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Covalent bonding of sulfur on Ni(001): S as a prototypical adsorbate catalytic poisoner

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The effects of sulfur, as a prototypical catalytic "poisoner," on the structural, electronic, and magnetic properties of Ni(001) are investigated with the highly precise full-potential linearzed augmented-plane-wave method. The Si-Ni interlayer distance is determined to be 1.36 Å. The poisoning is found to be caused by local Ni—S covalent-bond formation and the "lone-pair" density polarization on the S site. A nearly magnetically dead Ni surface layer ($0.12\mu_B$) is obtained. The indirect long-range (screening) interaction is manifested in a layer-dependent oscillatory on-site charge transfer between e_g and t_{2g} symmetry states for Ni inner layers.

Considerable experimental and theoretical work has revealed a complex role played by sulfur as an adsorbate on metallic surfaces. Thus, as a well-known catalytic "poisoner," S is observed to cause a drastic reduction in the surface reactivity and sticking coefficient of the metallic substrate. Experimental studies of the modification of chemisorptive and catalytic properties of Ni conclude that each adsorbed S affects ten neighboring surface Ni atoms.[1] On the other hand, evidence from studies of CO on S-modified Ni(001) surfaces supports a local interaction for the catalytic poisoning.[2] Thus, the catalytic poisoning effect of S on substrates and coadsorbed species appears to have different electronic origins. From a theoretical study of S adsorbed on Rh(001), Feibelman and Hamann[3] found features of a long-range S-Rh(001) interaction (i.e., unscreened charge density at E_F). Recently, a theoretical investigation of S+CO/Ni(001) by Wimmer *et al.*[4] gave evidence for a covalent-type short-range interaction between S-CO and S-Ni. Apparently, additional theoretical investigations are necessary to illustrate and understand the role played by S as a catalytic poisoner. Regarding structural aspects, $c(2\times2)$S/Ni(001) has been seen as a prototype for studying the adsorbate-substrate interaction by various experimental techniques.[5-10] A wealth of experimental data calls for the need of a first-principles calculation which takes into account both the short-range and long-range aspects of the metallic substrate.

In this paper, we present results of spin-polarized all-electron total-energy local-spin-density-functional studies of the poisoning effect due to an adsorbed $c(2\times2)$ S overlayer on Ni(001). The surface is modeled by a single-slab geometry and the local density one-particle equations are solved self-consistently by use of the full-potential linearized augmented-plane-wave (FLAPW) (Ref. 11) method. The catalytic poisoning of S is found to be understood in terms of the formation of a (short-ranged) S—Ni covalent bond and the "lone-pair" density polarization at the adsorbed S site. These effects lead to a modification of the surface density of states (DOS) at E_F (and thus the surface reactivity) and the magnetic moment of surface Ni atoms. The indirect long-range interaction, which is a response to the surface Ni-S covalent-type local interaction, is manifested in the layer-dependent oscillatory on-site charge transfer between e_g and t_{2g} symmetry states from surface to inner layers and the reduction of magnetic moments even for Ni atoms which are not nearest neighbors to the adsorbed S.

The single-slab consists of five Ni layers with a $c(2\times2)$ S overlayer adsorbed in the fourfold hollow sites of both surfaces. This geometry leads to 12 atoms per unit cell with two inequivalent sites for the subsurface Ni atoms (denoted as sites A and B, i.e., with and without S atoms directly above, respectively). The experimental lattice constant of 3.52 Å is used for the Ni substrate. The S—Ni bond length was determined from total-energy calculations. We use a total of 2×530 linearized augmented-plane-wave basis functions; angular momentum components up to 8 are employed to expand the full-potential and charge density, and the linearized wave functions within the muffin-tin (MT) spheres.

For the structural properties, we calculated the total energy as a function of S-Ni interlayer spacing ($d_\perp$) ranging from 1.2 to 1.45 Å. The resulting total energies behave harmonically in this range and yield an equilibrium $d_\perp=1.36$ Å. This value compares very well with the measured value by low-energy electron diffraction[5] (LEED, 1.3±0.1 Å), photoelectron diffraction[6] (1.3±0.044 Å), surface extended x-ray absorption fine structure[7] (SEXAFS, 1.37±0.03 Å), and angle-resolved-photoemission extended fine structure[8] (ARPEFS 1.31 Å), low-energy ion scattering (LEIS 1.40±0.05 Å), and an angle-resolved ultraviolet photoemission spectroscopy (ARUPS) analysis[12] (1.3 Å), and a very recent[13] electron-energy-loss spectroscopy value of 1.35 Å determined after the submission of our work. The curvature of the total-energy curve gives a normal stretching frequency of 310 cm^{-1} for S, which is in fair agreement with the result obtained from experiment.[10]

Figure 1 presents a charge-density contour plot of the clean Ni(001) surface [Fig. 1(a)] and $c(2\times2)$S/Ni(001) [Fig. 1(b)] in the (110) plane normal to the surface. Similar to that seen at other transition-metal surfaces, the electronic density above the Ni surface layer is very smooth and results from the charge expansion into the vacuum which serves to heal the charge discontinuity caused by formation of the surface. In contrast, the adsorption of S increases markedly the charge corrugation in the surface-vacuum region. Furthermore, Fig. 1(b) also reveals that the charge distribution at the S site is highly nonspherical with the density polarized toward the surface Ni atoms, indicating the formation of a S—Ni covalent bond. The work function (Φ) for the clean Ni(001) surface is 5.4 eV; upon S adsorption, Φ adsorption, Φ increases by 0.25 eV, which is consistent with experiment[14] (i.e., an increase of 0.38 eV). This result again indicates that the S-Ni interaction does not involve a large amount of intersite charge transfer between S and Ni, but instead, resembles covalent bonding.

To examine the charge redistribution and bonding effects upon S chemisorption and the strength of the S—Ni bond, we present in Fig. 2 a plot of the charge-density difference between $c(2\times2)$S/Ni(001) and a separately determined unsupported S monolayer and the clean Ni(001). The main features which can be drawn from this analysis are (1) the increased electronic density in the middle of the S—Ni bond (accompanied by a loss of $d_{xz,yz}$-like density delocalized at the surface Ni site) is evidence for a strong covalent bond between S and surface Ni atoms; (2) there forms a lone-pair electron density polarization at the S site (with the increased density directly above the chemisorbed S atoms); this may imply a chemically active region above S, and therefore, an inhibition of the direct interaction between Ni and other species (e.g., the S-CO interaction is predominantly local and direct); and (3) the increased density covers the Ni surface and may thus further reduce the reactivity of the substrate. These observations appear to explain the catalytic poisoning and site-blocking effects of S.[15]

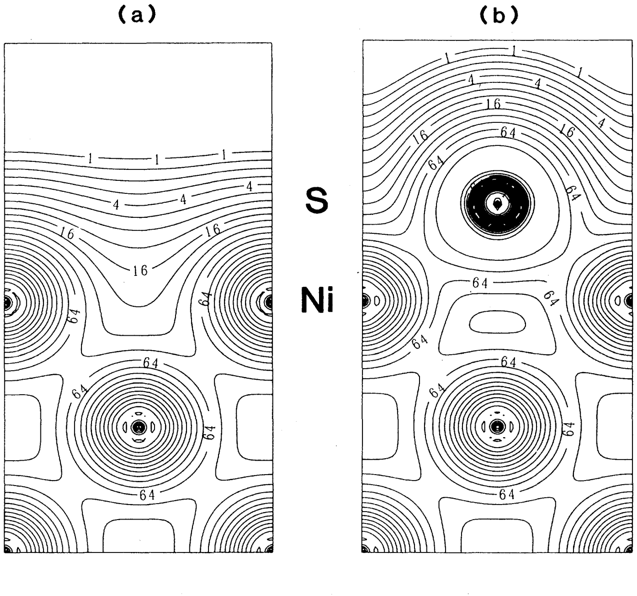

FIG. 1. Valence-charge density [in 10^{-3} $e/(\mathrm{a.u.}^3)$] of (a) the clean Ni(001) surface, and (b) the $c(2\times2)$S/Ni(001) in the (110) plane perpendicular to the surface.

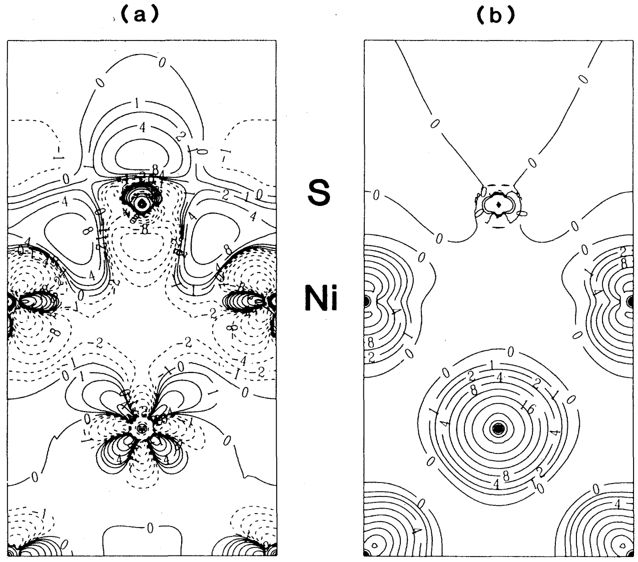

FIG. 2. (a) Charge-density difference [in 10^{-3} $e/(\mathrm{a.u.}^3$ units)] between $c(2\times2)$S/Ni and an unsupported S monolayer plus the clean Ni(001). (b) Spin density of $c(2\times2)$S/Ni in the (110) plane perpendicular to the surface. Solid (dotted) contours indicate gain (loss) of charge.

Although the change in the total number of valence electrons within the Ni muffin-tin (MT) spheres due to the S adsorption is predominantly localized to the surface layer, the density difference plot [cf. Fig. 2(a)] reveals that the catalytic poisoning effect on the charge redistribution actually shows long-range oscillatory behavior, i.e., while there is a decrease of t_{2g}-type symmetry electrons within the surface Ni MT sphere, an on-site counter charge transfer (screening) from e_g- to t_{2g}-type symmetry is seen at the subsurface Ni site [and vice versa for the center Ni layer, although the magnitude of the charge transfer is smaller than that of the surface Ni atoms; cf. Fig. 2(a)]. In their theoretical study of S adsorbed on Rh(001), Feibelman and Hamann[3] show that the charge density at E_F is not a screened quantity and conclude that a long-range interaction exists between S and substrates. This type of long-range interaction is also confirmed by our total-energy spin-polarized study: the modification of on-site d-orbital symmetry displays long-range features from surface to inner layers, but there is essentially no change in the total occupancy of electrons within the MT spheres [compared with those of clean Ni(001)] over distances larger than the S-Ni nearest neighbor's distance. Further, we demonstrate that this type of long-range interaction does not originate from a direct interaction between S and the subsurface Ni, but is instead a response to the change in surface electronic structure caused by the strong, direct surface Ni—S bonding. The evidence for this is the development of a layer-dependent screening charge, which shows an oscillatory charge transfer between e_g- and t_{2g}-type states from surface to center Ni layers [cf. Fig. 2(a)]. Not only is the d-type symmetry affected by the chemisorbed S, but the magnetization of Ni is strongly reduced by this type of indirect long-range interaction which ranges (at least) up to its third nearest neighbors (discussed below). This is not surprising, since the size of the magnetic moment

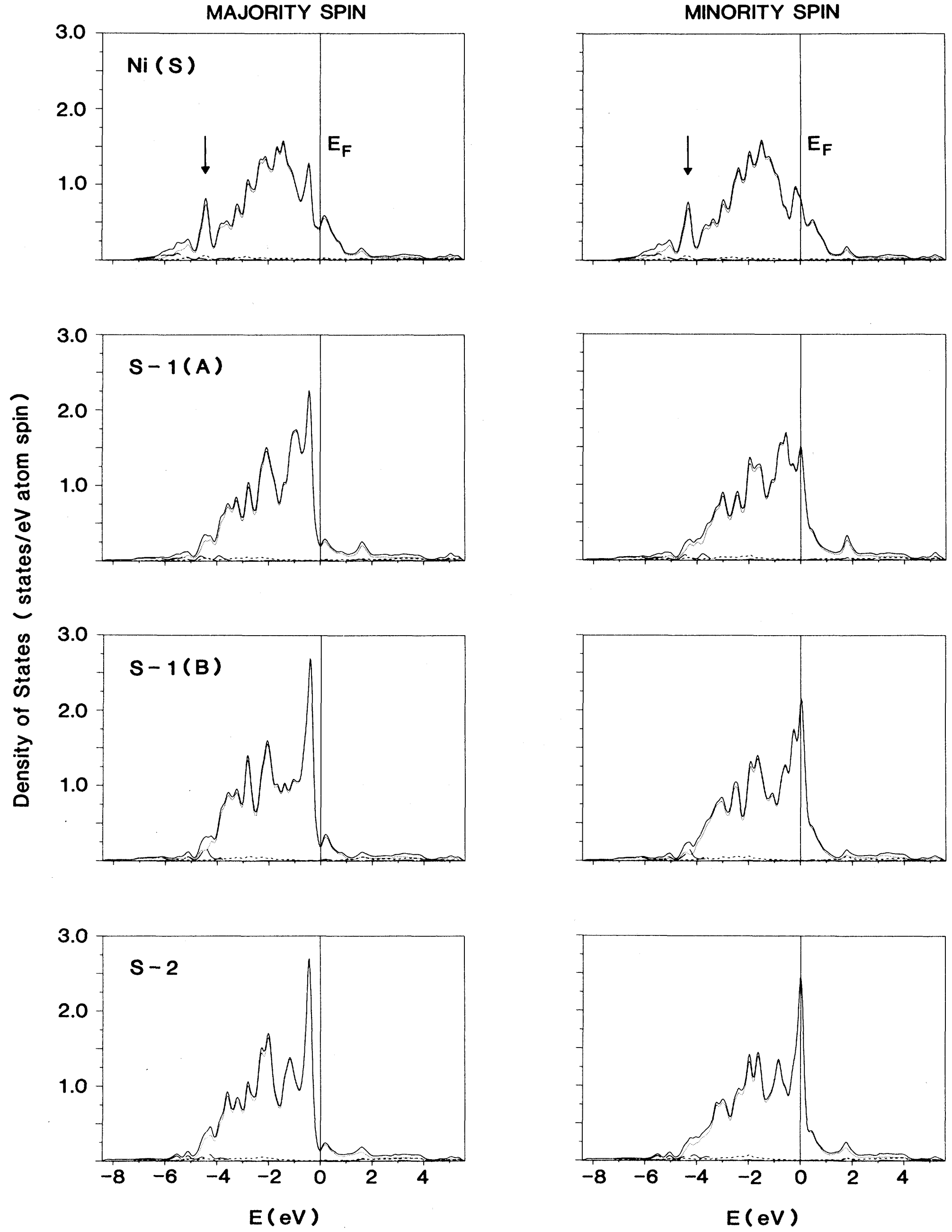

FIG. 3. Layer-by-layer projected DOS for the Ni(001) substrate of S/Ni(001) for majority-spin and minority-spin states. Ni(S) denotes the surface layer of Ni, $S-1$ (A) and $S-1$ (B) denote subsurface A and B sites (cf. text), and $S-2$ the next or center layer of the Ni slab. The down arrow (↓) denotes the position of the sulfur p state and emphasizes its effect through hybridization on the Ni surface-layer DOS.

depends on the local density of states at E_F, which is not a screened quantity.[3]

Consider now the catalytic poisoning effect on the magnetism of Ni(001). The theoretical study by Wimmer *et al.*[16] shows that the Ni(001) magnetization is enhanced by 20% at the surface with magnetic moments $0.68\mu_B$, $0.60\mu_B$, $0.59\mu_B$, and $0.56\mu_B$ from surface to inner layers. Now, since the interaction of the surface Ni with S forms strong covalent bonds, a decrease of magnetization is expected. Indeed, our spin-polarized calculation shows that the surface magnetic moment is drastically reduced to $0.12\mu_B$ due to the S poisoning (i.e., almost magnetically "dead"). A spin-density contour plot [cf. Fig. 2(b)] reveals that the spin density of the Ni surface is predominantly of d_{z^2}-type symmetry (the t_{2g}-type spin density has been completely quenched due to the formation of S—Ni covalent bonds). Interestingly, a manifestation of the long-range catalytic poisoning effect is the decrease of subsurface Ni magnetic moments to $0.40\mu_B$ (site *A*) and $0.54\mu_B$ (site *B*), and $0.54\mu_B$ for the center Ni layer. These values are all smaller than the corresponding values for the clean Ni(001) slab.

To gain a more in-depth understanding of the S poisoning, we now consider the electronic structure. Figure 3 displays the layer-projected density of states (DOS) for the majority and minority spins of the Ni substrate. The most striking feature shown is the strong suppression of the minority surface DOS at E_F caused by the S adsorbate [cf. Ref. 16, for pure clean Ni(001), and consequently, the surface reactivity]. A prominent peak in the DOS at 4.5 eV is identified in the band structure as being due to the S(p)-related state dispersed along the $\bar{\Gamma}\bar{X}$ direction and has odd parity. This result is in satisfactory agreement with photoemission measurements by Plummer *et al.*[17] Further, Fig. 3 also shows that S causes a decrease of magnetic exchange splitting for the surface Ni layer [compared to clean Ni(001)].[16] The states at E_F of Ni surface layer for the majority spin (cf. Fig. 3) are identified as catalytic "poisoned" Sp – Nid character.

Finally, comparing the S/Ni system with that of $c(2\times2)$O/Ni(001) studied by Chubb *et al.*[18] shows that the bonding natures of S—Ni and O—Ni are very different: the O—Ni bond is more ionic, whereas that of S—Ni is dominantly covalent. This difference manifests itself in a relatively larger change of the work function ($\Delta\Phi = 0.8$ eV) and a far smaller reduction in the surface magnetic moment for O/Ni. A key to understanding S catalytic poisoning is thus the strong covalent-bond formation and the deactivation of the d orbitals.

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