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Structural and dynamical properties of iridium surfaces: First principles and molecular dynamics investigations

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Abstract

The structural and dynamical properties of Ir(1 0 0) clean surface are investigated in the temperature range 100–1100 K. We performed molecular dynamics (MD) simulations using the interaction potential energies obtained from the density-functional theory (DFT) and plane-wave pseudopotential (PWPP) method. The obtained contraction of the first interlayer distance, d_{12} , decreases from −4.94% at 100 K to −4.84% at 1100 K. This decrease deviates by 11.8% at 100 K to 13.6% at 1100 K, from that at 0 K (−5.6%). The expansion of the second interlayer distance, d_{23}, however increases from 0.89% at 100 K to 1% at 1100 K, causing a deviation that ranges from −11% to 0% from that at 0 K (1%). The deviation of the calculated surface vibrational frequencies and surface relaxations over the entire range of temperatures (100–1100 K) is rather modest as a result of small anharmonic effects of the surface.

Keywords: Density functional calculations; Molecular Dynamics; Surface relaxation

1. Introduction

The investigation of temperature dependencies of the structure and the dynamics at solid surface is vital for many reasons. The surface itself due to the reduction of symmetry and coordination is a very good working ground for realizing atomic arrangements, geometrical structures, as well as local atomic bonding, which are generally different from those in the bulk. Consequently, structural changes such as relaxations and reconstructions as well as dynamics modifications of the vibrational modes are witnessed for surface atoms. Through anharmonic contributions to the interaction potential, anharmonic effects become significant for most of the systems with increasing temperatures. Thermal expansion and changes in surface vibrational frequencies are the most common signs of anharmonicity. In fact, anharmonic effects are expected to play an even more dominant role on the surface than in the bulk crystal because of reduced symmetry and atomic coordination at the surface. The issue of the strength of the surface anharmonicity, by itself and related to the bulk value, has thus been the subject of research for several decades [1–7].

The vast developments of the experimental techniques such as LEED [8], ion scattering [9], X-ray diffraction and atom-beam scattering [10] have provided information of the surface geometry. The vibrations, however, have been successfully measured by methods such as electron energy-loss spectroscopy [11] and inelastic helium beam scattering [12]. In addition, the progress in the computational techniques has been exploited to serve with an experiment, in order to give reliable description of the surface static and dynamic properties. The total energy calculations using density-functional theory were of great success in surface science to describe the optimum geometrical structures of real systems. As for vibrations, the situation was more complicated for surfaces due to expensive computational efforts. Early calculations used Leanard–Jones potentials for the interatomic interaction [13]. Afterwards, empirical studies such as the embedded-atom method (EAM) [14–16], the effective-medium theory (EMT) [17] and the glue model [18] have been used by fitting experimental-bulk-phonon-dispersion curves to obtain surface modes.

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However, such empirical methods may yield unphysical interpretations [19]. Such errors could be reduced by using the density-functional theory that provides reliable energies as functions of nuclear coordinates. The DFT prescriptions could be employed in plausible predictive methods such as frozen-phonon method [20], linear response [21,22] and dielectric-matrix approach [23], and density-functional perturbation theory [24].

However, all the previous ab-initio methods are valid at zero temperature. In order to include vibrations at an elevated temperature, the problem was tackled by two approaches. One approach was addressed by Car and Parinello [25] that proposed a scheme combining the accurate description of forces through DFT and the power of molecular dynamics (MD) techniques for applications at finite temperatures. Nevertheless, applications of this scheme to study the temperature dependence of real systems have been limited by the large computational time required, especially for noble and transition metals, which are characterized by the tightly bound valence electrons.

The idea behind the present methodology is to perform less expensive MD calculations than the ab-initio MD techniques, but with comparable degrees of accuracy. In this study, we use the DFT total energy points as an input for interpolation through two-dimensional thin-plate splines to obtain the forces needed to carry out classical MD calculations.

Platinum group metals are known to have excellent high-temperature characteristics, and Ir is an important catalyst that has been recognized as a potential candidate for a variety of high-temperature structural applications. And, since a deeper understanding of the relation between anharmonic phenomena and the characteristic temperatures at which these phenomena are initiated or accentuated is necessary for developing high-temperature structural applications of Ir. This paper comes to carry out an analysis of the structure and dynamics of Ir(1 0 0) in the temperature range 100–1100 K by examining the changes in the surface relaxations, vibrational frequencies and Debye temperature.

This paper is structured as follows: in Section 2, the method of calculation and computational details are described. In Section 3, we present and discuss the changes in the vibrational frequencies, Debye temperature and surface relaxations, and in Section 4 we summarize the main conclusions.

2. Method of calculation

Since our study involves dynamical processes, we combine the DFT with MD simulations. The ab-initio calculations were performed using the ABINIT code [26,27]. The total energies were computed using DFT calculations that are based on the planewave pseudopotential (PWPP) [28] method under the local density approximation (LDA) using Hartwigsen–Goedecker–Hutter (HGH) relativistic separable dual-space Gaussian pseudopotential [29] using the Teter–Pade parametrization, which reproduces the Ceperley–Alder data [30] for the exchange-correlation functional. The (1×1) surfaces were modeled by a supercell technique. The Ir(1 0 0) supercell consists of five atomic layers and vacuum equivalent to seven atomic layers. The bulk lattice constant was obtained by the structural minimization of the bulk system, which is followed by the Murnaghan fit [31] yielding a lattice constant of 7.29 Bohr. In the slab calculations a 30 ha cut-off energy is used for the expansion of the plane wave basis. The Brillouin zone (BZ) integrations were carried out using 42 k-points in the corresponding irreducible wedge, which corresponds to $(12 \times 12 \times 1)$ Monkhorst–Pack grid [32]. In order to obtain a better convergence of the BZ integration, the Fermi surface is broadened using a "cold smearing" with a smearing temperature of 0.02 ha [33].

The total energies were calculated for systems of different structural configurations by changing the perpendicular interatomic spacing of the outermost as well as the subsurface layer. These total energies are obtained by performing self-consistent calculations (SCF) with a tolerance of the total energy less than 10^{-6} Ha. We performed SCF calculations for 176 structural configurations. These energies could be interpolated using two-dimensional thin-plate splines and then mapped in a two-dimensional energy landscape from which the optimum structure is obtained at the global minimum.

The MD simulations of the surface were carried out classically using the Velocity Verlet algorithm to integrate the equations of motion for the Ir(1 0 0) system. The forces needed for these simulations are calculated from the gradient of the interpolated energies using the 176 DFT energy points for Ir(1 0 0) clean surface. The time step was taken to be 0.1 fs for all cases that leads to an excellent conservation of energy. The simulations have taken place at temperatures in the range 100–1100 K, where the runs last for 50 ps long for each temperature. By obtaining the trajectories on the landscape of the surface, which represent the time evolution of this system, we could calculate the vibrational modes by using the discrete Fourier-transform method for these trajectories.

3. Results and discussion

The energies of different structural configurations have been performed using DFT calculations. The relative values are interpolated in a two-dimensional landscape that represent relaxation of the first layer on the x-axis and the second layer on the y-axis, (Fig. 1). On this potential energy surface (PES), the minimum is located at $d_{12} = -5.6\%$ and $d_{23} = 1.0\%$. We observe a contraction of the first layer, which is the case for most clean transition metal surfaces and an expansion in the second interlayer distance. The contraction of the first layer is in agreement with other previous calculations [34,35] and with low-energy electron diffraction (LEED) analysis [36].