu.ac.uk

http://dx.doi.org/10.1016/j.cplett.2016.10.080
0009-2614/© 2016 Elsevier B.V. All rights reserved.

electronic issues arising in these fits, and the paper finishes with a conclusions section.

2. Theory

Investigations performed in this current work were of the Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt and Au systems. The structures investigated are summarised in Fig. 1. For the FCC systems – Ni, Cu, Rh, Pd, Ag, Ir, Pt and Au – the hexagonal (1 1 1) and square (1 0 0) surfaces were simulated, and the hexagonal HCP (0 0 0 1) and square BCC (1 0 0) surfaces were simulated for the HCP - Co, Ru, Os - and BCC – Fe – systems, respectively. The surfaces were strained uniformly in the surface-parallel direction by an amount σ.

Table 1
Summary of the equilibrium bulk lattice constants determined computationally in the current work (a_{theo}) and experimentally (a_{expt}). All dimensions are in Å.

Element	a_{theo}	a_{expt}
Fe	2.838	2.867
Co	2.491	2.507
Ni	3.518	3.524
Cu	3.680	3.615
Ru	2.698	2.706
Rh	3.850	3.803
Pd	3.962	3.891
Ag	4.073	4.085
Os	2.745	2.734
Ir	3.898	3.839
Pt	3.981	3.924
Au	4.073	4.078

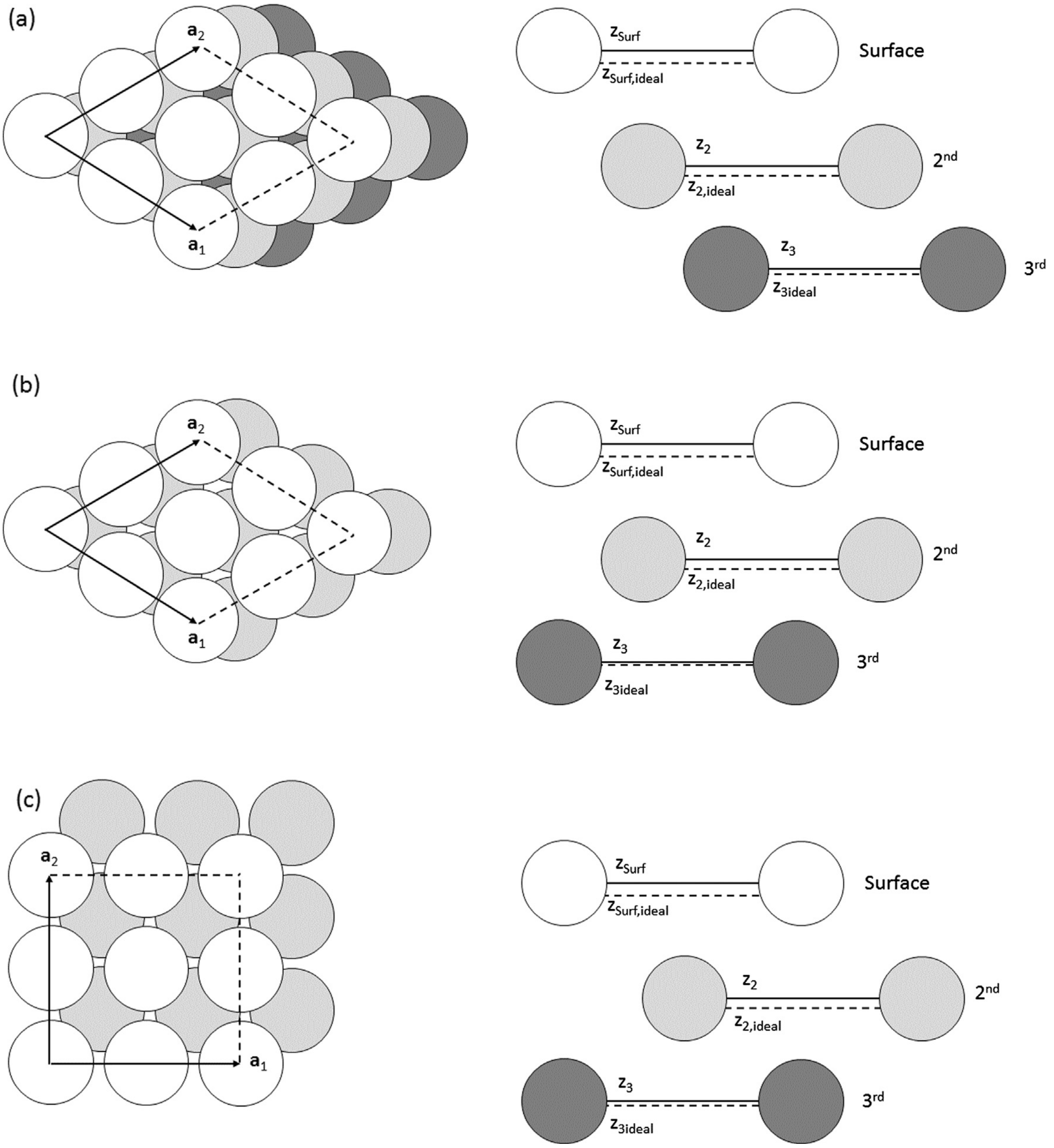

Fig. 1. Schematic showing (a) hexagonal FCC (1 1 1), (b) hexagonal HCP (0 0 0 1), and (c) square FCC (1 0 0) and BCC (1 0 0) surfaces. Surface (second/third) layer metal atoms are shown by white (light grey/dark grey) circles, respectively. a_1 and a_2 are the primitive surface vectors for each system, and are (2 × 2) for clarity. The dashed horizontal lines in the cross-sectional views show the ideal, bulk terminated plane heights $z_{L,ideal}$ where the subscript 'L' denotes 'Surf', '2', or '3', and the solid lines show the actual plane heights z_L.

Download English Version:

https://daneshyari.com/en/article/5378335

Download Persian Version:

https://daneshyari.com/article/5378335

Daneshyari.com