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SULFUR EFFECTS IN MULTIMETALLIC FISCHER-TROPSCH CATALYSTS: FINAL REPORT

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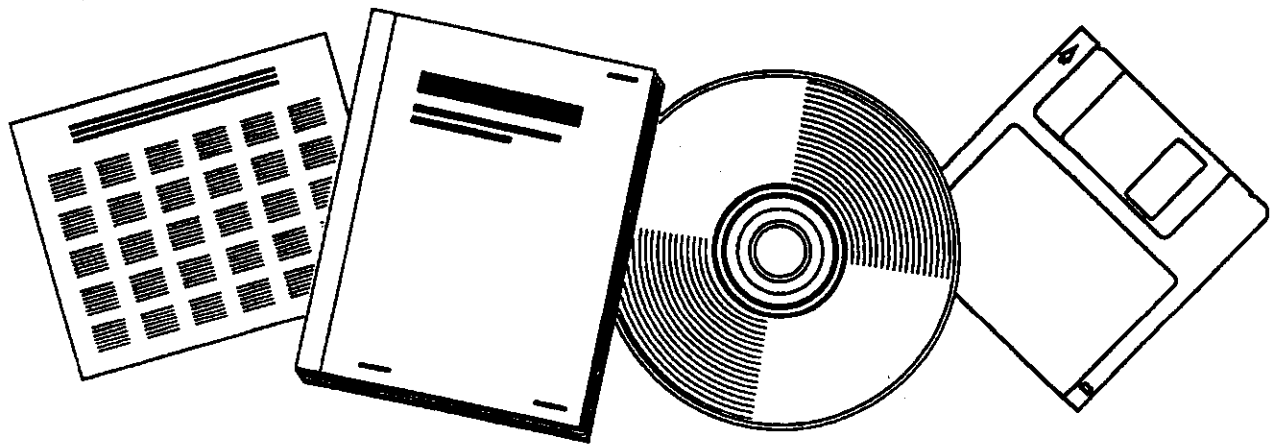

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SULFUR EFFECTS IN MULTIMETALLIC FISCHER-TROPSCH CATALYSTS

DE-FG22-84 PC 70800

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FINAL REPORT

DISCLAIMER

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1. INTRODUCTION

We have conducted a coordinated experimental and theoretical study of a novel bimetallic system prepared by molecular beam techniques. We have prepared fcc Fe expitaxially grown on Cu and investigated its properties using a diverse number of analytical techniques. The temperature stability of these novel materials was investigated as well as the properties of the surface towards chemisorption of CO and Fischer-Tropsch reactions. After carefully characterizing the Fe/Cu systems we investigated the effect of small amounts of sulfur on the chemisorption properties, specifically on the activity of the contaminated surface towards Fischer-Tropsch reactions. In the following pages we report the results of such a study. Finally, we give a detailed list of the scientific publications in peer reviewed journals that resulted from this support by the U.S. Department of Energy.

1. PRACTICAL METHOD FOR HIGHLY ACCURATE LARGE-SCALE SURFACE CALCULATIONS

(Quarterly Report October 16, 1985 - January 15, 1986)

Abstract

We have developed and tested a practical and accurate version of the Linearized Muffin-Tin Orbital (LMTO) technique for surface calculations. This has been done by extending the standard LMTO basis with a small number of independent plane wave orbital functions (PWO's). The basic advantage of the LMTO method, small basis size, is thus retained. This implies sufficiently great computational advantages of time and memory so as to extend the range of feasibility for high quality surface electronic structure calculations to larger problems (more atoms per two-dimensional cell) than hitherto possible.

The rapid progress of surface physics in the last decade has invariably demanded more reliable and more efficient calculational methods to study surface phenomena such as chemisorption and surface magnetism. However, it is still true that only simple surface electronic structure problems, with a fairly small number of atoms per two-dimensional unit cell, can be treated by the best available self-consistent first principles calculational methods such as the Linear Augmented Plane Wave (LAPW) method.[1-3] For example, problems involving the chemisorption of CO on a transition metal surface (even using only a three-layer slab to simulate the metal surface and other simplifications) can require[4] well over 1000 LAPW basis functions with consequent need for several tens (for simplified spectroscopic information) or hundreds (for total energies) of hours on a supercomputer such as a Cray X-MP, and indeed can have fundamental convergence problems.

Thus, there are severe limitations in computer time and memory that discourage the use of accurate first-principles methods for surface studies without substantial basic practical improvements. The Linear Muffin-Tin Orbital (LMTO) method,[1,5] because of its inherently small basis, offers a promising opportunity to overcome these limitations. While the LMTO method has been used very successfully[5] for a number of bulk calculations some of which have been for rather complicated compounds, it has proven difficult in practice[6] to realize the anticipated advantages of the LMTO method, in computational efficiency with high accuracy, for applications to surface problems. In this letter we report Film Linearized Muffin-Tin Orbital (FLMTO) calculations for three different (3d and 4d) transition metal films that use substantially smaller basis sets than LAPW calculations. Using about 60-70 basis functions instead of 300 as in LAPW, we have been able to

achieve results of very similar high quality for 5 layer slabs of Cu(001), Fe(001), and Ru(0001), including excellent results for the work functions and projected density of states, in slightly shorter (by perhaps a factor of two) computing time.

Our present results imply a great advantage for the FLMTO technique that will be shown in larger problems (more atoms per two-dimensional unit cell) than the simple 5-layer examples cited above. The smaller FLMTO basis needed for equally high quality results means that small matrix sizes are used, also implying decreased memory requirements. For a given computer, this reduction of computer time and memory makes it practical to study systems with a larger number of atoms in the two-dimensional unit cell.

Development of the FLMTO method in its present form is the culmination of our efforts,[6-9] to adapt the Linearized Muffin-Tin Orbital Method to the study of surface electronic structure through systematically exploring the question of finding the minimum size, and nature, of the extension of the muffin-tin-orbital basis used for bulk behavior necessary in order to have a high quality description of surface electronic behavior. Because of this systematic search to find the minimally sized basis necessary in practice to describe sensitive surface properties with experimental accuracy, we believe that the FLMTO method as here described has a strong claim to being the most powerful technique available for treating complex (large) surface problems realistically within local density approximation theory.

The conventional LMTO method is known to work well for bulk solids.[5] However, to apply this method to study surface electronic structure requires augmenting the basis set beyond the number of basis functions per atom that would be adequate for a bulk solid. The freedom created by the

open surface for the charge to move in the z (normal to the slab) direction has to be accompanied by somewhat of an increase in the variational degrees of freedom in order to capture the fine detail of the surface behavior and give quality results, especially good work function values. Our effort to implement the LMTO method for surface studies started with Krakauer and Cooper.[7] Subsequent applications of the method as described in Reference 7, and the difficulties associated with it, are reported in References 6, 8, and 9. The present treatment improves the variational freedom of the LMTO-PWO basis set described in References 7, 8, and 9 by discarding the vacuum tail cancellation condition (Equations 15(a) and 15(b) of Ref. 7 as subsequently modified) and treating the Plane Wave Orbitals (PWOs) as independent basis functions.[10] The PWOs of Ref. 7 now take the following form:

$$x^{\vec{k}}_{1m}(\vec{r}) = e^{i\vec{K}_m\cdot\vec{r}} \begin{cases} s_{1m}\phi_1(c_{1m},z) , & z \geq z_1 \\ s_{1m}e^{-iQ_m z} , & z_1 > z > -z_1 \\ s_{1m}\phi_2(s_{2m},z) , & -z_1 \geq z \end{cases} \qquad (1)$$

with

$$\phi_1(c_{1m},z) = -2iQ_m\{\dot{c}_{1m}u^{(1)}_{\vec{k},m}(z) - c_{1m}\dot{u}^{(1)}_{\vec{k},m}(z)\} \qquad (2)$$

and

$$\phi_2(s_{2m},z) = -2iQ_m\{\dot{s}_{2m}u^{(2)}_{\vec{k},m}(z) - s_{2m}\dot{u}^{(2)}_{\vec{k},m}(z)\} \quad . \qquad (3)$$

$x^{\vec{k}}_{2m}$ of Eq. (8b) of Ref. 7 is modified similarly. ($u^{\vec{k}}_{k,m}(z)$ is[7] the solution of the one-dimensional Schroedinger Equation in the vacuum. At the vacuum boundaries z_1 and $-z_1$, the coefficients c_{im}, $\dot{c}_{im}$, s_{im} and $\dot{s}_{im}$ (i=1,2) are chosen so as to give continuity of the functions and their first (spatial) derivatives. Dots designate energy derivatives; notation is as in Refs. 6-9.) The use of a linear combination of $u^{\vec{k}}_{k,m}$ and $\dot{u}^{\vec{k}}_{k,m}$ follows what is done[2,3] in film LAPW calculations.)

The spatial variation of the PWOs may be described as follows. Parallel to the slab their spatial dependence is plane-wave-like. Normal to the slab (i.e., along z) the spatial dependence varies according to whether $Q_m^2>0$ or $Q_m^2<0$. If $Q_m^2>0$, the z dependence of the PWO inside the slab is also plane-wave-like. If $Q_m^2<0$, the z dependence of χ_{im} is real and exponential on going from z_1 to $-z_1$. For both cases, outside the slab the PWO becomes a linear combination of $u^{\vec{k}}_{k,m}(z)$ and $\dot{u}^{\vec{k}}_{k,m}(z)$.

The part of the MTOs (tails) extending into the upper vacuum take the following form,

$$\chi^{\vec{k}}_{\alpha L}(\vec{r}) = \frac{\kappa^{\ell}}{c_{\alpha\ell}} \frac{2\pi i}{\Lambda} \sum_m \frac{e^{i\vec{K}_m\cdot(\vec{r}-\vec{\tau}_\alpha)}\, e^{-iQ_m\cdot\tau^z_\alpha}\, Y^*_L(m)}{Q_m} \phi_1(s_{1m},z) \quad (4)$$

(similarly for the lower vacuum); while the MTOs have Hankel (or Neumann) tails in the interstitial region.[6-9] Equation (4) "augments" the MTO in the way described in Reference 6. Inside the MT sphere the MTOs are still given by the form used in equation (3) of Ref. 8. However, the structure matrix[7,8] $A^{\alpha',\alpha}_{L',L}$ no longer contains the PWO tails.

The wave function $\Psi^{\vec{k}}_k(\vec{r})$ is expanded as

$$\Psi_{\vec{k}}(\vec{r}) = \sum_{\alpha,L} A_{\alpha L} \chi^{\vec{k}}_{\alpha L}(\vec{r}) + \sum_{m} A_{1m} \bar{\chi}^{\vec{k}}_{1m}(\vec{r}) + \sum_{m} A_{2m} \bar{\chi}^{\vec{k}}_{2m}(\vec{r}) \quad (5)$$

with $\bar{\chi}^{\vec{k}}_{1m} = \chi^{\vec{k}}_{1m}$, $\bar{\chi}^{\vec{k}}_{2m} = \chi^{\vec{k}}_{2m}$ everywhere except inside the spheres where $\bar{\chi}$ is the modified PWO, i.e., the PWO is "augmented" analogously to that of Eq. (4) for the MTO so as to be continuous and have continuous first derivative on going inside the spheres. (To do this, we use a linear combination of u_ℓ and $\dot{u}_\ell$, u_ℓ being the solution of the radial Schrodinger Equation in the muffin-tin sphere). The new feature contained in Eq. (5) is that, in addition to the $A_{\alpha L}$, A_{1m} and A_{2m} are now also independent variational parameters.

The obvious question is how many independent PWOs need to be added to an MTO basis to get results of the desired quality for sensitive surface properties such as the work function. We have found that 18 PWOs (counting both $\bar{\chi}_{1m}$'s and $\bar{\chi}_{2m}$'s) are sufficient (less than 1mRy changes in the eigenvalues upon further increases in the basis set size) in addition to 9 MTO's for each of the five atoms in the two-dimensional unit cell for 5 layers of Cu(001) and Fe(001), while addition of 26 PWO's provided satisfactory results for 5 layers of Ru(0001). This means that for the five layer problem, with five atoms per unit cell, we use only 12-15 basis functions per atom compared to 50-60 per atom for the LAPW method for transition metal slabs. For thicker slabs the number of PWOs needed should remain essentially constant. Thus the number of basis functions per atom will decrease with thickness. Clearly we can add PWOs until the energy eigenvalues are well converged, providing a new convergence check. Another desirable feature is that both the MTO's and the PWO's contribute a (possibly decaying along $\hat{z}$) plane-wave-like component in the interstitial. Thus this new method has a flexibility in handling interstitial spatial

variations not present in a purely MTO method or in a purely site-centered LCAO method.

The three self-consistent calculations described in this paper use the full potential in the vacuum and in the interstitial regions without any shape approximations.[6] In the spheres, however, we use an Andersen-type[11] approximation for the non-muffin-tin potential. The correlation potential used is that of Ref. 12.

Table 1 shows a comparison of some results from the new FLMTO surface method (nonmagnetic) with other recent calculations and with experiment. The work functions calculated by the new method show impressive agreement with experiment and with the best available calculations. The band widths and the sphere charges also show impressive agreement with other calculations. For Fe(001), although we have neglected spin polarization, our calculated work function agrees well with experiment. Ohnishi, Freeman, and Weinert[19] state that their FLAPW calculations show the importance of the magnetic effects in a surface sensitive quantity such as the work function. A close comparison of the recent work function measurements and theoretical values does not seem to suggest this. Figure 1 shows our calculated sphere-projected density of states (DOS) for a Fe(001) 5 layer film. The essential features in the DOS agree quite well with other thin film calculations[19,20] for Fe(001). This is also true for Cu(001) (DOS not shown here). For Ru(0001) the DOS calculated with the new method (not shown here) shows reasonable agreement with an 11 layer film calculation by Feibelman[24] used to study carbidic and graphitic carbon phases on Ru(0001).

In conclusion we have reported a powerful and efficient method for surface electronic structure calculations. In addition to retaining most of the desirable features of the LMTO method it now has a basis with

improved variational quality. By self-consistently calculating the electronic structure of three different transition metals having three different crystal structures and comparing the results with the available up to date experiments and theory we have demonstrated that the new method offers a desirable alternative to the LAPW thin film method, especially as one goes to complex systems involving a large number of atoms per two-dimensional unit cell.

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TABLE I. A comparison of some experimental and theoretical results with the ones calculated using our new FLMTO method, for three systems, Cu(001), Fe(001), and Ru(0001). The band width is defined as the energy difference between the Fermi level and the bottom of the lowest valence band. The sphere charges are given for the surface and center spheres of these 5-layer systems.

System	Work Function (eV)					Band Width (eV)			Center/Surface Sphere Charge (electrons)	
	New FLMTO	Other Theory		Experiment		New FLMTO	Other Theory		New FLMTO	Other Theory
Cu(100): fcc	4.93	4.5*	(13)	4.58	(16)					
		4.91*	(14)	4.76	(17)		9.0	(13)		
		4.94	(15)	5.10	(18)	8.9	8.9	(14)	10.32/10.14	10.38/10.21 (15)
Fe(001): bcc	4.77	4.86	(19)	4.4	(21)					7.05/6.81 (19)
				4.67	(22)	7.4	7.4	(20)	7.01/6.74	
		4.20	(20)	4.88	(23)					7.06/6.83 (20)
Ru(0001): hcp	5.43	5.4	(24)	5.2-5.4	(23)	7.1	7.1	(24)	6.74/6.58	---
				5.52	(26)		6.8**	(27)		

*These two values are obtained using the Gaussian Orbital Method. However, the second value (from Ref. 14) is from a numerically improved calculation.

**This value is for fcc crystal structure from a bulk calculation.

FIGURE CAPTIONS

Fig. 1. Sphere projected density of states for a system consisting of a five-layer (100) slab of bcc Fe. These curves have been smoothed by a Gaussian of full width at half maximum (FWHM) of 0.3 eV. The calculated work function for this system is 4.77 eV.

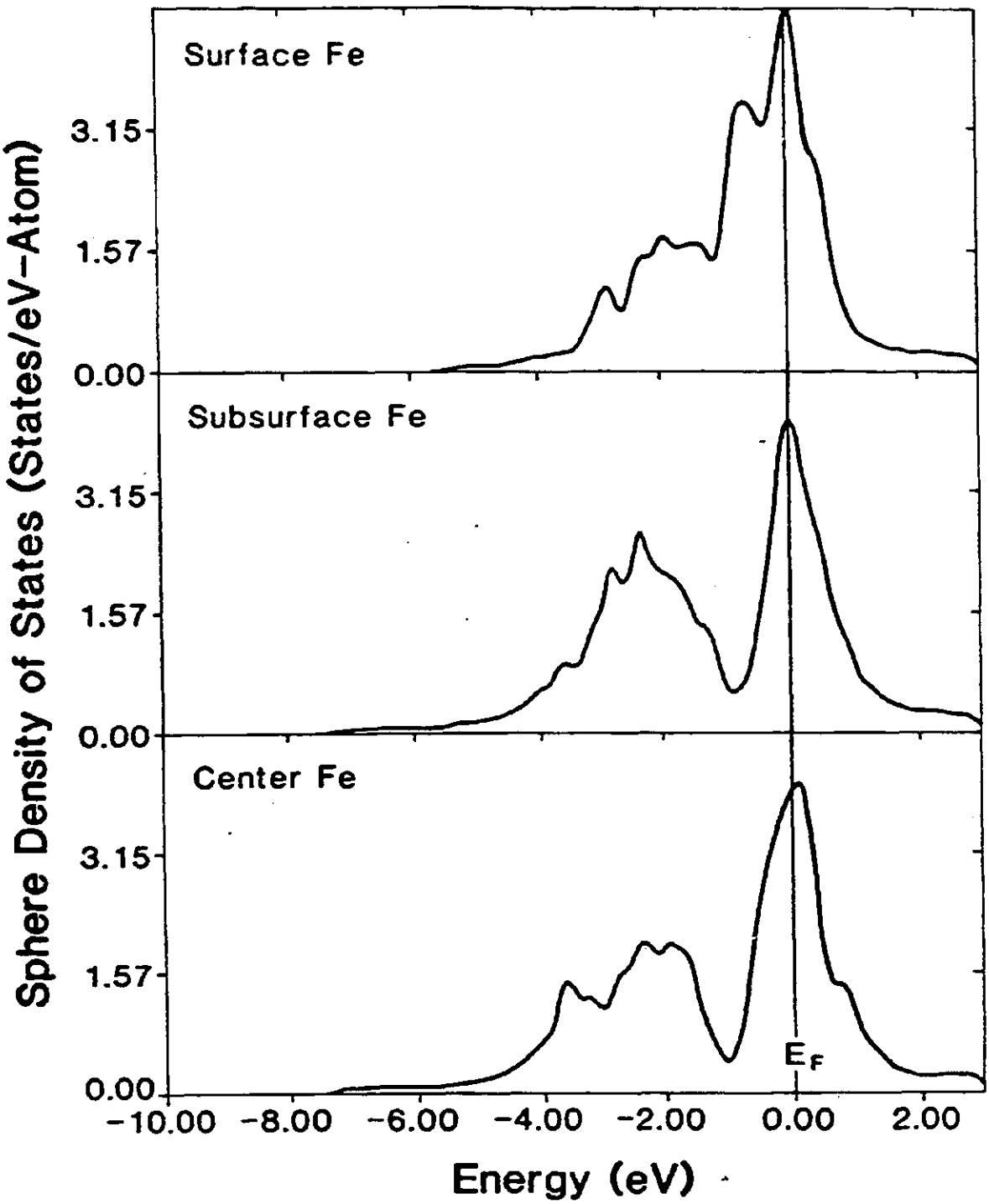
Surface Fe
Subsurface Fe
Center Fe
3.15
1.57
0.00
Sphere Density of States (States/eV-Atom)
E_F
-10.00
-8.00
-6.00
-4.00
-2.00
0.00
2.00
Energy (eV)

Fig. 1

2. THEORY OF ELECTRONIC STRUCTURE AND MAGNETIC BEHAVIOR OF Fcc IRON GROWN ON Cu(001)

(Quarterly Report January 16, 1986 - April 15, 1986)