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Comparison of chlorine and oxygen adsorption on the ferromagnetic Fe(001) surface: Density-functional theory study

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ABSTRACT

We compare chemisorption of Cl and O on the ferromagnetic Fe(001) surface by using density-functional theory calculation. $p(2 \times 2)$ and $p(1 \times 1)$ adsorbate overlayers are considered. The chlorine adsorption resembles in most respects the previously thoroughly studied oxygen deposition, although the Cl atom is well separated from the subsurface-layer Fe atom and, at low coverage, its induced magnetic moment is very small: 0.06 μ_B. For the $p(2 \times 2)$ structure, the spin-resolved local density of electronic states is dominated by exchange-splitted peaks of O(2p) or Cl(3p) character. The calculations are employed to discuss the data obtained recently by the new spin-polarized ion-scattering experimental technique [T.T. Suzuki et al., Surf. Sci. 602 (2008) 1688] for oxygen and chlorine adsorption on Fe(001). It remains to show whether the experimentally found significant difference between the signal from oxygen and chlorine, respectively, can be explained by the comparatively little differing electronic properties of the two adsorbates, or whether the signal from O does not rather reflect partly properties of the surface iron atoms. For chlorine, the latter mechanism might be suppressed due to its large atomic radius.

1. Introduction

Understanding chemisorption processes on iron surfaces is of importance in applications such as recording media, magnetic sensors, catalysis and metallurgical processes. Not long time ago, several theoretical papers have been published considering the interplay between atomic (C, N, O) chemisorption or subsurface deposition and magnetization of Fe atoms [1–4]. The adsorbates introduce serious deformations in their neighbourhood, and the C and N adatoms also cause some magnetization reduction at the close Fe atoms. The adatoms gain small magnetic moment that couples antiferromagnetically with Fe for C and N. In the above references, also information on experimental and other theoretical studies can be found. Another chemisorption system with technical applications is the adsorption of carbon tetrachloride CCl_4 on iron. It has been established that CCl_4 adsorbs dissociatively but the whole picture remains partly unclear. According to Ref. [5] carbon atoms remain at the Fe(001) surface which causes formation of incommensurate or long-period Cl overlayers. After heating, carbon is removed from the surface region. Later measurements [6] challenge this model: Some form(s) of surface iron chloride is formed, perhaps together with some amount of CCl_2 fragments. It seems that all the experiments agree [7] that on Fe(001), chlorine resides at the four-fold (hollow) positions or close to them. Let us remark that, based on previous experimental and theoretical experience, hollow adsorption sites (for adsorbates of "reasonable size" and not for too large coverage, at least) represent the most likely sites for atomic adsorption at the (001) face.

Quite recently, deposition of oxygen on Fe(001) has been studied [7,8] by the newly developed *element selective* spin-polarized ion-scattering spectroscopy with He^+ ions. It has been found that signal from both the surface Fe and O atoms, respectively, shows *negative* spin asymmetry, i.e. interaction with the surface *minority-spin* electrons prevails. For iron, this can be explained by the local density of electronic states (LDOS) with minority spins that is high close to the Fermi level E_F as revealed, e.g., by the detailed spin-polarized metastable deexcitation spectroscopy measurements [9,10] using excited He^* atoms, and confirmed also by the calculations [1]. Indeed, it is quite logical [8] that the delocalized electronic states of iron near E_F contribute most strongly to the Auger neutralization of He^+. For the oxygen signal, the situation is more involved. Although the electronic states from vicinity of E_F are likely to participate actively in the He^+ neutralization, for the adsorbed oxygen (and also for Cl, see below) the LDOS is low and the question arises whether rather the high LDOS O(2p) feature lying ~ 6 eV below E_F [9,10] is not the main actor.

For CCl_4 dissociated on Fe(001) the same technique detects again negative spin asymmetry for Fe that is, moreover, not sensitive to the Cl exposure. For Cl signal, however, virtually zero asymmetry is found in the Ref. [7]. The Authors suggest that absence of the chlorine magnetization might explain the result.

It follows from the previous discussion that for oxygen adsorption on Fe(001) detailed experimental and theoretical data are

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available (Refs. [1,9,10] and references given therein). For chlorine deposition, the experimental data are not complete and are partly controversial, and theoretical calculations are missing. Since the theoretical studies quoted above show that magnetic moment of adsorbates on Fe(001) changes sign when going from nitrogen to oxygen, one is tempted to speculate that an adatom with properties lying between those of O and N, respectively, might posses no or very small magnetic moment. According to the table of tight-binding parameters of Harrison [11] the effective atomic valence p-electron levels (in eV) read -8.97 (C), -11.47 (N), -14.13 (O) and -12.31 (Cl). The electronegativities of atoms grow in the sequence C–N–O in the revised Pauling [12] and Sandreson [13] schemes, and the electronegativity value of Cl falls between that of O and N, respectively. Hence, we find some simple argumets supporting our speculation. To shed more light upon the problem, we perform the density-functional theory calculations for Cl and O adsorption on the Fe(001) surface. One of the main purposes of the calculation is to check whether there are marked enough differences in the electronic and/or magnetic properties of the two adsorbates that might explain the difference in the measured spin-asymmetry.

2. Model and computational details

To analyze magnetic properties of Cl or O on Fe(001), the low-coverage ($\theta = 0.25$) $p(2 \times 2)$ and the high-coverage ($\theta = 1.0$) $p(1 \times 1)$ adsorbate phases are considered. The $p(1 \times 1)$Cl/Fe(001) structure is not a realistic one since in the experiment [5] the maximum Cl coverage of about 0.74 was reached. It might be, however, useful to elucidate general trends by performing also the analysis for θ(Cl) = 1. The details of calculation are identical to those in our previous studies [4], cf. also Ref. [1]. Particularly, the spin-polarized density-functional calculations are performed by utilizing the DACAPO code [14]. It is a plane-vawe code using ultrasoft Vanderbilt pseudopotentials to study periodic structures. The gradient-corrected Perdew and Wang form of the density functional (PW91) is chosen. The Fe(001) crystal is modelled by a six-layer slab with or without adsorbate. The adatoms are adsorbed at one surface of the slab only. The supercell geometry with periodically repeated slabs separated by vacuum wide about 14 Å is used. The dipole correction compensating the work-function jump when crossing the slab is included. The Monkhorst–Pack mesh in the Brillouin zone for the $(1 \times 1)((2 \times 2))$ structure is $(8 \times 8 \times 1)$ $((4 \times 4 \times 1))$ The energy cut-off is 400 eV. We use always the lattice constant $a = 2.855$ Å calculated previously [4] for bcc iron. In the same calculation, somewhat elevated value 2.29 μ_B of the magnetic moment at the iron bulk atoms was found. A more detailed discussion of numerical accuracy as well as comparison of our results for iron with those of other authors is presented in Refs. [1,3,4,15]. For the magnetic O_2 and non-magnetic Cl_2 free molecule we get the bond lengths 1.24 and 2.00 Å that compare rather well with experimental values 1.21 and 1.99 Å, respectively. The adsorbate atom resides always at hollow (four-fold) sites above the surface. The geometry optimization of adatom and iron-atom positions in the first three iron layers is performed. The calculated dissociative adsorption energy per adatom A is defined as $E_{ad} = E(Fe - slab\ +\ A) - E(Fe - slab) - 0.5E(A_2)$, where E($\cdots$) is the total energy per elementary cell. E_{ad} is negative for exothermic adsorption. To evaluate local magnetic moments, we use atomic sphere with the Fe bulk Wigner–Seitz radius $r_{WS} = 1.41$ Å for iron and the same value also for Cl since the Cl-Fe separations (see below) and Fe–Fe separations turn out to be similar. (Generally, the effective Cl radius can vary strongly [12] in dependence on the corresponding bond polarization.) For oxygen, we use the radius 0.8 Å close to typical oxygen covalent-radii values. Let us stress that, in accord also with our previous experience, the magnetic moment remains almost unchanged when the sphere radius varies in reasonable limits; e.g. by taking $r = 1.0$ Å instead of 1.41 Å for Cl, the moment value is reduced by about 0.01 μ_B. The reason is that we modify mainly the contribution from the free-electron-like states that are weakly magnetically polarized. Similar behaviour has been found also for oxygen. Let us note that the values of magnetic moments derived in the calculations [1–4] (and in the present one) for several atomic adsorbates on iron by using differing formalisms compare favourably.

3. Results and discussion

Data on the non-magnetic properties for O and Cl adsorption on Fe(001) are gathered in Table 1. In many respects, the changes when going from the $p(2 \times 2)$ to the $p(1 \times 1)$ structure are common for Cl and O, respectively. They follow mainly from the fact that for the $p(2 \times 2)$ structure, the four surface Fe neighbours of adatom can move also horizontally towards it lifting simultaneously the adatom higher above the surface. This results in a less urgent need to push the subsurface atoms away from adatoms (lowered value of Δ_{12} in Table 1). The results for the $p(1 \times 1)$O overlayer agree reasonably well with those of Ref. [1]; when comparison for the $p(2 \times 2)$ is done one should keep in mind that definition of the position (level) for the buckled subsurface layer is different in the latter paper from the definition used here. When properly recalculated, the Δ_{ij} values in the two studies differ by about 1%. The large drop in the adsorption energy for the θ (Cl) = 1 phase indicates a considerable repulsion between chlorine atoms.

The local magnetic moments are shown in Table 2. In accord with the theoretical study [1] we find some magnetization enhancement near the oxidized iron surface especially for $\theta = 1$. There is a quite moderate magnetic moment on oxygen that couples ferromagnetically to iron moments. For chlorine, the change of moments on neighbouring iron atoms is small. The magnetization of the Cl adatom (0.06 μ_B) in the low-coverage phase $\theta = 0.25$ is clearly suppressed as compared with oxygen. It is interesting that splitting of Cl(3p) majority- and minority-spin peaks (~0.4 eV, Fig. 1) is still considerable although smaller than for oxygen.

Table 1
Relaxations Δ_{ij} of the vertical interlayer distance for the iron (001) surface with or without adsorbates. Index $i = 1$ refers to the Fe surface. For $p(2 \times 2)$ structures, the level of the buckled second Fe layer is defined by the iron nearest to the adsorbate. The relaxations are calculated with respect to ideal bcc iron slabs. z is the height of adsorbed adatom (Cl or O) above the Fe surface, d_1, d_2 are the adsorbate distances to its Fe nearest neighbours in the surface and subsurface Fe layer, respectively. E_{ad} is the calculated adsorption energy per one adatom.

Structure	Δ_{12}(%)	Δ_{23}(%)	Δ_{34}(%)	z (Å)	d_1, d_2 (Å)	E_{ad} (eV)
$p(1 \times 1)$ Clean	-2.26	1.66	0.04			
$p(2 \times 2)$Cl	6.86	-5.08	1.55	1.65	2.58, 3.18	-2.56
$p(1 \times 1)$Cl	11.66	-1.67	0.85	1.49	2.51, 3.08	-1.33
$p(2 \times 2)$O	8.95	-6.11	1.09	0.59	2.08, 2.14	-3.47
$p(1 \times 1)$O	14.86	-1.18	0.68	0.43	2.07, 2.07	-2.94

Table 2
Magnetic moments (in μ_B) calculated for adsorbate (A = Cl,O) and the first three iron layers. For layers with non-equivalent Fe atoms, values for atoms closest to adsorbate are given.

Layer	$p(1 \times 1)$ Clean	$p(2 \times 2)$Cl	$p(1 \times 1)$Cl	$p(2 \times 2)$O	$p(1 \times 1)$O
A		0.06	0.19	0.12	0.18
1	3.05	3.00	3.03	3.00	3.26
2	2.38	2.36	2.35	2.51	2.58
3	2.35	2.42	2.47	2.44	2.46