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Segregation of Cr impurities at bcc iron surfaces: First-principles calculations

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The segregation of Cr impurities placed in different layers at four low-index iron surfaces is studied from first principles in the dilute limit of Cr concentration. The surface segregation depends strongly on the surface orientation. For a single Cr atom in the computational cell, configurations with Cr atom in the outer surface layers are found to be unfavorable. However, for higher bulk Cr concentration, the Cr-enriched surfaces are predicted. The magnetic moment on the Cr-solute atoms in surface layers is much increased and follows the trend observed for the Fe-host atoms.

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Iron and chromium form a perfect ferromagnetic FeCr alloy, which (for the Cr bulk concentrations up to around 10%) is the basic component of ferritic stainless steel. This binary system exhibits superior mechanical properties and an enhanced corrosion resistance due to formation of a Cr-rich oxide layer. A formation of this passive oxide layer at the surface of a diluted alloy must be a consequence of its enrichment by Cr atoms. Thus, the question arises about segregation of Cr at the surface of an FeCr system.

According to simple thermodynamic considerations, the surface should be enriched by a component with lower surface energy. The empirical surface energies, which were obtained by extrapolation of results for the liquid metal surface tensions to zero temperature, are reported to be higher for Fe than Cr: 2.41 and 2.35 $\mathrm{J/m^2}$ (Ref. 1) and 2.55 and 2.30 $\mathrm{J/m^2}$ (Ref. 2), respectively, thus predicting Cr segregation. This is in contrast to the results of first-principles calculations, which show that surface energy of (100) and (210) surfaces is distinctly lower for Fe than Cr [2.47 and 3.25 $\mathrm{J/m^2}$ and 2.60 and 3.40 $\mathrm{J/m^2}$ for (100) and (210) facets, respectively].[3,4]

Direct experimental investigations[5–7] of segregation have not clarified the situation. An angle-resolved x-ray photoelectron spectroscopy experiment reported a Cr enrichment of the $\mathrm{Fe_{87}Cr_{13}}$ and $\mathrm{Fe_{75}Cr_{25}}$ alloy surfaces.[5] The scanning tunneling microscopy study of a Cr monolayer grown on Fe(100) has shown[6] that after *in situ* heating at 973 K, only one out of the four deposited Cr atoms remained on the surface; the major part migrated into subsurface layers via an atomic exchange mechanism. Similarly, an angle-resolved Auger-electron-scattering experiment[7] for a half-monolayer Cr film grown on an Fe whisker reported a substantial mixing that occurred at room temperature in the first three Fe layers.

This controversy on Cr segregation has been addressed by several *ab initio* calculations. Full-potential Korringa-Kohn-Rostoker Green's function method calculations performed by Nonas *et al.*[8] within the local-density approximation (LDA) have suggested that segregation of Cr is unlikely. Although at 0 K segregation energy (SE) is negative, which means segregation, however, it is too small (-0.05 eV) to overcome energy barriers at higher temperature. All-electron calculations performed by Geng[9] within the generalized gradient approximation (GGA) yielded a very similar value of segregation energy (-0.03 eV). Another LDA calculation, within the Green's function linear muffin-tin orbital method, reported a larger and positive (0.16 eV) segregation energy.[10] In all those calculations the lattice relaxation effect was neglected.

More recently, by applying a simple Ising model to an FeCr system, Ackland[11] demonstrated that in the dilute limit, Cr does not segregate to the surface but as the concentration increases, segregation is possible. Plane-wave basis projector augmented-wave (PAW) calculations of Ponomareva *et al.*[12] showed that the segregation energy of Cr at Fe(100) is rather small (-0.04 to $+0.09$ eV) and is very sensitive to the supercell size—being positive (i.e., unfavored) for large supercells. Application of the exact muffin-tin orbitals method, which included the configurational entropy for $T>0$ K, showed that while in dilute alloys the surfaces were covered exclusively by iron, above the Cr bulk-concentration threshold ($\sim 10\%$) the surface became enriched with Cr,[13] and the stability of the Cr-enriched surface is due to magnetic interactions. The role of magnetic effects in the stability of FeCr system was also stressed by other authors.[14]

In this work we investigate the effect of Cr-solute atoms on the cohesive and magnetic properties of four different facets of the ferromagnetic α-Fe crystal. The segregation energies at various surfaces may be quite different due to the strong influence of the local atomic arrangements. Since almost all of the previous calculations considered segregation at Fe(100) only [and additionally at the (110) in Ref. 10], our principal goal is to see how the segregation process and magnetic properties of the system are influenced by the reduced coordination in different surface layers of various orientations. Finally, we discuss the effect of higher bulk Cr content on surface segregation.

Our total-energy calculations utilized density-functional theory within the plane-wave basis approach.[15,16] The exchange-correlation energy functional was treated in the PW91 version[17] of GGA. The electron-ionic core interactions were represented by PAW potentials[18] with the Fe $3d^7 4s^1$ and Cr $3d^5 4s^1$ states treated as valences. The kinetic-energy cutoff for the plane-wave basis was set equal to 400 eV, which is sufficient to yield good energy convergence for both Fe and Cr. The Brillouin-zone integrations were performed using an $8\times 8\times 1$ k-point mesh of the Monkhorst-Pack scheme[19] and the first-order

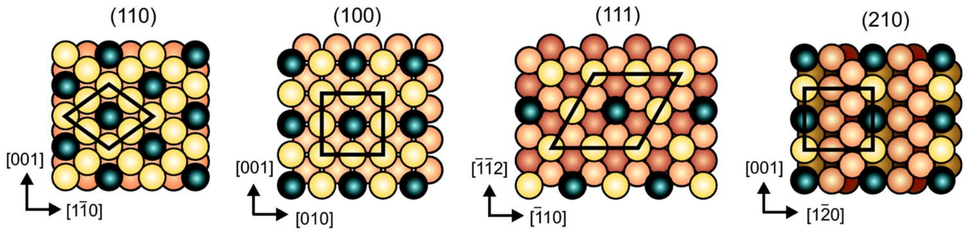

FIG. 1. (Color online) Top view of the considered low-index Fe surfaces showing the 2×2 and 1×2 surface cells applied to calculate segregation. The colors are darker for deeper lying layers. Black-blue balls represent Cr atoms. The in-plane nearest-neighbor distances between Cr atoms are, respectively, equal to $\sqrt{3}a$ at (110), $2a$ at (100) and (210), and $2\sqrt{2}a$ at (111) surfaces. The in-plane Cr concentrations per a^2 are 0.354 at the (110), 0.250 at (100), 0.144 at (111), and 0.224 at (210) surfaces.

Methfessel-Paxton[20] method for the Fermi-surface smearing of 0.2 eV. Free (100) and (110) surfaces were modeled by slabs of 11 layers, while the (111) and (210) surfaces were represented by slabs of 15 and 20 Fe layers, respectively, separated by $\simeq 15$ Å of vacuum. The resulting structure was repeated periodically in space. We used the theoretical lattice parameter ($a = 2.844$ Å) of ferromagnetic iron,[3] which is slightly smaller than the experimental value of 2.867 Å. The thicker vacuum of $\simeq 20$ Å was chosen for the (100) surface in order to facilitate comparison of our results with those of previous calculations.[12] Full relaxation of atomic positions was carried out until the forces on each atom converged to less than 0.01 eV/Å. We employed the 2×2 surface unit cell, except for the (210) oriented slab, where the 1×2 cell was applied (Fig. 1). A dilute FeCr system was modeled by replacing one or two Fe atoms of the central layer by Cr and then moving one Cr to the surface or subsurface layer. The resulting asymmetry of the electrostatic potential in the vacuum region was compensated by the dipole correction.[21,22]

The surface SE is defined as

$$E_{\mathrm{segr}} = E_{\mathrm{Cr,surf}}(n\mathrm{Cr}) - E_{\mathrm{bulk}}(n\mathrm{Cr}), \tag{1}$$

where $E_{\mathrm{bulk}}(n\mathrm{Cr})$ is the total energy of the supercell, which contains n Cr atoms, and $E_{\mathrm{Cr,surf}}(n\mathrm{Cr})$ is the total energy of the slab with one Cr atom moved to the surface layer. The negative/positive E_{segr} means that the impurity does/does not segregate to the surface.

The calculated segregation energies are displayed in Fig. 2 as a function of layer depth. For all surfaces considered the SE is positive or equal to zero, i.e., Cr-free surfaces are more favorable than the ones containing Cr and, consequently, Cr stays in the Fe interior. As already noticed previously,[10] the calculated SE depends strongly on the surface orientation. The values of segregation energy are most differentiated in the topmost surface layer, where its anisotropy can vary by as much as ~0.3 eV, and the segregation is least favored for the (210). At the remaining three surfaces there is a high-energy barrier for Cr segregation, which has a maximum in a second or third Fe layer. For the topmost layer, the SE is largest at the (100) and (210) planes, which suggests that it depends both on the volume concentration of Cr and the coordination of surface atoms. For the applied supercells, the average volume of Cr concentration (per supercell) is similar and amounts to 2.27% for the (110) and (100), 1.67% for the (111), and 2.5% for the (210) orientations. The highest SE for the (210) facet may result from the fact that the Cr impurity sitting in the [001] oriented row of the topmost layer of the (210) surface is less screened by Fe atoms from the Cr-Cr interaction.

According to Aldén *et al.*[10,23] the main contribution to the surface SE originates from the difference in surface energy in the pure alloy component. Using the surface energy values calculated previously,[3,4] one gets for the Fe(100) and (210) facets the SEs equal to 0.39 and 0.94 eV, which are much larger than those presented in Fig. 2. In general, the SEs increase with openness of the surface. An exception is the (111) where the SE is close to zero. In agreement with Ref. 10, our results show that SE at the (100) is distinctly larger than that at the (110).

For the topmost layer of the (100) facet, the SE of 0.076 eV is very close to that (0.069 eV) reported by Ponomareva *et al.*[12] The remaining small discrepancy results from a difference in the lattice parameters applied. In agreement with Ref. 12, we find that for large supercells (which mean more dilute alloys), Cr should not segregate toward the surface. Some of our results may be influenced by the long-range repulsion between Cr atoms, which is of nonmagnetic nature[24] and amounts to ~0.1 eV at the distances of $\simeq 2a$. However, it was also found that at such distances, the Cr-Cr interaction is negligible.[9] Thus, also at the Cr-Cr separations

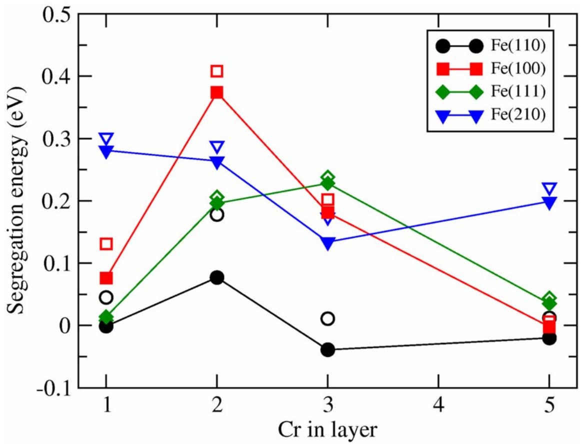

FIG. 2. (Color online) Segregation energies calculated for Cr, substituting one of the Fe atoms in the surface or subsurface layer at different iron surfaces. Open symbols represent the values calculated for a sparser (4×4×1) k-point mesh.

TABLE I. Surface segregation energy of Cr (in eV) at the topmost layer of four Fe facets, calculated for Cr concentrations involving one (Fig. 2) and two Cr atoms per supercell. The surfaces are ordered from the most to the least densely packed.

	(110)	(100)	(111)	(210)
1 Cr	−0.001	0.076	0.014	0.281
2 Cr	−0.267	−0.193	−0.119	−0.042

encountered at most of the surfaces considered (see caption to Fig. 1), the Cr-Cr interaction is rather small and the only surface which may be affected is the (110). In fact, this is illustrated in the latter case, where the relatively high in-plane concentration of Cr ($0.354/a^2$) is the cause. The SE is smallest of all and, in some layers, turns negative when calculated for a denser k-point mesh (Fig. 1). This is in line with the observation[12] about the importance of small in-plane concentration of Cr for a good estimation of the SE. If small unit cells are applied, then the surface SE of Cr becomes negative because of a significant concentration of the effective pair interaction between atoms in the bulk material.[12] Furthermore, our results (Fig. 2) show that the higher the Cr concentration at the facet (Fig. 1), the finer the mesh of k points required to obtain well-converged estimates of the SE

At open surfaces, for the (111) oriented slab, SE decreases when a Cr atom is placed in an outer Fe layer and becomes very small when Cr is substituted for one of the surface-layer atoms. This is in contrast to the (210) surface where SE is positive and is largest for the Cr atom placed in the surface layer. This suggests that there is an orientation effect due to a different coordination of surface-layer atoms at these surfaces. At the (210) surface the bulk coordination is achieved only for the atoms of the fifth atomic layer. Consequently, the energy of the Cr atom at the fifth (210) layer is still much different from that of the system with Cr at the middle of the slab (Fig. 2). However, it converges to the bulk value in deeper layers. The energy of Cr placed in the seventh layer differs from that in the bulk only by 0.058 eV.

The calculated relaxations of interlayer distances for the clean surfaces agree well with those determined by us previously.[3] A disturbance of relaxation due to a Cr atom placed in different Fe layers is rather limited to the nearest planes; however, the pertinent average relaxations can be decreased/increased by 40%–50%. There is also a substantial buckling of the Fe planes containing Cr (0.05–0.25 Å), which induces the buckling in the neighboring Fe planes. Note, however, that even substantial relaxations (~20%), which appear at open Fe surfaces,[3] have a relatively small effect ($\lesssim 5\%$) on the calculated surface energies, so their effect on SE is also small.

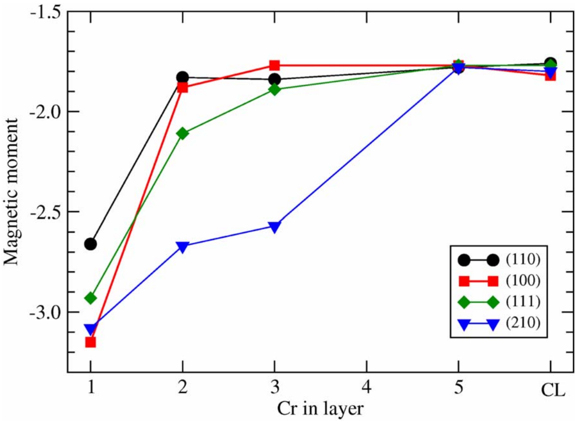

FIG. 3. (Color online) Magnetic moment (in μ_B) on a Cr atom placed in different layers of the slab. CL labels the central layer of the slab [i.e., 6th layer for the (110) and (100) slabs, and 8th and 10th layers for the (111) and (210) slabs, respectively].

In order to see how the SE is changed for higher bulk Cr concentrations, and to verify the existence of the bulk-concentration threshold[11,13] for the surface Cr enrichment, we have performed calculations for two Cr atoms placed originally at the center of our slabs and then for one of the two Cr atoms moved to the surface. The results for SE are collected in Table I. As can be seen, already at these, relatively low bulk concentrations of Cr [i.e., 4.55% at the (110) and (100), 3.33% at the (111), and 5.0% at the (210) oriented slabs] segregation is clearly favored. The magnitude of SE is higher on close-packed surfaces than on the open ones. This correlates with a decline in the coordination of Cr atoms in the surface layers of different orientation. Reduced coordination of the topmost-layer atoms, in turn, correlates with the reduced spacings between the (210) and (111) planes compared to those between the close-packed ones. Fe atoms of the bulk (210) and (111) layers screen more effectively the pair interaction between Cr atoms placed in the same layer than those in the close-packed (110) and (100) planes. Thus, the magnitude of interaction between two Cr atoms in the middle layer is not much different from that between one Cr in the middle layer and the other one moved to the surface. Consequently, when one of the Cr atoms is moved to the surface layer, the first term on the right-hand side of Eq. (1) may remain smaller or comparable to the second one, making the segregation unlikely. Our additional calculations for the (111) oriented slab showed that increasing bulk Cr composition to three, seven, or nine Cr atoms in a slab yields SEs of −0.072, −0.152, and −0.182 eV, respectively. The Cr atoms were placed in the slab following the patterns: 000100010001000, 001010111010100, and 001011111110100, where 0 and 1 stand for the pure Fe layer and the layer containing one Cr atom, respectively. For each composition the Cr atom from the middle layer was swapped with the Fe atom from the outermost layer. The latter calculations applied a $4\times4\times1$ k-point grid, which for the (111) facet assures a good convergence of the energies with respect to the number of k points (Fig. 2). Since in all considered cases (Fig. 2) the results for a sparser k-point mesh are higher in energy than those for $8\times8\times1$ k points, they provide an upper bound for the converged SE values. Thus, we get a clear indication of surface enrichment at a higher Cr content in bulk FeCr.

By discussing the effect of magnetism, let us note that while for the close-packed (110) and (100) surfaces we find (in line with Ref. 12) that the magnitude of segregation energy is correlated with the magnetic moment of Cr (Fig. 3), and is larger for the larger magnetic moment, the correlation breaks down for open surfaces. A Cr atom in a dilute concentration in the Fe surrounding becomes antiferromagnetically aligned with respect to the host atoms. In the pure bcc iron the moment on atoms of the outermost surface layer is enhanced[3] up to 2.96 μ_B and it converges to that characteristic of the bulk Fe ($\simeq$2.20 μ_B) in the middle of the slab. The local moment of Cr impurity also changes substantially for the position in different layers and follows the trend observed for Fe atoms.[3] It is most increased for Cr in the outermost layer, achieving -3.14 μ_B at the (100) surface. This is in good agreement with the measured value[25] for the first complete monolayer of Cr on Fe(100). Its diminishing with layer depth is monotonic, but even in the center of the slab, the moment is about three times larger ($\simeq -1.80$ μ_B) than the characteristic of bulk Cr ($|0.59|$ μ_B),[4] independent of the slab orientation. This agrees very well with the moment of -1.88 μ_B from the diffuse neutron-scattering experiment[26] for the low-volume concentration of Cr (1.46 at. % Cr). For the compact (110) and (100) surfaces, the effect of enhancement due to termination is limited to the topmost-layer atoms (Fig. 3).

The above changes can be linked[3] to the reduced coordination of surface-layer atoms. For Fe surfaces, the magnitude of the magnetic moment on Fe atoms in the outermost surface plane depends on the coordination number of this atom, in the first place. At surfaces with the lowest coordination of the topmost-layer atom [i.e., (100), (111), and (210)], where four bonds are missing, the magnetic moment is largest. Then, coordination of the second layer atom is relevant. Every atom in the second layer of (210) is only sixfold coordinated and, thus, its moment is more enhanced than that of the sevenfold coordinated atom of the (111) surface. Consequently, the number of unsaturated bonds in particular layers decides on the ordering of enhancement of magnetic moments on the surface atoms. By segregating Cr to the surface, the Fe-Fe bonds are replaced by Cr-Fe bonds and a similar argument holds for the local moments on Cr.

In summary, the segregation of Cr impurities at four different facets of the diluted FeCr alloy was studied from first principles. In all cases, a single Cr impurity prefers the bulk to the surface-layer position. The energy of segregation depends both on the impurity concentration and the reduced coordination of an impurity atom in the surface layers. Our results demonstrate that for a little higher bulk Cr concentration, involving more than one Cr atom per computational cell, the Cr-enriched surfaces become favorable. The magnetic moment on Cr impurity is greatly increased in the surface layers.

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