

SURFACE SCIENCE LETTERS

**S AND Fe BINDING TO THE Fe(100) SURFACE AND IN THE BULK:
MOLECULAR ORBITAL THEORY FOR SURFACE SEGREGATION
OF S**

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The ASED-MO theory and large cluster models are used to predict and analyze the formation energies for bulk vacancies in iron and S atom adsorption and dissolution energies in bulk substitutional sites. The driving force for surface segregation of S is shown to result from the vacancy formation energy and a strong S3s–Fe valence band closed shell repulsion for dissolved sulfur.

Sulfur is a ubiquitous impurity in transition metals and their alloys. Above 700°C it segregates to surfaces and grain boundaries, displacing all other segregated elements [1], poisoning catalysts [2], and causing grain boundary embrittlement [3] and adhesive failure of protective oxide scales [4]. Sulfur atoms bind substitutionally in iron and its alloys [5]. The thermodynamic driving force for S segregation in Fe may be seen by comparing the dissolution energy of S atoms in the bulk, 2.56 eV [6], to the adsorption energy, 4.29 eV on powdered iron at 0.6 monolayer coverage [7] and 4.20 eV at saturation half-monolayer $c(2 \times 2)$ coverage on the (100) surface [2]. The difference, 1.64 eV, is the segregation energy. A direct determination based on a Langmuir–McLean plot [8] yields a similar value of 1.71 eV for the segregation energy. The reason for the greater stability of S at the surface has not been previously known and is uncovered by the use of molecular orbital theory in this paper.

The atom superposition and electron delocalization molecular orbital (ASED-MO) theory [9] and cluster models representing the Fe(100) surface and a bulk Fe substitutional site are employed. The clusters are superimposable on the bcc bulk Fe structure; the nearest neighbor Fe–Fe distance is 2.48 Å. The S and Fe valence orbital parameters used in the calculations are given in table 1. They are based on those from a diatomic FeS study [9] with modifications to produce Fe(111) surface structure relaxations [10]. Electrons are unpaired throughout the cluster d bands according to a spin unpairing rule

Table 1

Parameters used in the calculations: IP (eV), Slater orbital exponents, ζ (a.u.) and linear coefficients, c

Atom	Orbital	IP	ζ_1	c_1	ζ_2	c_2
Fe	4s	7.87	1.85			
	4p	5.44	1.55			
	3d	9.00	5.35	0.5366	1.80	0.6678
S	3s	19.20	2.122			
	3p	9.36	1.827			

wherein each Fe atom contributes a spin polarization dependent on its coordination to neighboring Fe and S atoms [10].

A sulfur atom is calculated to bind to Fe(100) at a height of 1.11 Å above the surface layer as shown in fig. 1. The experimental height from low energy electron diffraction is 1.09 ± 0.05 Å [11]. The binding energy when 4 other S atoms are present, modeling $c(2 \times 2)$ coverage, is 3.98 eV, which underestimates the experimental value by 5%.

A bulk substitutional site is modeled with a Fe_{46} cluster as shown in fig. 2. The binding energy of S in this site is 3.06 eV. A slight 0.04 eV gain in stability is achieved when the S atom relaxes to equilibrium by moving 0.36 Å in the [100] direction.

The calculated 0.88 eV energy difference, which is a part of the surface segregation energy, can be understood on examination of molecular orbital correlation diagrams of the mixing of the filled S 3s orbital with cluster orbitals. Simplified clusters are used to generate the diagrams. An Fe_{14} cluster is used to model the substitutional bulk site. This cluster is a cube of 8 Fe atoms with each face capped by an Fe atom. The S atom is placed in the center of the cube. As fig. 3 shows, the cluster has two doubly-occupied and one singly-occupied orbital with the proper symmetry to interact with the S 3s orbital; other cluster orbitals interact with S 3p orbitals and are not shown. The net result of the S 3s + cluster interaction is a closed-shell repulsion. The 3s orbital is stabilized by bonding to a cluster orbital of predominately Fe 4s character and three cluster orbitals are destabilized. By removing the S 3s

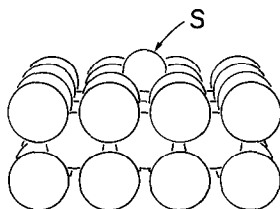


Fig. 1. Structure of S on Fe_{41} model of the (100) surface.

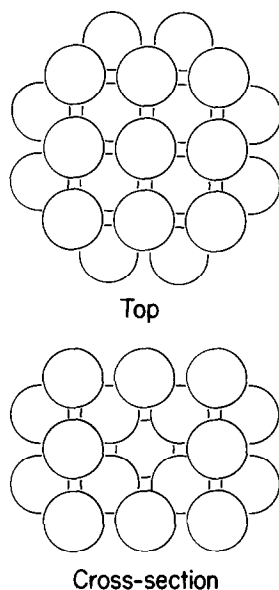


Fig. 2. Top and cross-section views of Fe_{46} model of a bulk substitutional site in Fe.

orbital from the interaction, accomplished by moving its level down to -50 eV and shrinking it with a Slater exponent of 20 a.u., this closed-shell repulsion is found to be 1.92 and 1.58 eV respectively for the Fe_{14} and Fe_{46} clusters when S is in the equilibrium position.

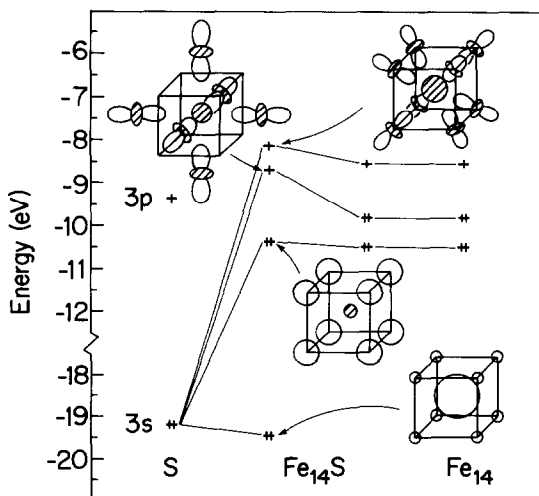


Fig. 3. Interactions of S3s orbital with surrounding metal orbitals in the Fe_{14} cluster. The third column of energy levels has the S3s interaction removed.

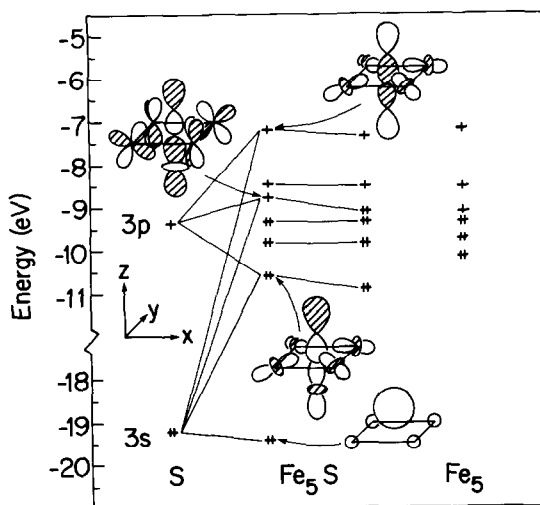


Fig. 4. Interactions of S3s orbital with surrounding metal orbitals in the Fe_5 (100) surface cluster. The third column of levels has the S3s interaction removed and comparison with the Fe_5 column shows bonding stabilizations caused by mixing with the S3p_z orbital.

On the (100) surface the corresponding closed-shell repulsion is less because the symmetry of the bulk site is broken, allowing the S3p_z orbital to mix and stabilize the antibonding counterparts to the S3s bonding orbital. This is shown in fig. 4 for a simplified Fe_5 cluster model of the (100) surface consisting of a square pyramid of Fe atoms. When the S3s interaction is again removed, its closed-shell repulsion is found to be 0.82 and 0.66 eV with the respective Fe_5 and Fe_{41} clusters.

From the above, the 0.92 eV decrease in closed-shell repulsion fully accounts for the calculated 0.88 eV energy differences gain for S binding in bulk and surface sites. Removal of the closed-shell repulsion results in a S adsorption energy of 4.53 eV and a binding energy of 4.67 eV for S at the equilibrium bulk site. Taking into account the two body S–Fe repulsion energies of the ASFD-MO theory, 0.97 eV for S on the surface and 1.21 eV for S in the bulk, it is evident that the S3p orbitals contribute 5.50 eV to the chemisorption energy and 5.88 eV to the binding energy in the equilibrium bulk substitutional site.

Iron atoms bind more strongly in the bulk than on the surface; 4.86 eV is calculated for bulk binding, which, as expected, is greater than experimental atomization energy, 4.29 eV [12]. On the surface, the binding energy is calculated to be 4.07 eV, substantially less. The vacancy formation energy is the difference, 0.79 eV. An experimental value for this property is not available.

Taking into account the vacancy formation energy, the predicted dissolution energy of S in bulk Fe is 2.31 eV, underestimating the experimental value by 10%. The difference between this and the surface adsorption energy is 1.67 eV, which is very close to the experimental values of 1.64 and 1.71 eV.

It is expected that the 3s + metal band closed-shell repulsion will also be an important factor leading to the segregation of P, which also binds substitutionally in the bulk metals [13], to the surface. The P 3s IP is 16.15 eV [14], placing its 3s level closer to the metal band than is the case for S, which has a 3s IP of 20.20 eV [14]. Thus, the repulsion should be strong.

In conclusion, this study shows that about half of the driving force behind the segregation of dissolved S to the surface of Fe is the closed-shell repulsion between the occupied S 3s orbital and occupied metal band orbitals. At the surface the S 3p_z orbital is allowed by the surface symmetry to mix with and stabilize the antibonding counterparts to S 3s + metal band interaction. The S 3p contributions to the binding are nearly the same in the bulk and on the surface. Iron atoms, on the other hand, are found to bind more strongly in the bulk than on the surface since there is no similar closed-shell repulsion. The displacement of a bulk Fe atom by the substitutionally dissolved S atom accounts for the other half of the segregation energy.

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