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LDA theory of the coverage dependence of the local density of states: Li adsorbed on Ru(001)

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To understand recent β-decay NMR experiments on Li atoms chemisorbed on a Ru(001) surface, the work-function changes and the local density of states (LDOS) at E_F and at the Li nucleus are determined from first-principles local-density full potential linearized augmented plane wave calculations for three coverages (Θ =1, 0.25, and 0.11) and two possible sites for Li (fcc and hcp). From full structure optimizations by means of total energy and atomic force calculations, both a surface and in-plane relaxation are found, and Li chemisorption site preferences are determined as a function of coverage. The calculated LDOS is constant for low coverage whereas the work function changes substantially—both in very good agreement with the β-decay NMR experiments. In contrast, the LDOS at high coverage is predicted to increase by a factor of 2. [S0163-1829(98)01120-5]

I. INTRODUCTION

Experimental and theoretical investigations of phenomena at surfaces and interfaces continue to grow at a rapid pace, driven in part by new discoveries and their importance for many device applications. Since the interface strongly determines the properties of such a device, a determination and understanding of the local as well as global electronic structure are necessary. Among others, the chemisorption of alkali-metal atoms on metal surfaces is an example of the importance of understanding local electronic properties at surfaces: The catalytic promotion of chemical reactions on metal surfaces in the presence of alkali-metal atoms is well known,[1] and a famous example is the Haber-Bosch process. The lowering of the work function upon alkali-metal chemisorption and its vast technological applications was first recognized by Taylor and Langmuir.[2] Since the early days of the Gurney model,[3] extensive discussions have centered on the type of bonding of the alkali-metal atom to the metal surface, centered on the question of charge transfer from the alkali-metal atom to the metal. While various calculations of the charge density in the vicinity of the adsorbed alkali-metal atom were performed to clarify this question, unfortunately different authors have come to different results and both covalent and ionic pictures of the alkali-metal adsorption have been reported.[4–6]

Still, despite enormous advances, there are few experimental techniques for probing local electronic properties of surfaces and interfaces. Recently a novel type of experiment, β-decay detected NMR, was developed[7] and applied to investigate the chemisorption of Li atoms on a Ru(001) surface. One of the quantities determined by these NMR experiments is the so-called spin-lattice relaxation time T_1. The hyperfine interaction between the nucleus of the NMR probe and the surrounding electrons give rises to a nuclear spin relaxation. For a NMR probe with s electrons, like the Li atom, the dominant part of the hyperfine interaction is the Fermi contact interaction. Theoretical investigations of a relaxation process under the assumption that the Fermi contact term is the relevant interaction lead to the following relation between T_1 and the local density of states at the Fermi energy and the position of the nucleus of the probe $n(E_F,0)$:[9,8]

$$\frac{1}{T_1}=\frac{256\pi^3}{9}\mu_e^2\left(\frac{\mu_n}{I}\right)^2\frac{kT}{\hbar}n(E_F,0)^2, \tag{1}$$

where μ_e is the Bohr magneton and μ_n is the magnetic moment of the nucleus. Now, such measurements of the spin lattice relaxation time (T_1) provide information about the local density of states (LDOS) at the Fermi energy and at the position of the Li nucleus. Thus, the very local electronic structure of the chemisorbed alkali-metal atom is determined through the LDOS and its understanding provides new physical insight into the chemisorption process. It also offers a severe challenge for modern *ab initio* local-density-approximation (LDA) calculations.[7] Unlike the charge density profile around the alkali-metal atom, which is not a well defined quantity and is not easily accessible through experiments, the LDOS allows a direct comparison between experiment and theory.

A particularly characteristic feature of the alkali-metal chemisorption, which has been exploited extensively since the early days of Langmuir, is the considerable lowering of the work function even at very low coverages. Thus one striking result of the β-decay NMR experiments (β-NMR for short) is a constancy of the LDOS over a coverage region of $\Theta=0.0$ to 0.2, while the work function changes by about -2 eV.[7] So far, no realistic calculations of the LDOS for Li on Ru(001) (or other systems) including the atomic structure of the substrate have been performed; only model calculations for a jellium surface have been reported.[8]

In this paper, we present results of fully self-consistent local-density calculations for Li chemisorption on Ru(001). Using our full potential linearized augmented-plane-wave (FLAPW) method[12] for thin films, we investigated the Li chemisorption for three different coverages $\Theta=$ 0.11, 0.25, and 1.0, and for both the fcc and hcp sites, since both these threefold symmetry sites were found for low coverages in LEED investigations.[10,11] For a coverage of $\Theta=0.25$, Li was reported to occupy the fcc site in a 2×2 structure while for $\Theta=0.33$ the hcp site was occupied.[10] For each coverage we performed full structure optimizations, including possible surface relaxation and surface reconstruction, by means of total energy and atomic force calculations. In Sec. II, we describe the method and details of the calculations. In Sec. III we present results for (i) the clean surface, (ii) Li chemisorbed on the fcc site, and (iii) for Li chemisorbed on the hcp site. Section IV provides a summary and conclusion.

II. METHOD AND DETAILS OF CALCULATION

The all-electron *ab initio* FLAPW method for thin films makes no shape approximations for the potential and charge density. The exchange-correlation effects are treated within the local-density approximation (LDA) using the Hedin-Lundqvist[13] parametrization of the exchange-correlation potential. The thin film (or single slab) approach uses two-dimensional symmetry in the plane; along the z direction no artificial periodicity is imposed, which makes it highly advantageous in treating surface related problems, such as chemisorption. Our present implementation of the FLAPW method for thin films includes total energy[14] and atomic force calculations,[15] which allows full structure optimization. For each self-consistent structure, the forces on all atoms were determined. A stable configuration is found, when the $3n$-dimensional force vector of the system (with n atoms) is zero. A Broyden[16] scheme was used to find the multidimensional zero. We considered a structure relaxed, when the force on each atom was smaller than 1 mRy/a.u.

To make the calculations for very low coverages still feasible and for meaningful comparison of the results for different coverages, we used a four-layer slab for the Ru substrate for all three coverages, the Li atom adsorbed on both sides of the slab. A muffin-tin radius of 2.4 a.u. for the Ru and of 1.6 a.u. for Li was chosen in order to allow the system to relax without overlap of the spheres. A $k_{\mathrm{max}}=$ 3.3 and 9.0 a.u. for the plane-wave basis and the potential representation was found to be sufficient, and 12 (two-dimensional) special k points in the irreducible BZ were used to achieve self-consistency. A theoretical description of the LDOS is very similar to the DOS, except that it is a local quantity:

$$n(E,\vec{r}) = -\frac{1}{\pi}\mathrm{Im}\; G(\vec{r},\vec{r},E) = \sum_i |\psi_i(\vec{r})|^2 \delta(E-E_i), \quad (2)$$

where G is the Green's function of the system. The latter expression was used to calculate the LDOS from the self-consistent, fully optimized structure.

At a coverage of $\Theta = 0.25$ and 0.11, an in-plane relaxation of the substrate atoms is possible due to the larger two-dimensional unit cell employed. For a coverage of $\Theta = 0.11$, this gives 9 Ru atoms in the surface layer and a total of 38 atoms in the system. To obtain a reliable result for the LDOS at E_F, both the band structure and the Fermi surface have to be determined accurately. To determine the number of k points necessary to achieve convergence, we used the following procedure: A 40 meV temperature broadening of E_F was used to calculate the LDOS. We increased the number of k points and a well converged result for the LDOS was obtained for special k point sets of more than 400 k points in the irreducible BZ (IBZ) We therefore used about 500 (two-dimensional) special k points in the IBZ to calculate the LDOS from a previously converged potential. Neither the work function nor the force calculation and therefore the structure optimization were significantly affected by this procedure.

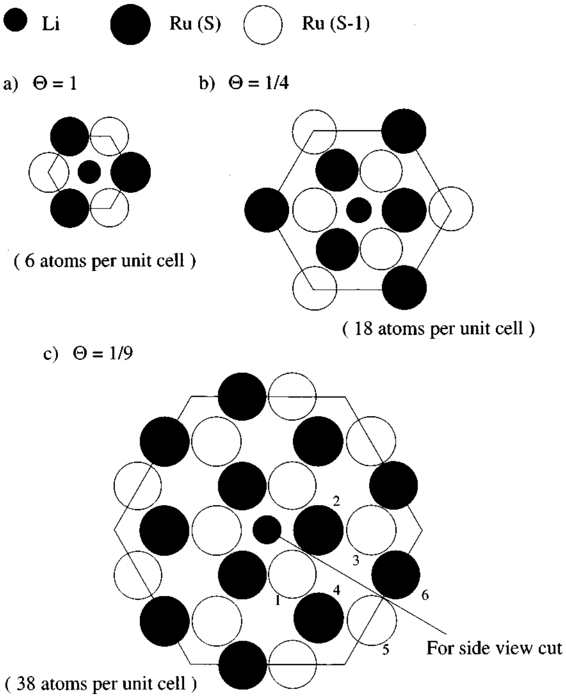

FIG. 1. Schematic top view of the different coverages for Li on the fcc site. The labeled Ru atoms (1–6) are shown in Fig. 2 and are used for a surface relaxation.

III. RESULTS

A. Clean metal surface

In order to determine the effects of Li chemisorption, we first investigated the bare metal substrate. To cover possible in-plane relaxation, we use a two-dimensional unit cell of twice the size required to describe the clean metal system. The Ru substrate was set up with its bulk lattice constant; employing atomic force and total energy calculations, the system was allowed to relax, including possible in-plane relaxation. For the clean surface we find a surface layer that is contracted by about 3.2% with respect to the bulk value. In order to avoid artificial relaxation effects due to the relatively small number of Ru layers, we compared this result with that from a six-layer slab calculation: The result was a 3.4% contraction of the surface layer. The clean metal surface was found to show no in-plane relaxation and to keep its perfect hexagonal structure. Since the work-function change, $\Delta\Phi$, due to the Li chemisorption is of some importance, we calculated the work function Φ of the clean Ru(001) surface: A value of 5.42 eV was found, which agrees well with the experimental value of 5.35 eV for this surface.[17,18] Again, we compared this result with that for a six-layer slab and found the same value of $\Phi = 5.41$ eV. These results indicate that a four-layer slab covers the relevant physical properties of interest in the present work.

B. Coverage-dependent Li-induced surface relaxation: fcc site

The chemisorption of Li atoms onto the Ru(001) surface was investigated for three coverages, $\Theta = 1.0$, 0.25, and 0.11.

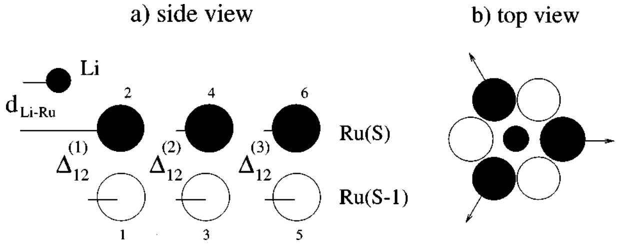

FIG. 2. Side view cut along the line shown in Fig. 1 with the same labeled atoms.

First, we discuss the results for a Li chemisorption on the fcc site. For $\Theta=0.25$ and 0.11, we doubled and tripled the two-dimensional unit cell necessary to describe the monolayer coverage ($\Theta=1.0$); the resultant (schematic) top views of the different coverages are shown in Fig. 1. The surface and subsurface atoms are shrunk in order to better show both the surface and subsurface layers. Unlike the case of lower coverages, no in-plane relaxation is allowed for $\Theta=1.0$ in the calculations due to the symmetry of the unit cell.

Upon Li chemisorption, the Ru surface relaxation shows a strong coverage dependence; the relative changes in their atomic positions are given with respect to the relaxed clean metal. To discuss these effects, we define the following notation: The relative distances between the surface and subsurface Ru atoms are denoted by $\Delta_{12}^{(i)}$. The additional index i refers to the first, second, and third nearest-neighbor Ru atoms with respect to the Li atom. Of course, $\Theta=1.0$ has only first nearest-neighbor Ru atoms, while the lower coverages of $\Theta=0.25$ and 0.11 also have second and third nearest neighbors, respectively (cf. Fig. 1). Figure 2 presents a schematic side view cut along the plane shown in Fig. 1(c). Note that the surface and subsurface Ru atoms are not on top of each other [cf. Fig. 1(c)]. For the relaxed clean metal, $\Delta_{12}^{(i)}$ is the same value for all i.

The results of the structure optimization are summarized in Table I. For the very low coverage of $\Theta=0.11$, we find a reduction of $\Delta_{12}^{(1)}$ by 1.02%, a small expansion of $\Delta_{12}^{(2)}$ by 0.35%, and also a reduction of $\Delta_{12}^{(3)}$ by 0.53%. In addition, no significant in-plane relaxation of the Ru atoms was found. The Li atom is found to have an equilibrium distance of 4.50 a.u. from the Ru surface. In contrast, a coverage of $\Theta=0.25$ shows a quite different behavior. While $\Delta_{12}^{(1)}$ is also reduced by 1.30% (which is comparable to that for $\Theta=0.11$), $\Delta_{12}^{(2)}$ is expanded by 2.71%. Here we find a significant in-plane relaxation of the Ru atoms by 1.82% along the directions shown in Fig. 2. This change in the relaxation of the Ru surface has to be discussed in connection with the Li-Ru distance, which for $\Theta=0.25$ is 4.23 a.u. Thus, the Li atom moves closer to the surface and pushes the Ru atoms apart. As a result of the in-plane relaxation, the second nearest Ru atoms are affected and cause the outward relaxation.

TABLE I. Surface relaxation due to Li chemisorption versus coverage for the fcc site.

	$d_{\text{Li-Ru}}$	$\Delta_{12}^{(1)}$	$\Delta_{12}^{(2)}$	$\Delta_{12}^{(3)}$	In-plane
$\Theta=0.11$	4.50 (a.u.)	−1.02%	+0.35%	−0.53%	0.0
$\Theta=0.25$	4.23 (a.u.)	−1.30%	+2.71%		1.82%
$\Theta=1.0$	4.04 (a.u.)	+2.00%			

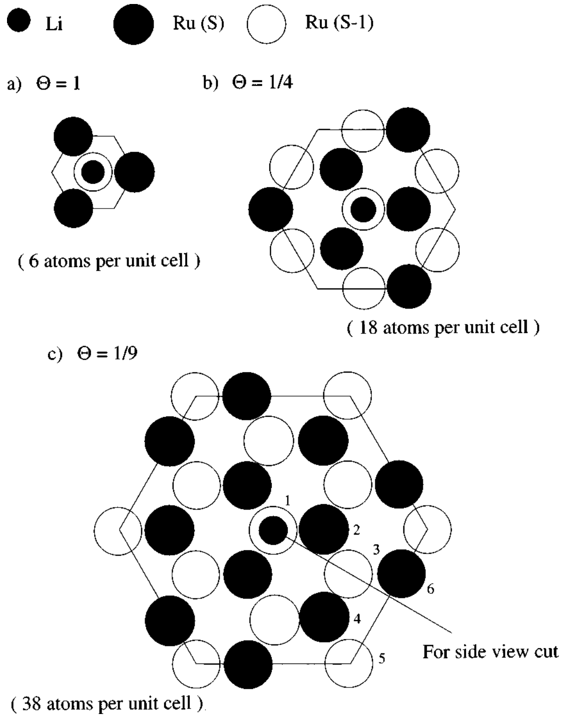

FIG. 3. Same as Fig. 1 for the hcp site.

In the case of $\Theta=1.0$, a further interesting result is found: In contrast to $\Theta=0.11$ and 0.25, the high coverage causes a 2% expansion of $\Delta_{12}^{(1)}$ [which means a restoration closer to the bulk (unrelaxed) value]. The Li-Ru equilibrium distance is given by 4.04 a.u., which means a further reduction compared to $\Theta=0.25$ and 0.11.

C. Coverage-dependent Li-induced surface relaxation: hcp site

We give here the results for the Li chemisorption on the hcp site. In Fig. 3 we show a schematic top view of the system as in Fig. 1, but now for Li chemisorbed on the hcp site. Also, in Fig. 4, a side view along the plane indicated in Fig. 3(c) is shown. The results are summarized in Table II. Note that the distances $\Delta_{12}^{(i)}$ are not the same as for the fcc site; they are chosen to reveal the influence of the Li chemisorption on the first, second, and third nearest Ru atoms with respect to the Li atom. Also here, as in the case of the fcc adsorption site for Li, we find a strong surface relaxation of the Ru substrate upon chemisorption. For $\Theta=0.11$, we find a contraction of $\Delta_{12}^{(1)}$ by 0.41%, an expansion of $\Delta_{12}^{(2)}$ by 0.40%, and of $\Delta_{12}^{(3)}$ by 0.57%. Also here we find a small

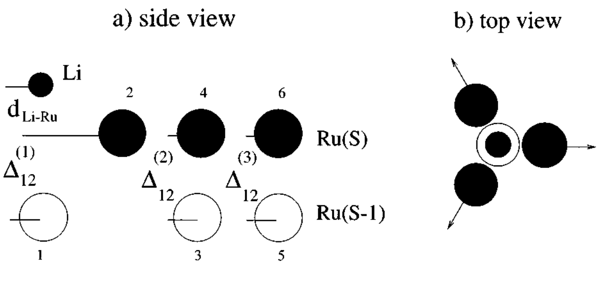

FIG. 4. Same as Fig. 2 for the hcp site.

TABLE II. Surface relaxation due to Li chemisorption versus coverage for the hcp site.

	$d_{\text{Li-Ru}}$	$\Delta_{12}^{(1)}$	$\Delta_{12}^{(2)}$	$\Delta_{12}^{(3)}$	In-plane
$\Theta=0.11$	4.46 (a.u.)	-0.41%	$+0.40\%$	$+0.57\%$	$+0.20$
$\Theta=0.25$	4.21 (a.u.)	-1.84%	$+0.67\%$		$+1.03\%$
$\Theta=1.0$	3.94 (a.u.)	-0.05%			

in-plane relaxation of 0.2% along the directions indicated in Fig. 4. The Li-Ru distance (4.46 a.u.), which is smaller compared to the fcc site, causes the in-plane relaxation; indeed, the Li atom pushes the Ru atoms slightly apart. As a consequence, $\Delta_{12}^{(3)}$ shows an outward relaxation.

In the case of $\Theta=0.25$, we find a reduction of $\Delta_{12}^{(1)}$ by 1.84% and an expansion of $\Delta_{12}^{(2)}$ by 0.67%, i.e., similar to the case of the fcc site. As in the case of the fcc site, we find an in-plane relaxation but of a smaller amount (1.03%), along the directions indicated in Fig. 4. In this case, the Li-Ru distance is 4.21 a.u. Finally, for the high coverage of $\Theta=1.0$ we find a small reduction of $\Delta_{12}^{(1)}$ of 0.05%. Here, the Li-Ru distance is 3.94 a.u.

The calculations for both sites include the determination of the total energy of the system. To investigate the site preference at 0 K, we calculated the total energy difference ΔE_{tot} between the fcc and hcp sites; a negative value of ΔE_{tot} predicts the fcc site to be favorable. We find ΔE_{tot} for $\Theta=0.25$ and 1.0 to be about +47 meV and −350 meV, respectively. Thus our calculations predict the fcc site to be favorable for high coverage and the hcp site to be favorable for $\Theta=0.25$. By contrast, experiments suggest the fcc site for a coverage of $\Theta=0.25$ and the hcp site for $\Theta=0.33$,[10,11] which indicates the sensitivity of site preference to coverage. Indeed, in Ref. 10, a thermal instability was observed once a temperature of 80 K was reached. For $\Theta=0.11$, the ΔE_{tot} value is so small (−4 meV) as to suggest that both sites are likely to be occupied.

D. Coverage dependence of the LDOS for Li/Ru(001)

Having obtained the optimized structures of the three Li coverages, we then calculated the electronic properties of the chemisorbed system for both the fcc and hcp sites. As mentioned above, the experiments focus on the LDOS at E_F at the Li nucleus for a very low coverage region. Therefore, our coverages of $\Theta=0.11$ and 0.25 allow a comparison of theory and experiment. We show the LDOS at the position of the Li nucleus as a function of the band energy for Li chemisorbed on the fcc site in Fig. 5 and on the hcp site in Fig. 6. The zero in the energy scale refers to E_F, for the three Li coverages of physical interest here. Table III summarizes the results for the Li LDOS of both sites. The interesting result is that in the low coverage region the Li LDOS has a constant value of 0.10 $\text{eV}^{-1}/\text{Å}^3$ in the case of Li on the fcc site and 0.11 $\text{eV}^{-1}/\text{Å}^3$ for the hcp site. In contrast, the high coverage of Li results in a value of the LDOS that is about two times larger than in the low coverage region, 0.23 for the fcc site, and 0.21 for the hcp site.

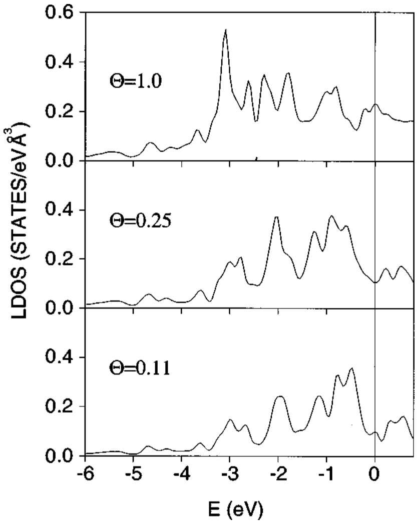

FIG. 5. LDOS at the position of the Li nucleus at E_F, for the fcc site. The zero in energy scale refers to E_F.

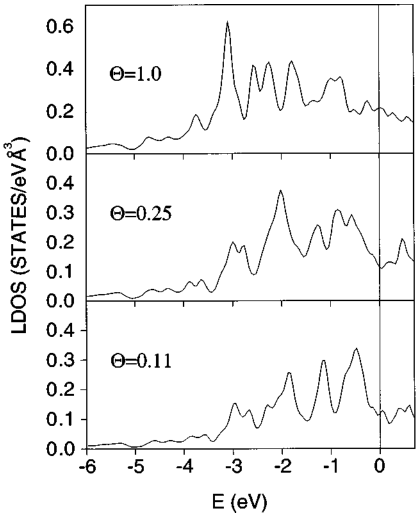

FIG. 6. Same as Fig. 5, for the hcp site.

From Figs. 5 and 6 and the result for the LDOS at E_F, one can see that both threefold symmetry sites reveal essentially the same local electronic properties—a constant LDOS at E_F of about the same value, which is predicted to be two times larger for high coverages. The experiments find a value of 0.13 $\text{eV}^{-1}/\text{Å}^3$ for a coverage region of $\Theta=0$ to 0.2. Thus, the calculated LDOS for the low coverage region agrees favorably with experiment with respect to both the absolute value and, perhaps more important, the constancy over a coverage of $\Theta=0$ to 0.25. The smaller theoretical value of the LDOS can be explained by the fact that other possible relaxation mechanisms may be present, which give a higher experimental value for the relaxation rate than a pure Fermi contact interaction would give. A further interesting result of our theoretical calculations of the LDOS is a more than two times greater value for the high coverage region, a prediction that needs to be confirmed by future experiments.

TABLE III. Coverage dependence of the LDOS at E_F in $\text{eV}^{-1}/\text{Å}^3$.

Θ		0.11	0.25	1.0
LDOS	fcc	0.100	0.103	0.231
LDOS	hcp	0.115	0.113	0.212

TABLE IV. Work-function change due to Li chemisorption in eV.

Θ		0.11	0.25	1.0
$\Delta\Phi$	fcc	-0.72	-2.33	-2.01
$\Delta\Phi$	hcp	-0.61	-2.41	-2.20

In addition, for the fcc site the calculated work-function change $\Delta\Phi$ ranges from -0.72 to -2.33 eV over a coverage change from $\Theta=0.11$ to 0.25, and increases again to -2.01 eV for $\Theta=1.0$. For the hcp site, the result is very similar and we find $\Delta\Phi$ changes from -0.61 to -2.41 for $\Theta=0.11$ and 0.25 and again increases to -2.20 for $\Theta=1.0$. Table IV lists the results for $\Delta\Phi$ for both sites, to be compared with the experimental $\Delta\Phi$ of more than -2 eV.[7]

Finally, we also calculated the Li projected density of states in order to compare it with the LDOS for both the fcc and hcp sites (cf. Figs. 7 and 8, respectively). The solid line is the projected *s* DOS and the broken line the *p* DOS. One can see for both chemisorption sites that the *s* projected DOS shows a very similar energy dependence to that of the LDOS, since only *s* states have a contribution to the LDOS at the position of the Li nucleus. In general, the DOS shows the strong interaction of the Li atom with the Ru substrate, even at very low coverages: Due to hybridization with the metal *d* states, new states are formed below E_F, which can be seen from Figs. 7 and 8. Also with increasing coverage, the *p* projected DOS near and below E_F increases. These states are responsible for an increased dipole layer, which causes a shift in the electrostatic potential and a lowering of the work function.[4] At low coverages ($\Theta=0.11$ and 0.25), the *s* projected DOS and the LDOS show essentially the same features with respect to their energy dependence, while for high coverage ($\Theta=1.0$) the shape and maxima of the curve change significantly; the states with *s* character are more occupied and the maxima in the *s* projected DOS shift to lower energies. This clearly explains the significant change in the LDOS upon going from low to high coverages.

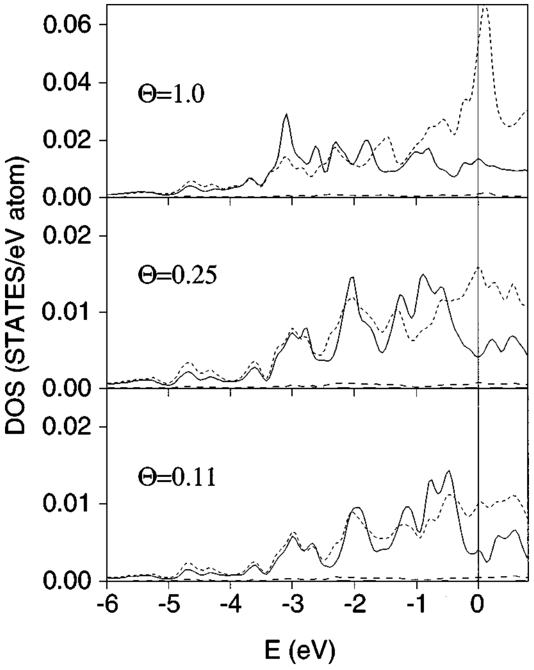

FIG. 7. Projected density of states. The zero in energy scale refers to E_F. Solid line refers to the *s* states, short-dashed line refers to the *p* states.

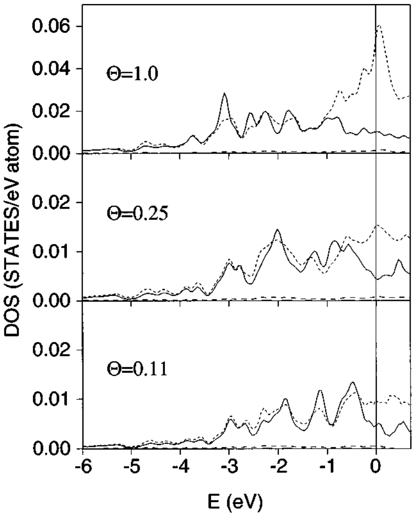

FIG. 8. Same as Fig. 7, for the hcp site.

IV. SUMMARY AND CONCLUSIONS

We have presented *ab initio* calculations for the coverage dependence of the LDOS at E_F and the Li nucleus. The Li chemisorption on Ru(001) was investigated for three different alkali-metal coverages ($\Theta=1.0$, 0.25, and 0.11) and the two threefold symmetry sites (fcc and hcp) for the chemisorbed Li atom. Structural and electronic properties of the Li chemisorption were determined. We find a rather strong surface relaxation of the Ru substrate due to Li chemisorption for all coverages and both sites. At very low coverages ($\Theta=0.11$) no in-plane relaxation of the Ru surface layer was found for the fcc site and a small value (0.2%) for the hcp site. At $\Theta=0.25$, our calculations showed a 1.82% and 1.03% in-plane expansion for the fcc and hcp sites, respectively, caused by the smaller Li-Ru distance. Also, our calculations show that the surface relaxation is not only limited to the next-nearest-neighbor atoms with respect to the Li atom, but that there exists a rather long range effect. As shown for the case of $\Theta=0.11$, both Li adsorption sites cause a surface relaxation of the second and even third nearest-neighbor Ru atoms.

For each optimized structure, we calculated the projected DOS and the LDOS at E_F of the Li atom. The local electronic properties of the Li chemisorption are essentially the same for both the fcc and hcp adsorption sites. The remarkable result we find is a constancy of the LDOS in the low coverage region but a large change in the work function, both in accordance with experiment. At high coverages ($\Theta=1.0$), we furthermore predict a value of the LDOS that is more than two times larger compared to the low coverage region.

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