

## Energetics of 3d Impurities on the (001) Surface of Iron

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We present a detailed *ab initio* study of the alloying process in the dilute limit for 3d atoms on the Fe(001) surface. The calculations are based on local density functional theory and apply a KKR-Green's function method for impurities on surfaces. For practically all 3d transition metal impurities on Fe(001) we find a strong tendency for a direct exchange mechanism into the first surface layer. The early 3d impurities V, Cr, and Mn strongly repel each other on neighboring positions within the first layer, while Ni and Cu atoms show a moderate repulsion. The *ab initio* results are in good agreement with STM studies for Cr/Fe(001) and present valuable predictions for all 3d/Fe(001) systems. [S0031-9007(98)06045-1]

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Over the last several years experimental methods like ion field and scanning tunneling microscopy made it possible to discern individual atoms on surfaces and to observe to a certain extent diffusion and formation processes on the surface of materials. Together with various calculational methods a good understanding of growth modes on an atomic scale has been achieved [1,2]. For a few substrate-adsorbate combinations the formation of surface alloys is found even though the adsorbates are principally immiscible in the substrate [3,4]. In a recent STM study the growth and alloying of chromium on the Fe(001) surface has been investigated [5]. The authors find that under a layer-by-layer growth condition substantial alloying occurs at the Fe/Cr interface. For instance, adsorbed Cr atoms are directly incorporated into the first layer and also interdiffusion into deeper layers is observed. Further statistical analysis of the data yields direct information about the interactions of Cr atoms in the surface layer; e.g., the absence of nearest neighbor (NN) dimer pairs shows a strong repulsion between neighboring Cr atoms.

Motivated by these STM results for Cr on Fe(001) we present here an *ab initio* study of the alloying process for 3d impurities on the Fe(001) surface, where we will concentrate on the energetic properties in the dilute limit. In particular we consider the elemental processes sketched in Fig. 1 and ask the following specific questions: Is it for an impurity adatom [Fig. 1(a)] energetically favorable to exchange with an Fe surface atom ["direct" exchange, Fig. 1(b)], and is the resulting complex (b) stable or likely to dissociate ["complete" exchange, Fig. 1(c)], so that effectively a migrating 3d adatom (a) is replaced by a migrating Fe adatom as in (c)? Do two 3d impurities in the first layer cluster as in (d) or are distant configurations (e) more stable? And finally, does the 3d impurity stick to the surface layer or does it interdiffuse into the Fe bulk? We will show that our results are in good agreement with the recent STM studies for Cr on Fe [5] and represent valuable predictions for the whole 3d series on Fe(001).

The calculations are based on density functional theory in the local density approximation with the parameters of Vosko *et al.* [6], and apply a Korringa, Kohn, and Rostoker (KKR) Green's function methods for surfaces [7] and impurities on surfaces [8]. The atomic potentials as well as the potentials in the vacuum region are approximated by spherically symmetric potentials. However the "full" charge density including all nonspherical terms is evaluated and used in the calculation of the total energies. Angular momenta up to  $\ell_{\max} = 3$  are included in the expansion of the wave functions (and up to  $2\ell_{\max} = 6$  in the charge density expansion). We start from the self-consistently calculated Green's function of the ideal surface which serves as the unperturbed reference system. To describe the impurity or the impurity dimers on the surface we consider a cluster of perturbed potentials which includes the potentials of the impurities and the perturbed potentials of several neighbor shells, with typical sizes ranging from 19 perturbed sites for the segregation

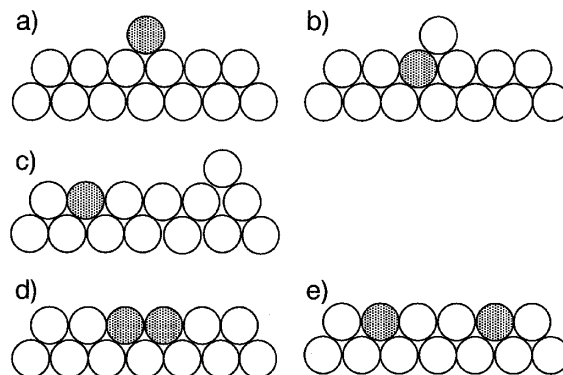


FIG. 1. Schematic representation of different configurations of 3d impurities (shaded) at the surface: (a) 3d adatom, (b) the direct-exchange complex consisting of a 3d surface atom and a neighboring Fe adatom, (c) the complete-exchange complex with a "free" Fe adatom, (d) two 3d surface atoms at NN sites in the first layer, and (e) two noninteracting 3d surface atoms.

energies to 58 for the interaction of NN impurities. To overcome finite size effects due to the restricted finite extension of the perturbation, the total energy of the perturbed system is evaluated as the energy difference with respect to the reference system by applying Lloyd's formula (adapted to complex energies [9]). In this way all single particle contributions are summed up in whole space. We checked the accuracy of our calculations by using different cluster sizes and by changing the reference system. In general we find that screening is less efficient at the surface than in the bulk, so that the spatial extent of the perturbed cluster plays here a greater role. Nevertheless reliable total energy results can be obtained if (i) at least two shells of perturbed potentials around each impurity are considered, (ii) Lloyd's formula is used for the single particle energies, and (iii) all calculated total energy differences refer to the same cluster sizes. For instance, for the interaction energy of two impurities the larger "dimer cluster" has also to be used for the energy of the single impurity. Our calculations neglect the lattice relaxations at the surface and around the impurities. For the 3d impurities on the Fe surface this should be well justified. For instance, recent calculations for 3d impurities in bulk Fe [10] show that the relaxation energies are very small, e.g., for Cr and Mn impurities 0.02 and 0.002 eV, respectively. At the surface relaxations are in general larger, but the relaxation energies are also small. Recent calculations [11] for 3d monolayers on Fe(001) give typical relaxation energies of 0.02 eV.

Figure 2 summarizes the calculated energies for the exchange mechanism at the Fe(001) surface. Plotted are both the energies for the "direct exchange" process defined by the energy difference between the 3d adatom configuration shown in Fig. 1(a) and the exchanged pair configuration of Fig. 1(b), as well as the energies for the "complete exchange," defined by the energy difference between configuration (a) and configuration (c) consisting of the 3d

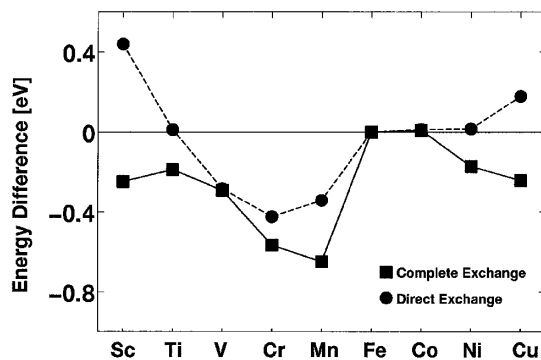


FIG. 2. The differences in total energy for the exchange process. The *direct-exchange* energy is the total energy difference between the exchange complex of Fig. 1(b) and the 3d adatom of Fig. 1(a). The *complete-exchange* energy includes the dissociation energy of the complex and represents the total energy difference between configurations 1(c) and 1(a).

surface atom and a free Fe adatom. Our definition of the exchange energy does not include the additional energy gain due to the possible adsorption of the Fe adatom at a step or an island, since we are interested only in the exchange probability during diffusion on the terrace, which for the present purpose is considered as infinitely large. Moreover we calculate only the equilibrium configuration, but not the activation barrier, which we assume to be sufficiently small that the exchange process actually occurs. By definition both exchange energies vanish for an Fe "impurity." Surprisingly we find that for all 3d impurities the complete-exchange configuration (c) is more stable than the 3d adatom (a). The only exception is the Co impurity, which has a nearly vanishing exchange energy and behaves in this respect like an Fe adatom. The energy gain is particularly large for the Cr and Mn adatoms, i.e., 0.57 and 0.65 eV, respectively. Our result for Cr explains the STM observations [5], showing that all Cr atoms are incorporated directly into the iron surface without moving to steps. One can see from Fig. 2 that (with the exception of Co and V adatoms) the direct exchange configuration (b) is considerably less stable than the complete exchange configuration (c), so that substantial energy is gained by breaking up the pair complex. In fact, at both ends of the series, i.e., for Sc and Cu, the pair configuration is energetically higher than the 3d adatom configuration. The reason for the instability of this complex will be discussed later on. The calculated exchange energies are strongly affected by magnetism, which we illustrate for a Mn impurity. The local moment of the Mn adatom couples ferromagnetically to the substrate moments, while for the Mn surface atom the antiferromagnetic configuration [12] is most stable, lying 0.34 eV lower than the ferromagnetic one. Therefore the complete exchange energy of 0.65 eV for Mn is reduced to 0.31 eV, if we consider the transition from the ferromagnetic Mn adatom to the (metastable) ferromagnetic surface atom. While magnetism strongly affects the calculated energies, the local moments of the impurities do not change much for the different geometries and magnetic configurations.

We now consider the interaction of two 3d surface atoms by calculating the interaction energies on nearest neighbor (NN) and next-nearest neighbor (NNN) sites in the surface and comparing with the calculated interaction energies at the same distances in the bulk. The interaction energies are defined as the total energy difference between the dimer complex and two isolated impurities at infinite separation. Thus by construction a negative energy means attraction and a positive energy repulsion between the two atoms. For the single surface impurities the preferred magnetic states are [12]: ferromagnetic coupling ( $\uparrow$ ) to the substrate for Fe, Co, and Ni and antiferromagnetic coupling ( $\downarrow$ ) for Ti, V, Cr, and Mn; the Mn and Fe impurities may also align in the respective other (metastable) configuration. Thus for the pairs we can in principle have three different collinear states, the antiferromagnetic configuration ( $\uparrow\downarrow$ ) with both impurities coupling ferromagnetically to each other, but

TABLE I. Interaction energies of 3d impurities on the nearest neighbor (NN) and next nearest neighbor (NNN) sites in the surface layer of Fe(001) and at the same distance as the surface NN sites in bulk Fe (bulk: NNN). The energies are given in eV with positive energies referring to repulsive interactions.

	V	Cr	Mn	Fe	Co	Ni	Cu
Configuration	( $\Downarrow$ )	( $\Downarrow$ )	( $\Downarrow$ )	( $\Downarrow$ )	( $\Downarrow$ )	( $\Downarrow$ )	( $\Downarrow$ )
Surface: NN	0.214	0.208	<b>0.214</b>	-0.011	-0.010	0.041	0.0
Bulk: NN	0.127	0.082	...	...	-0.031	...	...
Surface: NNN	-0.016	0.023	<b>-0.014</b>	...	-0.007	-0.059	...

antiferromagnetically to the substrate, the ferrimagnetic configuration ( $\Downarrow$ ), and the ferromagnetic one ( $\Uparrow$ ). The last one is realized for the Co and Ni NN pairs, while the antiferromagnetic configuration is found for Ti, V, and Cr pairs. Mn and Fe pairs are boundary cases, for which all three configurations exist, with the antiferromagnetic one being most stable for the Mn dimer and the ferromagnetic one for Fe. The interaction energies for all these surface dimers on NN and NNN sites are listed in Table I together with the corresponding NN dimers in the bulk (in the bulk terminology these are NNN dimers). For Mn and Fe the bold numbers indicate the stable configuration. The most important result of Table I is that the interaction for the NN dimers of Ti, V, Cr, and Mn is strongly repulsive with a magnitude of about 0.2 eV, while the interaction for the NN dimers of Co, Ni, and Cu is relatively weak, being slightly attractive for Co and repulsive for Ni and Cu. A similar trend, in particular the repulsion of the Ti, V, and Cr dimers, is also found in the bulk, although the values are reduced due to the better screening in the bulk. The interaction of the NNN surface dimers is much weaker, repulsive for Cr and Ni and attractive for V and Mn. As noted already above for the exchange energies, magnetism plays also a large role for the interaction energy. The repulsion of the ( $\Downarrow$ ) configurations is a consequence of frustration: the two atoms would like to couple antiparallel to each other, which can however not be realized due to the strong antiferromagnetic coupling of each atom to the substrate moments. The above results are in very good agreement with the recent STM studies for the growth process of Cr on the Fe(001) surface [5]. In the statistical analysis of these data, no NN Cr pairs are found, while the probability for the formation of Cr dimers on NNN sites is reduced by  $0.4 \pm 0.2$  as compared to a random distribution, which would occur in the noninteracting case. Since the pair correlation function between impurities is determined for small concentrations by the factor  $e^{\Delta E/k_B T}$ , where  $\Delta E$  is the impurity interaction energy, we obtain from our calculations a reduction to 0.01 for the NN Cr dimers and a reduction to 0.6 for the NNN dimers which agrees with the above results within the statistical errors.

We now proceed to the calculation of the surface segregation energies, i.e., the energy difference between the 3d impurity in the first surface layer and in the bulk. The calculated surface segregation energies are plotted in Fig. 3. Negative energies mean that the impurities segregate to the

surface, while for positive energies the surface position is unfavorable. The results show a parabolic behavior, however, with a depletion in the middle of the row. The parabolic behavior with negative values at the beginning and end of the series is expected from simple bonding arguments or from the trend of the surface energies. However instead of the expected maximum with positive values for Cr and Mn, we obtain a slightly negative value for Cr and a stronger negative value for Mn. This anomaly is due to magnetism which also shows up in the two values obtained for the Mn impurities. The stable antiferromagnetic configuration segregates to the surface, while the metastable ferromagnetic one has a vanishing segregation energy. For the well studied case of Cr/Fe(001) Venus and Heinrich [13] report at room temperature an intermixing up to three monolayers, while the STM studies [5] show that in the dilute limit about 25% of the Cr atoms stay in the first layer. This agrees with the nearly vanishing segregation energy obtained in the calculations which means that there is no energetic driving force to or away from the surface. Our results also agree reasonably well with the semiempirical formulas of Miedema [14]. Recent calculations of segregation energies based on the linear muffin-tin orbitals (LMTO) method in the coherent-potential approximation (CPA) [15] for 3d impurities on Fe(110) yield a similar trend as in the present studies. However the results for Ti, V, Cr, Mn, Ni, and Cu are about 0.5 eV higher than our values for Fe(001). Most of the difference seems to be due to numerical approximations in evaluating the CPA total energies [16]. The calculated segregation energies offer an

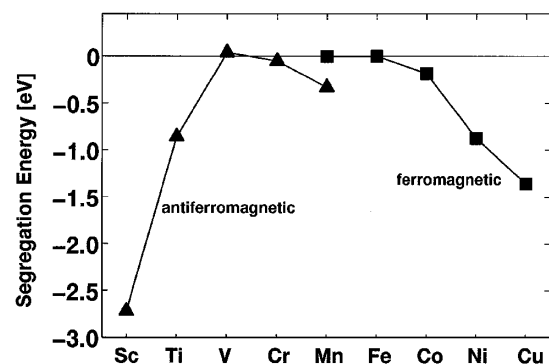


FIG. 3. Surface segregation energies of 3d impurities with respect to the Fe(001) surface; negative energies mean segregation at the surface.

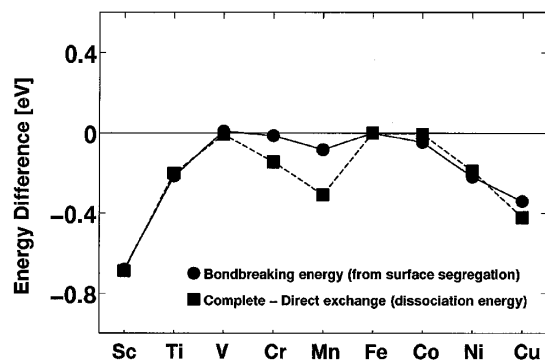


FIG. 4. The dissociation energy of the exchange complex (total energy difference between the configurations 1(c) and 1(b) and the energy per broken impurity-iron bond, as calculated from the segregation energy.

easy explanation for the instability of the direct-exchange complex shown in Fig. 1(b). The negative surface segregation energy, e.g., of the Cu impurity can be modeled by Fe-Cu bonds being weaker than Fe-Fe bonds, since by segregating to the (001) surface four NN Fe-Cu bonds are replaced by Fe-Fe bonds. The same process occurs in the dissociation of the complex (b), since one Fe-Cr bond is replaced by an Fe-Fe bond. For this reason we have plotted in Fig. 4 the dissociation energy, as given by the difference of the complete-exchange and direct-exchange curves in Fig. 2, in comparison to the bond-breaking energy, as defined by 1/4 of the segregation energy. The close agreement supports the simple bond-counting picture.

In summary we have performed *ab initio* studies for the energetic behavior of 3d impurities on the Fe(001) surface. Using the local density approximation and the KKR-Green's function method we calculated the energy gain for the exchange process, the interaction of the impurities within the first layer and the surface segregation energies. The surprising result of our calculations is that with the exception of Co all 3d impurities prefer the surface position to the adatom one. Our results for Cr/Fe(001) are in excellent agreement with recent STM studies, showing the stability of the surface configuration, the strong repulsion of NN pairs, weak repulsion of NNN pairs, and a nearly vanishing surface segregation energy. For the other impurities we predict interesting trends: for V and Mn the incorporation into the surface layer, equally strong repulsion of NN pairs as for Cr, but contrary to Cr weak attraction of NNN pairs, a nearly vanishing segregation energy for V, but a moderate segregation energy for

Mn. A Co impurity behaves energetically very much like an Fe atom. On the other hand for Ni and Cu impurities the surface position should be more stable; first neighbors in the surface repel each other, while second neighbors are weakly repulsive for Ni and attractive in the case of Cu. Both Ni and Cu show a strong tendency for surface segregation. We hope that the present calculations encourage further experimental studies of these systems.

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