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Dipole model for the linear response of adsorbed overlayers

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This paper present theoretical calculations of reflectance anisotropy spectra (RAS) for overlayers of alkali atoms adsorbed on a crystalline metallic surface. We assume that the overlayer is formed by an ordered two-dimensional (2D) array of adatoms that respond to the local electric field like point-like harmonic oscillators. We consider overlayers with several rational coverages, assuming that the adsorbates occupy high symmetry sites which form a Bravais lattice that is commensurate with the substrate [1,2]. RAS spectra are obtained for the five 2D Bravais lattices. We found that RAS can be used to observe ordered phases when the ordered phase has a rectangular, centered-rectangular or oblique symmetry.

1 Introduction Adsorption of alkali metals on various substrates has been widely investigated because of the simplicity of the interface formation and because of its technological applications such as low-temperature and low-field electron emission sources or catalyzers of silicon dioxide growth on silicon surfaces [3,4]. Such adsorption has been investigated in detail in the case of metallic substrates [3] and gives rise to a wealth of regimes which have been described through phase diagrams as a function of coverage and temperature. The richness of the phase diagram arises from the competition between the adsorbate-substrate interaction, which favors adsorption at specific sites of the surface, typically those of high symmetry, and the adatom-adatom interaction, which typically contains a long range repulsive part. The resulting phases may be ordered or disordered, and they may be commensurate or incommensurate with the substrate. Low temperature experiments, some of them regarding the adsorption over fcc(001) surfaces on which we concentrate our attention, have been performed in the past [5–9] and show that the overlayers of K on Ir (001) and Cs on Rh(001) show a particularly rich set of ordered phases [6,7].

In this work we study theoretically the possibility of observing the overlayer and its phase transitions through the optical technique of reflectance anisotropy spectroscopy (RAS). This technique probes the surface and interface structure of cubic materials [10], and measures the difference between the normal-incidence optical reflectance of light polarized along the two principal axes in the surface plane as a function of photon energy. Since the bulk optical properties of cubic crystals are isotropic, any observed anisotropy must be related to the lower symmetry of the surface and/or the adsorbed overlayer. We use a polarizable dipole model [11] to describe the response of each adatom and we assume that the substrate may be described as a homogeneous semiinfinite system described by a local dielectric function. For concreteness, we concentrate our attention on ordered alkali overlayers adsorbed on a (001) nominally isotropic metallic surface, and in particular, we consider the case of K atoms on a clean Ir(001) surface. Nevertheless, our approach may be applied to other systems. We evaluate the direct and the substrate mediated interaction between the polarized adatoms and we show that it yields a RAS signal that changes as the coverage is varied and the system evolves through a series of 2D ordered phases; we show how the RAS spectra changes as a function of the two dimensional (2D) arrangement of

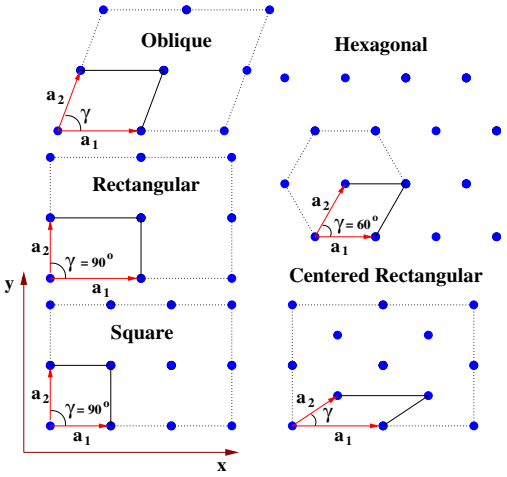

Figure 1 (Color online) The five 2D Bravais lattices, with the choice of the primitive unitary cell for each lattice (solid lines). x, y are the system's coordinates, $\mathbf{a}_1$, $\mathbf{a}_2$ represent the primitive lattice vectors and γ is the angle between them.

the adlayer. The results show that RAS can be used for monitoring disorder-order phase transitions.

The article is organized as follows. In Sec. 2 we describe the polarizable dipole model, we discuss how the geometrical arrangement of the adatoms is taken into account, and explain the procedure to obtain RAS. Then, in Sec. 3 we present and discuss the theoretical results for different geometries. Finally, in Sec. 4 we present our conclusions.

2 Theory We consider a system composed of a 2D array of adsorbed atoms forming a 2D Bravais lattice with primitive lattice vectors $\mathbf{a}_\zeta$ ($\zeta = 1, 2$) which make an angle γ between them (see Fig. 1), lying on top of a metal substrate.

Let $z_0 = d/2$ be the separation between the adsorbed layer and the metal surface, where the metal is presumed to occupy the half-space $z < 0$. We assume that the frequency dependent polarizability $\alpha(\omega)$ of an absorbed atom is isotropic while the response of the metal is described by a local, complex dielectric function $\epsilon(\omega)$. We let polarized light of angular frequency ω to illuminate the system at normal incidence and we choose the electric field as $\mathbf{E} = (E_x, 0, 0)$ or $\mathbf{E} = (0, E_y, 0)$. The external field polarizes the substrate and the adsorbed atoms. The latter thus acquire oscillating dipole moments which act on neighboring atoms and which induce image dipoles in the substrate metal. Furthermore, the images act back on the adatoms modifying their dipole moments. We assume d and $a_\zeta \ll \lambda$, where λ is the wavelength of light, so we may calculate the response of the surface in the quasi-static approximation. On exposure to light, then, the adsorbed layer consists of an array of oscillating dipoles each of moment $\mathbf{p}^A_{nm}$, located at $r^A_{nm} = n\mathbf{a}_1 + m\mathbf{a}_2 + \hat{z}d/2$,

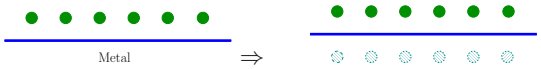

Figure 2 (Color online) In the left hand, we show the overlayer on top of the substrate, green circles are adatoms, and in the right hand, we show its corresponding system with the plane of image dipoles (blue circles).

where n and m are integers with $-\infty < n, m < \infty$. This choice implies that the z axis goes through one of the adatoms. In addition, there appears another array of dipoles located in the image plane $z = -d/2$ (see Fig. 2), each having a dipole moment $\mathbf{p}^I_{nm} = (\epsilon - 1)/(\epsilon + 1)\mathcal{S}\mathbf{p}^A_{nm}$ located at $r^I_{nm} = n\mathbf{a}_1 + m\mathbf{a}_2 - \hat{z}d/2$, where the tensor $\mathcal{S} = \mathrm{diag}(-1, -1, 1)$ yields the correct orientation of the image dipoles.

We assume that each adatom responds to the local electric field $\mathbf{E}^L_{nm}$ at site nm as

$$\mathbf{p}^A_{nm} = \alpha \mathbf{E}^L_{nm}, \tag{1}$$

where

$$\alpha(\omega) = f_0 \frac{e^2/m}{\omega_0^2 - \omega^2 - i(\omega/\tau))}, \tag{2}$$

is the polarizability of a harmonic oscillator with resonance frequency ω_0, damping parameter τ related to the width of the resonance, oscillator strength f_0, and where m and e are the electron's mass and charge, respectively. The local field is given by

$$\mathbf{E}^L_{nm} = \mathbf{E}^M + {\sum_{n'm'}}' \mathbf{M}^{AA}_{nm,n'm'} \mathbf{p}^A_{n'm'} + \sum_{n'm'} \mathbf{M}^{AI}_{nm,n'm'} \mathbf{p}^I_{n'm'}. \tag{3}$$

The first term is the sum of the incoming field and the field reflected by the substrate, i.e., it would be the total field at the surface in the absence of the adlayer, and at normal incidence is independent of the position along the surface. The second term is the dipolar field produced by all other adatoms, and the prime in the sum means that the term $n = n', m = m'$, being the self interaction, is omitted from the sum. Similarly, the third term is the interaction of the images of all the adatoms on the adatoms themselves. In this case, we have to keep the interaction of an adatom with its own image. The tensor

$$\mathbf{M}^{AN}_{nm,n'm'} = \nabla\nabla \left. \frac{1}{|\mathbf{r} - \mathbf{r}^M_{n'm'}|} \right|_{\mathbf{r}=\mathbf{r}^A_{nm}}, \ (N = A, I) \tag{4}$$

is the dipolar interaction matrix between the adatom nm and either the adatom $n'm'$ ($N = A$) or its image ($N = I$). The summations over $n'm'$ in Eq. (3) can be carried out using standard plane-wise schemes [12]. Therefore, the local field can be written as

$$\mathbf{E}^L = \mathbf{E}^M + \left(\mathbf{T}^{AA} + \frac{\epsilon - 1}{\epsilon + 1} \mathbf{T}^{AI} \mathcal{S} \right) \mathbf{p}^A, \tag{5}$$

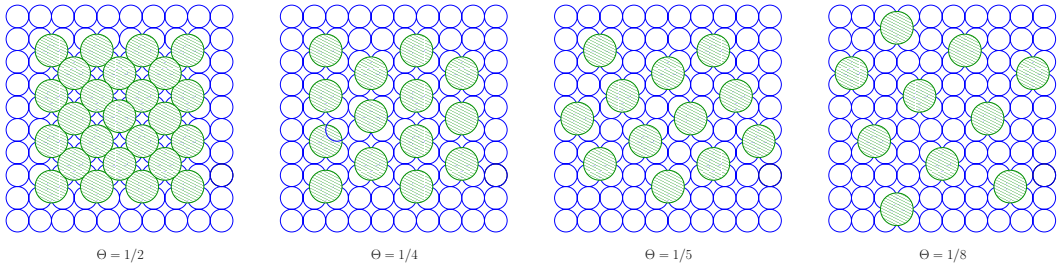

Figure 3 (Color online) Some ordered overlayer structures found experimentally for K atoms adsorbed on a Ir(001) surface for different values of coverage θ [6].

where we eliminated the indices n, m as the system has periodicity along the surface. The *inter-plane* and the *intra-plane* dipolar interaction tensors are given by $\mathbf{T}^{AA} = \sum'_{n'm'} \mathbf{M}^{AA}_{nm,n'm'}$ and $\mathbf{T}^{AI} = \sum_{n'm'} \mathbf{M}^{AI}_{nm,n'm'}$ respectively.

Then, we can rewrite Eq. (1) as

$$\mathbf{p}^A = \alpha \mathbf{E}^L. \tag{6}$$

As $\mathbf{E}^L$ depends in turn on $\mathbf{p}^A$, Eq. (6) defines a system of linear equations that may easily be solved for $\mathbf{p}^A$.

We now follow Ref. [13] to calculate the RAS signal of the system, $\mathcal{R} = 2(R_x - R_y)/(R_x + R_y)$, i.e., the normalized change in the reflectance R_x and R_y between the principal directions x and y, through

$$\mathcal{R} = 8\pi \left(\frac{d}{\lambda}\right) \mathrm{Im} \frac{p_x - p_y}{p_0}, \tag{7}$$

with λ the wavelength of the incident light, $\mathbf{p} = \mathbf{p}^A + \mathbf{p}^I$, and $p_0 = (\epsilon - 1)E^M |\mathbf{a}_1 \times \mathbf{a}_2| d/4\pi$ a complex normalization factor with the units of dipole moment, proportional to the bulk polarization of the substrate and used to set the scale of $\mathcal{R}$. Notice that $\mathcal{R}$ depends on the 2D geometry of the array of dipoles through the dipolar tensors $\mathbf{T}^{AA}$ and $\mathbf{T}^{AI}$.

3 Results In Fig. 3 we show some ordered superstructures found experimentally for K adsorbed on Ir(001) [6] for different values of coverage θ. The white circles represent Ir atoms while the dark circles are the K adsorbed atoms. The separation between Ir atoms is $a = a_0/\sqrt{2}$, where $a_0 = 3.84$Å is the lattice constant of Ir, as we are seeing the top view of an fcc (001) surface. Notice that when the coverage is $\theta = 1/2$ or $\theta = 1/5$ the adsorbed atoms occupy a square Bravais lattice array with $a_1 = a_0$ or $a_1 = \sqrt{5/2}a_0$ respectively, and when the coverage is $\theta = 1/4$ or $\theta = 1/8$ they form a centered rectangular Bravais lattice array with primitive lattice vectors $a_1 = \sqrt{11/2}a_0$ and $a_2 = (3/2)a_0$, and $a_1 = 4a_0$ and $a_2 = \sqrt{5}a_0$ respectively. Having recognized the type of lattice structure, we calculate from Eq. (7) the corresponding RAS spectra for each coverage. In Fig. 4 we show the RAS spectra of these configurations.

Table 1 Parameters employed in Fig. 5

Lattice	a_1 (Å)	a_2 (Å)	γ
square	3.84	3.84	90^0
hexagonal	4.13	4.13	60^0
rectangular	10.86	1.36	90^0
centered rectangular	3.96	3.96	70^0
oblique	9.40	2.05	50^0

We take in all the above cases a separation $d/2 = 2$Å between the overlayer and the substrate. For the polarizability of the adatom we use their free-atom properties, e.g., the oscillator strengths for single-electron transitions as given by Weisheit [14] and experimentally obtained excitation energies. We can see that the RAS spectra of the centered rectangular lattices show two structures, the first of which is located at 4.0 eV and the second at 8.0 eV. The intensity of these peaks is larger for $\theta = 1/4$ than for $\theta = 1/8$. Notice that for $\theta = 1/2$ and $1/5$ we obtained a null RAS signal, which we can easily understand as the square Bravais lattices are isotropic in the plane.

In Fig. 5 we show the RAS spectra for the five lattices shown in Fig. 1. To compare on equal grounds the RAS spectra for different geometries, we take a constant 2D unit cell area $A \approx 15$ Å^2. The parameters corresponding to each curve are shown in table 1.

As in Fig. 4, we took $d = 4$ Å.

Finally in Fig. 6 we compare the RAS spectra of an oblique lattice with the same parameters as in Fig. 5 but for two different values of the separation between the adsorbed layer and the metal surface, $d = 4$ Å and $d = 8$Å.

4 Conclusions We have calculated the RAS spectra of K atoms adsorbed on Ir(001) surfaces forming different ordered overlayers, corresponding to different values of the coverage θ [6]. We found that for both $\theta = 1/2$ and $\theta = 1/5$ K adatoms form a square Bravais lattice which yields a null RAS signal, since the square lattice, as the hexagonal lattice, is isotropic. On the other hand, for $\theta = 1/4$ and $\theta = 1/8$ the adsorbed atoms form an centered rectangular lattice and that this kind of lattice, as well as

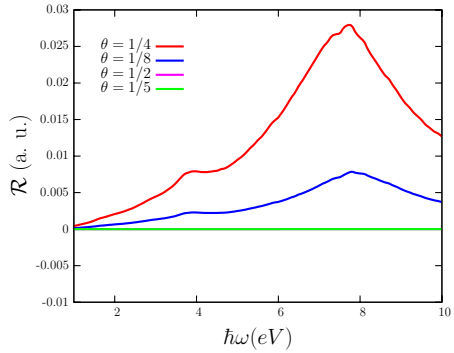

Figure 4 (Color online) RAS spectra for the ordered overlayer structures of Fig. 3.

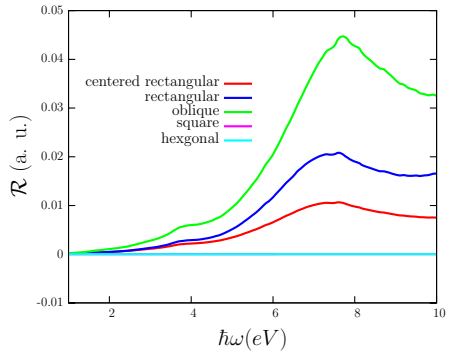

Figure 5 (Color online) RAS spectra for the ordered overlayer structures of Fig. 1.

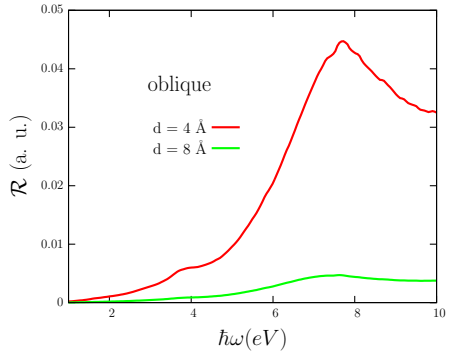

Figure 6 (Color online) RAS spectra for two different values of d of an oblique structure.

the rectangular and oblique lattices, are anisotropic in the plane and yield a RAS signal. Thus, RAS measurements may be employed for monitoring optically the presence and the transitions among some of the ordered overlayer structures as well for observing the transitions between ordered and disordered phases. Although our results were obtained for particular alkali atoms on a particular metallic substrate, our scheme may be employed to calculate the RAS spectra of many other systems for which we expect similar results. Our main approximation is that of using the free-atom polarizability for the adatoms, which we expect to be valid for physisorbed atoms whose electronic structure is not too strongly modified by the substrate. Although we expect the polarizability to be strongly modified in the case of chemisorbed atoms, we believe that our results would be qualitatively robust, namely, that overlayer phase transitions may be monitored through the observation of the RAS spectra.

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