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Segregation of substitutional bulk S to the Fe(100) surface and the Fe–Fe oxide interface: Molecular-orbital theory

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A molecular-orbital study of the binding of S atoms in bulk iron and on the (100) surface is performed with Fe_{47} bulk and Fe_{41} surface cluster models to understand the commonly observed surface segregation of impurities. An atom-spin-polarization rule for ferromagnetic iron is suggested wherein each atom's contribution to the cluster-spin polarization is dependent on its coordination number. Its predictions are in satisfactory agreement with recent theoretically calculated values for Fe(100) and Fe(110) surfaces. The calculated binding energies are found to agree best with experiment when S is included in determining the Fe coordination number, thereby decreasing the spin polarization. The interaction of the filled S 3*s* orbital with occupied *a*-symmetry orbitals in a bulk substitutional site results in a closed-shell repulsion, while on the surface the S $3p_z$ orbital is symmetry allowed to mix with the S 3*s* orbital, reducing the repulsion. The S 3*s* orbital is largely responsible for sulfur bonding more strongly on the surface than to a bulk substitutional site; respective calculated values are 3.98 (4.20) eV and 3.10 eV, where the value in parentheses is experimental. Taking into account the predicted vacancy-formation energy of 0.79 eV, the calculated S dissolution energy 2.31 eV is close to the experimental value (2.56 eV). The difference, 1.67 eV, compares well with experimental estimates (1.64 and 1.71 eV). It is concluded that half of the S segregation energy is caused by the closed-shell repulsion and the other half by the bulk Fe-vacancy-formation energy. The fact that S dissolves substitutionally in Fe suggests an explanation for a recent experimental observation that S will not segregate to an Fe–Fe-oxide interface: doing so would break strong Fe—O bonds and might introduce repulsive O^{2-}-S^{2-} interactions.

INTRODUCTION

It has long been known that impurities such as C, N, O, S, and P in metals segregate to the surfaces and to grain boundaries, and affect the chemical and mechanical properties of metals. Many experiments have demonstrated that the segregation of S in iron-based alloys[1,2] and in nickel-based alloys,[3] P in iron-based alloys,[1,4] and O in Mo (Ref. 5) induces the embrittlement of grain boundaries in these materials. Recent work[6,7] on the oxidation of Ni-Cr-Al alloys shows that S segregates to the alloy surface and weakens bonding at the alumina-metal interface, causing the exfoliation of the alumina layer during cyclic heating.

Impurity segregation and induced embrittlement are not well understood theoretically. Losch[8] ascribed the grain-boundary embrittlement of a metal to the weakened metal-metal bonds caused by the perturbation of metal-metal bonding orbitals by the formation of strong covalent bonds with the impurity atoms. Others have focused on the large charge transfer from metal atoms to impurity atoms, which would also weaken metal bonding,[9] and the formation of the impurity-centered small clusters at grain boundaries.[10] Painter and Averill[11] calculated the strain energies to accommodate S and B in the center of a Ni_6 cluster, and suggested that the metal-metal bonds are weakened by a large strain caused by S. A recent quantum-mechanical study of the effect of interfacial S on the bonding of α-alumina to the Ni(111) surface[12] showed that S at the interface does not bind to the alumina anion layer because of a closed-shell interaction between the doubly filled Ni—S bonding orbitals and the completely filled O 2*p* band. Though Al^{3+} was found to bind strongly to S^{2-} on the metal surface, the relatively low concentration per unit surface area of these bonds resulted in reduced interfacial bond strength.

The exact interfacial structures have not been determined. This makes it difficult to quantum mechanically model the effects of impurities on properties of interface, though in Ref. 12 a comprehensive attempt was made. However, it is relatively easy to model the segregation of impurity atoms to metal surfaces. In a recent theoretical study[13] the binding energies of a sulfur atom in a bulk iron substitutional site and on the (100) surface were calculated, producing a segregation energy close to experimental values. About half of the segregation energy was found to be due to the bulk Fe formation energy and the other half was due to weaker binding of S to the vacancy site than on the surface. The latter contribution was due to a closed-shell repulsion between the filled S 3*s* orbital and occupied metal bond orbitals. The purpose of the present paper is to give a detailed discussion of the results in the earler communication[13] and to consider S segregation to an Fe—Fe-oxide interface. Critical to this work is an electron unpairing rule for one-electron transition-metal cluster molecular-orbital calculations, which is

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presented. Predictions of this rule are compared to experimentally and theoretically determined surface magnetizations.

Sulfur has been chosen because it is the most deleterious element. It is ubiquitous and is extremely difficult to remove from metals and alloys. It has strong tendency to segregate to grain boundaries, and to surfaces at temperatures above 700 °C, displacing all other segregated elements,[14–16] poisoning catalysts,[17] as well as causing embrittlement of grain boundaries[1,2] and reducing adherence of protective oxide layers.[6,7]

THEORETICAL MODEL

For this study, as in recent investigations of interfacial bonding,[12,18] cluster models and the atom superposition and electron delocalization molecular-orbital (ASED MO) theory are employed. A brief outline of the theoretical method is given here; details appear elsewhere.[19,20] The theory is based on partitioning a molecule's electronic charge density, ρ, into rigid free-atom parts, ρ_a, which "follow the nuclei perfectly" and a bond charge density, ρ_{npf}, which is delocalized and "nonperfectly following:"

$$\rho = \sum_{a}^{\text{atoms}} \rho_a + \rho_{\text{npf}} \; . \tag{1}$$

The ρ_a cause a repulsive electrostatic force on nuclei of other atoms and ρ_{npf} produces an attractive force of the nuclei. Corresponding repulsive and attractive energy components E_R and E_{npf} are obtained by integrating these forces as atoms come together to form a molecule. The molecular-bonding energy E is then the sum

$$E = E_R + E_{\text{npf}} \; . \tag{2}$$

The pairwise components of E_R are easily evaluated from atomic electron density functions but since ρ_{pnf} is not a known function, E_{npf} cannot be obtained straightforwardly from the attractive force. Nevertheless, a molecular-orbital delocalization energy can replace it as an approximation:

$$E = E_R + \Delta E_{\text{MO}} \; , \tag{3}$$

where ΔE_{MO} is the total one-electron molecular-orbital energy minus the total one-electron atomic energies; it is calculated using a one-electron Hamiltonian which is similar to the extended Hückel Hamiltonian:

$$\begin{aligned} H_{ii}^{aa} &= -(V_{\text{VS}})_i^a \; , \\ H_{ij}^{aa} &= 0 \; , \\ H_{ij}^{ab} &= -1.125[(V_{\text{VS}})_i^a + (V_{\text{VS}})_j^b] S_{ij}^{ab} \exp(-0.13R) \; , \end{aligned} \tag{4}$$

where S_{ij}^{ab} is the overlap integral for orbital i on center a and orbital j on center b, and R is the distance between nuclei a and b. Valence-state-orbital ionization potentials (V_{VS}'s) and Slater-orbital exponents (ζ) are the input data for calculations with this method. These parameters are based on V_{VS} values for free atoms[21] and ζ values from atomic self-consistent-field calculation[22] with adjustments to produce the equilibrium bond lengths and reasonable charge transfers in diatomic fragments.[20] Double-zeta functions are used for the Fe-atom d orbitals.

For the determination of spins for the iron clusters employed in this study, it is assumed that the spin polarization (SP) of an Fe atom monotonically decreases with increasing coordination number (CN) from the experimental values of 4 for a free iron atom (with a CN of 0) to 2.12 for an atom in the bulk (with a CN of 8). An exponential function is chosen and its two parameters are determined by fitting to these two spin values. The resulting relationship between the SP of an Fe atom and CN is summarized in Table I. The total SP of an iron cluster is determined from the cluster's structure simply by summing up the SP of each atom. The calculated cluster molecular orbitals are then occupied with this number of unpaired electrons. When the total number of unpaired electrons is noninteger, the energies of two states are averaged as follows. Suppose orbital n is the highest doubly occupied orbital and orbital m is the lowest empty one, and k orbitals between n and m are singly occupied. Let the number of unpaired electrons given by the rule be $k+x$. Then it is assumed there is a mixture of configurations:

$$\Psi_{k+x} = a\Psi_k + b\Psi_{k+2} \; . \tag{5}$$

From the normalization condition,

$$a^2 + b^2 = 1 \; . \tag{6}$$

Let $\hat{O}$ be an operator whose eigenvalue is the number of unpaired electrons. Then

$$\langle \hat{O} \rangle = k + x = a^2 k + b^2 (k+2) \; . \tag{7}$$

TABLE I. Spin polarization of ferromagnetic Fe atoms.

CN	This rule	Reduced-charge matrix[a]	Other theoretical work
0	4.00 (89)[b]		
1	3.69 (74)		
2	3.41 (61)		
3	3.15 (49)	3.09,[c] 2.87[d]	
4	2.91 (37)	2.91,[e] 2.97[f]	2.90,[g] 2.98[h]
5	2.69 (27)		
6	2.48 (17)		2.55[i]
7	2.29 (8)	2.47	
8	2.12	2.34,[j] 2.41[k]	

[a] Calculated using the $Fe_{47}(100)$ cluster model.
[b] Percentage of enhancement of spin polarization with respect to a bulk value.
[c] Edge site.
[d] Corner site.
[e] Face center.
[f] Face off center.
[g] (100) surface, Ref. 33.
[h] (100) surface, Ref. 34.
[i] (110) surface, Ref. 33.
[j] Center of cluster.
[k] Off center.

TABLE II. Parameters used in the calculations: principal quantum number n, ionization potentials IP (eV), and Slater exponents (a.u.), with linear coefficients c for double-zeta d orbitals.

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

From Eqs. (6) and (7)

$$b^2 = x/2 ,$$

$$a^2 = 1 - x/2 .$$

The energy for this mixture of configurations is then

$$E_{k+x} = a^2 E_k + b^2 E_{k+2} = (1 - x/2) E_k + (x/2) E_{k+2} . \quad (8)$$

Parameters used in this study are in Table II. The Slater-orbital exponents for the Fe 4s and 4p orbitals are chosen to give a calculated contraction of 0.14 Å for the topmost layer of the six-layer Fe_{38}(111) cluster (Fig. 1). This relaxation matches the experimental low-energy electron-diffraction (LEED) results of -0.137 ± 0.025 Å (Ref. 23) and -0.127 ± 0.03 Å (Ref. 24) for the relaxation of the top atom layer in the Fe(111) surface. With these parameters, the contraction of the topmost layer of a three-layer Fe_{34}(100) cluster (Fig. 2) is calculated to be 0.03 Å. This predicted value agrees with the LEED determination of 0.023 ± 0.04 Å.[25]

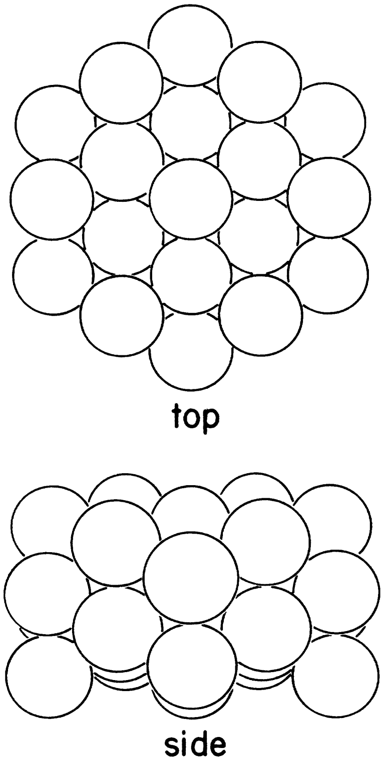

FIG. 1. Top and side views of the Fe_{38} cluster model for the Fe(111) surface.

RESULTS

S in bulk iron

From studies of diffusion in iron and its alloys,[26] S is believed to bind substitutionally. The five-layer Fe_{14}(100) and Fe_{46}(100) cluster models (Fig. 3), which have vacant substitutional sites in their centers, are used. The Fe_{14} cluster is the smallest cluster that defines the bulk substitutional site and the Fe_{46} cluster is the largest symmetric cluster defining this site that was calculationally treatable. When it is initially assumed that there is no change in the SP of the iron clusters due to the introduction of S, the binding energy (BE) of S in the Fe_{14}(100) cluster is calculated to be 0.12 eV. The BE of S in the Fe_{46}(100) cluster is 1.84 eV. The calculated BE is therefore influenced by the cluster size. If it is assumed that SP's of S neighboring Fe atoms are reduced by coordination of S to them, i.e., S has a "ligand effect," and S itself does not contribute a SP, the BE's of S in the Fe_{14} and Fe_{46} clusters become 1.47 and 3.06 eV, respectively. The BE of S in the Fe_{46} cluster should be closer to the experimental

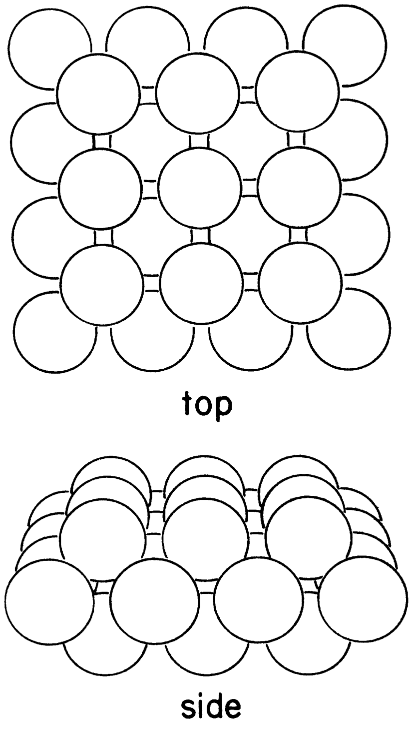

FIG. 2. Top and side views of the Fe_{34}(100) cluster model.

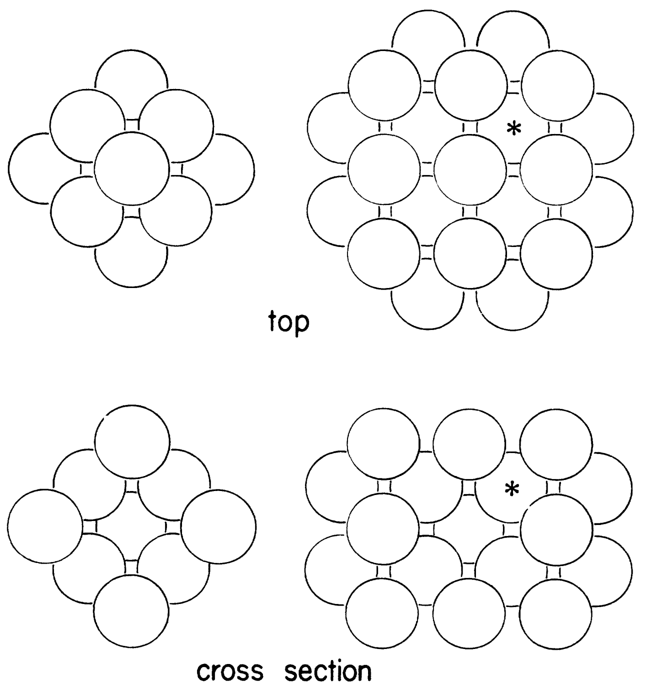

FIG. 3. Top and cross-section views of Fe_{14} and Fe_{46} cluster models. The atom labeled * is removed when modeling S binding to a substitutional site with an adjacent Fe vacancy.

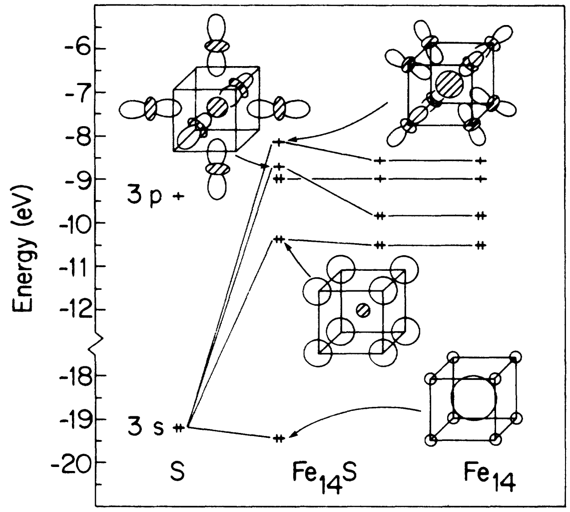

FIG. 4. MO correlation diagram for S in the Fe_{14} cluster model. The third column of energy levels has the S 3*s* interaction removed.

value. The increase in binding energy when S is treated as a ligand stems from the decrease of the cluster SP by 1.36 when the eight neighboring Fe atoms decrease their coordination from 8 to 7. The width of the singly occupied cluster bands is about 1.5 eV, so decreasing the cluster SP by 1.36 leads to stabilization.

From a molecular-orbital analysis of the bonding, it is found that S 3*p* orbitals interact with the triply degenerate metal orbitals, contributing to the binding energy. The S 3*s* orbital has a bonding interaction with the Fe $4s+3d$ band but also destabilizes all occupied *a*-symmetry orbitals of the iron *d* band, resulting in a net repulsive S $3s+$ Fe interaction. To find the destabilizing energy due to the interaction of the S 3*s* orbital with metal orbitals, the zeta and ionization potential (IP) of the S 3*s* orbital were increased to 20 a.u. and 50 eV, respectively. When these values are used, the S 3*s* orbital does not interact with the *a*-symmetry orbitals at all, and the BE's of S in the $Fe_{14}(100)$ and $Fe_{46}(100)$ clusters are calculated to be 3.67 and 4.75 eV, respectively, when the S ligand effect is included. Consequently, the destabilization energies are 2.20 eV for the $Fe_{14}(100)S_{bulk}$ cluster and 1.69 eV for the $Fe_{46}(100)S_{bulk}$ cluster. The molecular-orbital (MO) correlation diagram for the $Fe_{14}(100)S_{bulk}$ cluster model is shown in Fig. 4. The correlation diagram for the large cluster model is not shown because of the large number of orbitals, but the interactions are the same.

The S atom in the substitutional site of the $Fe_{46}(100)$ cluster is calculated to move 0.36 Å in the [100] direction. The energy barrier for S to move from one site to the other through the center is small (about 0.04 eV). Iron-atom relaxations around substitutional S are not included, but they should be small because the Fe-S distance in bulk Fe-S is 2.45 Å, close to the bulk Fe-Fe distance of 2.48 Å.

Introduction of an Fe atom in the substitutional site of the $Fe_{46}(100)$ cluster produces a BE of 4.86 eV.[27] This calculated bond energy is, as expected, larger than the thermodynamic value of 4.29 eV (Ref. 28) for the sublimation enthalpy of iron.

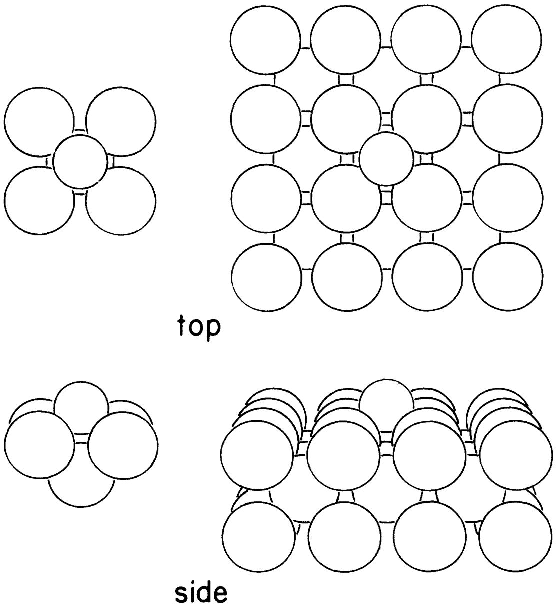

FIG. 5. Top and side views of $Fe_5(100)S_{ad}$ and $Fe_{41}(100)S_{ad}$ cluster models.

S on the Fe(100) surface

The S atom is known experimentally to be adsorbed at the fourfold site on the Fe(100) surface.[29] To study the adsorption of S on this iron surface, the $Fe_5(100)$ and $Fe_{41}(100)$ cluster models of Fig. 5 are used.

When it is assumed that chemisorbed S atoms do not induce a change in SP of the iron clusters, the calculated height of S from the $Fe_{41}(100)$ surface layer is computed to be 1.12 Å. This agrees well with the experimental value of 1.09 ± 0.05 Å from LEED analysis.[30] The same S height is used for the chemisorption of S on the $Fe_5(100)$ surface. The BE's of the S on the $Fe_5(100)$ and $Fe_{41}(100)$ clusters are calculated to be 2.25 and 2.99 eV, respectively. These values underestimate the experimental values[31] of 4.29 ± 0.10 eV at 0.6 saturation coverage normalized to CO uptake on the powdered iron surface in the temperature range of 547–855 K (Ref. 32) and 4.20 eV at a saturation coverage [0.5 monolayer with $c(2\times2)$ structure] on the Fe(100) surface.[17] When the S ligand effect is assumed, reducing the SP of its neighboring Fe atoms, the height above the $Fe_{41}(100)$ surface reduces to 1.11 Å and the BE's are 3.27 and 3.87 eV for the $Fe_5(100)$ and $Fe_{41}(100)$ clusters, respectively. The BE of S on the large cluster is close to the experimental value. When four S atoms are placed in a square array on the Fe_{41} cluster, the BE of a fifth atom at the center, modeling high coverage, increases by 0.11 to 3.98 eV, which is closer to the experimental value.

For simplicity, the MO correlation diagram for only the $Fe_5(100)S_{ad}$ cluster is given (Fig. 6). The more complicated diagram for $Fe_{41}(100)S_{ad}$ has the same types of interactions, but many more of them. On adsorption of S on Fe(100), the S $3p_x$ and $3p_y$ orbitals form π-type bonds with doubly degenerate Fe surface d orbitals. It might be expected that the S $3p_z$ orbital would strongly interact with a-symmetry orbitals of the surface clusters, leading to a strong σ bond. However, the resultant MO's are pushed slightly higher in energy, due to the destabilization of the low-lying S $3s$ orbital.

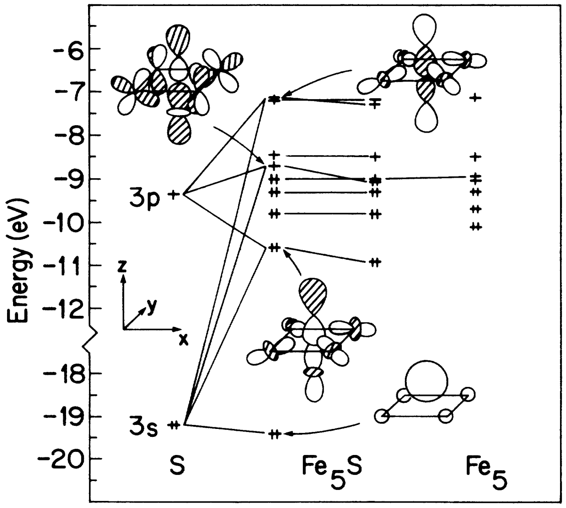

FIG. 6. MO correlation diagram for the adsorption of S on the $Fe_5(100)$ cluster. The third column of levels has the S $3s$ interaction removed, and comparison with the Fe_5 column shows bonding stabilizations caused by mixing with the S $3p_z$ orbital.

To avoid the destabilization due to the filled S $3s$ orbital, the shifted zeta (ζ) and IP values were again used. With these parameters, the BE's are 4.09 eV for the $Fe_5(100)S_{ad}$ cluster and 4.53 eV for the $Fe_{41}(100)S_{ad}$ cluster. The respective net destabilization energies are, consequently, 0.82 and 0.66 eV. Such small destabilization energies, compared to those for S in the bulk iron, are not surprising since the symmetry of the metal surface allows the mixing of the S $3p_z$ orbital with the a-symmetry orbitals of the surface band. This greatly stabilizes the a-symmetry antibonding counterparts to the S $3s$ + Fe $s+d$ bands bonding orbitals, and allows bonding with the cluster, as shown in Fig. 6. The participation of the $4s$ and $3d_z^2$ orbitals of the Fe atom directly below S shown in Fig. 6 has also been predicted from linearized-augmented-plane-wave (LAPW) calculations of Fernando and Wilkins.[33]

The BE for an Fe atom on the four-fold site of the $Fe_{41}(100)$ surface is calculated to be 4.07 eV, which is, as expected, substantially less than that in the bulk substitutional site. The difference between this and the energy for removing an Fe atom from the bulk, 0.79 eV, is the predicted vacancy-formation energy.

S segregation from bulk Fe to the (100) surface

The ability of S dissolved in Fe to segregate to the surface can be anticipated by comparing the measured adsorption energy, 4.29 eV on powdered Fe at 0.6 coverage[32] normalized to CO uptake or 4.20 eV at saturation $c(2\times2)$ 0.5 monolayer coverage on the (100) surface,[17] with 2.56 eV, the dissolution energy of S in the bulk.[34] In the case of the (100) surface the difference is 1.64 eV. Independent direct determinations by means of Langmuir-McLean plots yield an enthalpy of 1.71 eV for segregation of S to the surface of α-iron at coverages of $\frac{2}{3}$ to full saturation (assumed to be 0.5 monolayer),[15] which is remarkably close to the difference between the S dissolution and adsorption energies and 0.95 eV at coverages from 0.15 to 0.2 saturation (assumed to be 25 at. %),[35] an estimate based on just three data points.

The calculated binding energy of S on the 0.5-monolayer-covered Fe(100) surface, 3.98 eV, underestimates the experimental value by 5%. The vacancy-formation energy of 0.79 eV must be subtracted from the 3.10 eV calculated for binding to a bulk vacancy site to give 2.31 eV for the predicted dissolution energy of S in the bulk. This underestimates the experimental value by 10%. The 1.67-eV difference may be compared with the experimental difference of 1.64 eV and the segregation energy at high coverage, which is 1.71 eV. On the basis of this comparison it is probable that the predicted vacancy-formation energy in iron and binding energy of S in a bulk vacancy site are accurate. Neither value is experimentally available.

It has been suggested that sulfur segregation to the surface of iron is vacancy aided,[26] though it has not been proved. The interaction of the substitutional S atom with a vacancy has been modeled using an Fe_{45} cluster (Fig. 3). It is found that S binds most stably in the center of the two-vacancy site and it attracts the vacancy with a 0.29-eV stability gain. The weakness of this attraction suggests that at the temperatures of segregation, ~800 °C, mobile vacancies will on occasion collide with a substitutional S, and may help it diffuse for a while before departing.

DISCUSSION

A new method has been introduced to determine the spins of metal clusters from their structures for use in ASED MO studies. The less coordinated an atom is in a cluster, the greater its spin polarization. This spin rule is similar to the nearest-neighbor argument of Falicov[36] for the spin polarization of metal surfaces, but must be regarded as an empirical discovery. From the reduced charge matrix for the $Fe_{47}(100)$ cluster, the SP of each atom is obtained as given in Table I. These values are in satisfactory agreement with those from the spin rule. The enhancement of the surface magnetism of ferromagnetic materials with respect to bulk magnetism has been observed experimentally.[37] Waller and Gradmann performed spin-polarized LEED experiments on ferromagnetic Fe(110) films on a W(110) substrate, and found an enhancement of the surface magnetism by $34\pm10\%$.[38] Also, Tamura and Feder reported an enhancement of the Fe(110) surface magnetism by calculating the exchange- and spin-orbit-induced scattering asymmetry of the ferromagnetic Fe(110) surface using dynamic theory.[39] Recent calculations of surface SP's show satisfactory agreement with our predicted values: Victora *et al.*[40] calculate 2.90 for the Fe(100) surface and 2.55 for the Fe(110) surface with a seven-layer infinite slab, and Ohnishi *et al.*[41] predict 2.98 for the Fe(100) surface. These findings, when compared to our predictions in Table I, support the exponential dependence of SP on coordination that has been chosen; a linear dependence would clearly be in poorer agreement.

The change of the surface magnetization due to adsorption of foreign atoms, i.e., the ligand effect proposed for S, is less certain. A ferromagnetic resonance absorption study of Ni and Fe surfaces showed that chemisorption of reactive gases such as H atoms and CO molecules reduced the surface magnetic moments.[42] Polarized electron-diffraction calculations[43] on $p(2\times2)$S on Fe(110) also revealed changes in surface magnetization. Recently, Fernando and Wilkins calculated a reduction of surface magnetic moment in a LAPW study of S chemisorption on Fe(100).[33] However, Kirschner[44] concluded from a measurement of spin-polarized electron diffraction from clean and adsorbate-covered Fe(110) surfaces that the adsorption of O and S in small amounts (a coverage of up to a quarter of a monolayer) did not change the magnetization of the substrate. On the other hand, the recent film-FLAPW (full-potential linearized—augmented-plane-wave) calculation of Chubb and Pickett[45] predicted that the adsorption of O on Fe(100) with coverage of a monolayer induced approximately 10% enhancement of the surface Fe-atom moment.

In the present work the assumption of Fe-atom SP reduction by neighboring S atoms yielded BE's for S that are comparable to the experimental values both on the (100) surface and in the bulk substitutional site. Without a reduction in SP, these values are underestimated by about 1 eV. This seems to support the hypothesis that foreign atoms can induce the reduction of SP of ferromagnetic Fe atoms, though the simplicity of the ASED MO method is such that this is not a proof.

This study shows that a closed-shell interaction is produced between the occupied S 3*s* orbital and *a*-symmetry orbitals of the substitutional site when S is in bulk iron, while on surfaces this repulsive interaction is greatly reduced by symmetry-allowed mixing of the S $3p_z$ orbital. The calculated moving of S off center in the bulk substitutional site decreases the destabilization due to the S 3*s* closed-shell interaction by allowing participation of a S 3*p* orbital. The closed-shell repulsion is found to be reduced by 0.92 eV for S going from the equilibrium bulk substitutional site to Fe(100) surface. Since this reduction is comparable with our calculated total-energy difference of 0.88 eV, the filled S 3*s* orbital plays an important role in the segregation of S to iron surfaces. Taking into account the two-body S-Fe repulsion energies of the ASED MO theory, 0.97 eV for S on the surface and 1.21 eV for S in the equilibrium bulk site, it is evident that the S 3*p* orbitals contribute 5.50 eV to the chemisorption energy and 5.88 eV to the binding energy in the bulk substitutional site. These values are nearly the same. When S is in the center of the bulk site the two-body repulsion energy drops to 0.76 eV and the 3*p*-orbital contribution to bonding is 5.51 eV, essentially the same as for adsorbed S. The 0.36 Å shift in the [100] direction balances an increase in two-body repulsion and a decrease in orbital energies.

From the above results, it can be deduced that if valence *s* orbitals of other nonmetallic impurity elements can strongly interact with *a*-symmetry orbitals of metal bulk substitutional sites, then these elements will also bind more strongly in open spaces such as surfaces and grain boundaries. Therefore, reviewing the IP's (Ref. 21) and orbital sizes[22] of valence *s* orbitals of well-known segregants like C, N, O, P, and S suggests a greater bulk-site destabilization by 3*s* orbitals of P and S than by 2*s* orbitals of C, N, and O. Experimental studies,[14–16,35] in fact, show a stronger tendency for segregation of S and P compared to C, N, and O, though the effects of interstitial binding of C, N, and O must also be considered.

Larger enrichments of impurities are observed on metal surfaces than at grain boundaries.[46] This implies that the destabilization by the closed-shell interaction of valence *s* orbitals of impurities with the surroundings is larger at grain-boundary contacts than at surfaces. This would be expected because of the higher coordination. Oku *et al.*[47] have found from the Auger- and electron-energy spectra of a grain-boundary fracture plane of bicrystal molybdenum that O exists as if it were adsorbed. This suggests that impurities may act as bridges at grain boundaries.

It was noted in Ref. 35 that when sulfur was present on an Fe(110) surface prior to oxidation, it remained localized at the metal-oxide interface after oxidation. In contrast, when a clean surface was oxidized, sulfur was not observed to segregate to the interface. These findings can be explained by the mechanism of S segregation. When S segregates to a surface it brings at least one Fe vacancy with it. When the surface is already oxidized, S will be repelled by the interface because to enter the interface would require breaking strong Fe—O bonds and forming repulsive O^{2-}-S^{2-} closed-shell interactions. When the S-covered surface is oxidized, S is either oxidized to immobile sulfate anions or, if its diffusion is vacancy assisted, it lacks the vacancies it needs to move.

CONCLUSIONS

This study reveals quantum mechanically why dissolved sulfur in bulk iron segregates to the surface. In bulk iron the filled S 3*s* orbital is involved in a closed-shell repulsion with the occupied *a*-symmetry orbitals of the substitutional site, while on a surface the hybridization of S $3p_z$ orbital with the S 3*s* orbital becomes symmetry allowed, and this stabilizes the antibonding counterpart of the 3*s*-substitutional site interaction. This accounts for about half of the segregation energy and the Fe vacancy-formation energy is responsible for the other half. These results have implications for another nonmetallic impurity, P, which is large enough to bind substitutionally and has 3*s*-orbital parameters similar to those of S.

In addition, a spin rule for ferromagnetic iron is proposed. It assumes an exponential decrease in SP of a ferromagnetic iron atom with increasing CN, going from SP of a free atom to that of a bulk atom. It predicts surface SP's that are in close agreement with recent theoretically calculated SP's for Fe(100) and Fe(110) surfaces. Comparison of the calculated BE for S in the bulk and on the surface with experimental values suggests that S should be counted in the coordination sphere of Fe in determining the SP contribution of an Fe atom.

Finally, a general argument explains why S does not segregate to the Fe-Fe-oxide interface: to do so would require breaking strong Fe—O bonds and forming repulsive O^{2-}-S^{2-} interactions.

ACKNOWLEDGMENTS

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