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On-surface and sub-surface oxygen adsorption on Ag(2 1 0): Vibrational properties

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Abstract

In this work we investigate the vibrational properties of atomic oxygen on Ag(2 1 0) in a mixed on-surface + sub-surface adsorption configuration using density-functional perturbation theory. In particular, we consider a geometry in which oxygen decorates the steps and an additional O species is located in an octahedral sub-surface site just below an Ag step atom. This structure presents a mode at 55 meV due to the coupled vibration of on-surface and sub-surface O species, which is close to that observed in HREEL spectra.

Keywords: Density-functional calculations; Silver; Oxygen; Stepped single crystal surfaces

1. Introduction

Inclusion of oxygen atoms into sub-surface sites of metals is a phenomenon which plays an important role in many processes such as catalytic reactions, corrosion, and metal-oxide formation. Unfortunately, sub-surface species are quite difficult to detect with usual surface-science techniques and their chemical nature as well as the mechanisms governing the access to sub-surface sites are still unclear.

In a recent work [1], Rocca and coworkers have investigated the interaction of oxygen with the Ag(2 1 0) surface using high-resolution electron energy loss spectroscopy (HREELS). The vibrational spectra thus obtained suggest that oxygen can occupy a sub-surface site when a certain amount of O adatoms are adsorbed on-surface. In particular, their HREEL spectra show three distinct peaks at 31, 40 and 56 meV which are due to different

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oxygen species. The frequencies of the two low-energy peaks are close to those reported for O/Ag(1 0 0) (33 meV) [2] and for the added-row reconstructed O/Ag(1 1 0) surface (40 meV) [3], respectively. Due to this similarity, the peak at 31 meV has been assigned to O adatoms occupying the (1 0 0) terrace sites, while that at 40 meV is thought to correspond to atomic oxygen decorating the (1 1 0) steps. The feature at 56 meV appears on Ag(2 1 0) surface only at high oxygen coverage and it has never been observed on other O/Ag systems. Moreover, this peak has a strong impact scattering component and its frequency is too low for an internal stretch of O_2 molecules and too high for an adatom–surface vibration. Such arguments led the authors of Ref. [1] to propose that this feature could be the fingerprint of sub-surface oxygen adsorption. They also suggested that the oxygen atoms could occupy interstitial tetrahedral sites because an atom too deep into the metal—such as in an octahedral site—should have a very small dipolar activity.

In previous works we studied the on-surface [4] and sub-surface [5] atomic oxygen adsorption on Ag(4 1 0) and Ag(2 1 0). In particular, we showed that on Ag(2 1 0) the step decoration is much more stable than any other on-surface adsorption configuration. Moreover, we found that the inclusion of oxygen into interstitial sub-surface sites can be stabilized by O adatoms pre-adsorbed on the surface and that—at high enough coverage—the mixed on-surface + sub-surface O adsorption is more stable than purely on-surface one. For the on-surface adsorption geometries we analyzed also the vibrational properties and our results support the proposed assignment of the HREEL peaks at 31 and 40 meV. However, among the investigated configurations, no vibrational feature around 56 meV was found.

In this paper we study the vibrational properties of an adsorption configuration in which oxygen decorates the steps and additional O atoms occupy octahedral sub-surface sites just underneath an Ag step atom. This structure is more stable than the geometry in which the additional O atoms occupy a tetrahedral sub-surface site, and it presents interesting spectral features. In particular, it has a mode at 55 meV due to the coupled vibration of sub-surface and on-surface O atoms which could be responsible of the peak at 56 meV observed in HREEL spectra.

The paper is organized as follows. In Section 2 we describe the theoretical approach and computational details of our work. In Section 3 we present the vibrational properties of the investigated system. The last section is devoted to our conclusions.

2. Computational details

Our calculations have been performed within density-functional theory (DFT) using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [6]. Vibrational properties have been calculated using density-functional perturbation theory (DFPT) [7–11]. We have used the pseudopotential method with ultra-soft pseudopotentials [12] and plane-wave basis sets up to a kinetic-energy cutoff of 27 Ry (216 Ry for the charge-density cutoff). Details about the Ag and O pseudopotentials are the same as in Ref. [13]. All the calculations have been performed using the `PWscf` and `PHONON` packages [14], while molecular graphics has been generated with the `XCRYSDEN` package [15].

The Ag(2 1 0) surface is modeled by 10 (2 1 0) layers and adjacent slabs are separated by a vacuum region of at least 16 a.u. Oxygen is adsorbed on both sides of the slab and the structure is fully relaxed. We have used a (2×1) surface super-cell and the Brillouin zone integrations have been performed using a $3 \times 5 \times 1$ uniform shifted k mesh [4], with a Gaussian smearing parameter of 0.03 Ry [16,17].

The procedure to calculate the vibrational properties of the system is discussed in detail in Refs. [4,18].

3. Results and discussion

In a previous work [5] we showed that the adsorption configuration in which the oxygen adatoms decorate the step edge of the surface and an