Segregation in Strongly Ordering Compounds: A Key Role of Constitutional Defects

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For the example of the *B*2 CoAl(100) surface, we demonstrate that even slight deviations from an ordered alloy's ideal stoichiometry in a subsurface region or in the bulk can drastically affect its surface composition. By experimental surface analysis and first-principles calculations, we show that Co antisite atoms segregate to the very surface, driven by the same strong interactions which enforce order in the bulk. Our findings are consistent with the lack of antisite segregation we found earlier for the much weaker ordering FeAl(100), and resolve contradictory reports for NiAl(100).

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The versatility of metallic alloys in everyday applications is due to the easy manipulability of their chemical composition. Often, very small chemical modifications can influence material properties drastically, their effect being mediated by small, localized regions of reduced dimension: free surfaces for catalysis and corrosion, grain boundaries for fracture, and dislocations and small precipitates for plastic deformation. So, even minor alloying additions may reach the macroscopic world by affecting such a localized region through segregation—the enrichment of one component at a free surface or interface.

In the present paper, we address the issue of surface segregation in ordering alloys, which are frequently encountered as candidates for high-temperature structural applications. *Both* by experiments and first-principles calculations, we show that small deviations from the ideal stoichiometry in an extended region below the surface or in the bulk can crucially shape surface segregation in these materials—completely unlike the behavior of more often studied disordered alloys. Our findings receive additional support from recent theoretical work by Ruban for fcc Ni_3Al and Pt_3Fe, based on coherent potential calculations in the approximation of geometrically unrelaxed lattices [1].

To demonstrate the effect, we concentrate on the (100) surface of the strongly ordering alloy CoAl, which crystallizes in the *B*2 (or, equivalently, CsCl-type) structure, and compare it to the same surface orientation of the isostructural, less or similar strongly ordering alloys FeAl and NiAl, respectively. We show that strong ordering causes structural defects—which exist below the surface or in the bulk due to some slight deviation from the ideal stoichiometry—to segregate to the surface (or to an interface). Paradoxically, this means that the surface composition of an ordered alloy may be least well-defined just near the bulk's ideal composition, because the dominant structural defect type changes here. This effect is fundamental for our understanding of the surface and interface physics of ordering alloys, and also of considerable practical importance, as no real sample will have ideal stoichiometry.

Experimentally, we apply quantitative low-energy electron diffraction (LEED), i.e., the measurement and full multiple-scattering analysis of intensity vs energy spectra, $I(E)$, to retrieve the surface geometrical and chemical structure of CoAl(100) [for FeAl(100) and NiAl(100), published results are available [2–9]]. For the measurement, a computer controlled video method was applied [10]. Model intensity calculations were performed using the Tensor LEED method for the easy variation of geometrical, chemical, and vibrational parameters [10,11] as implemented in the TensErLEED package [12]. The latter includes a structural search [13] which is guided by Pendry's reliability factor, R_P [14], to quantify the comparison of experimental and calculated spectra. Its variance, var(R_P) [14], is used to estimate error limits for the parameters determined. On the theory side, first-principles results were obtained by applying density functional theory (DFT) in the generalized-gradient approximation (GGA) [15] including spin polarization. Ultrasoft pseudopotentials were used for the fast solution of the Kohn-Sham equations by means of the VASP computer code [16]. As a test of accuracy for this approach, the formation enthalpies of bulk CoAl, FeAl, and NiAl were calculated (-570, -300, and -660 meV/atom). They compare favorably to the respective experimental values (-550 [17], -260 [18], and -640 meV/atom [19]).

In order to determine the surface segregation of subsurface defects, one must either know that there are intrinsic defects in the bulk due to some deviation from the ideal stoichiometry or one can create such defects below the surface and follow their segregation behavior upon annealing. We chose the second strategy as our CoAl sample was nominally stoichiometric and there was no safe knowledge whether possible small deviations in the bulk were in favor of Co or Al. After routine cleaning of the sample by cycles of 1 keV Ne^+ ion sputtering at room temperature, a contamination-free surface was ascertained by Auger electron spectroscopy. As the sputtering is preferential with respect to Al, a Co-enriched surface slab of some nm thickness resulted. To disperse the Co antisite atoms to an extended region below the surface (or to the bulk), the sample was annealed at rather high temperatures, yet not above 1300 K where Al evaporation sets in. This procedure resulted in a clear (1×1) LEED pattern with sharp integer order spots. Additionally, there were some weak and diffuse centered intensities indicative of some lateral short-range order. $I(E)$ spectra were recorded at normal incidence of the primary beam, and the sample cooled to liquid nitrogen temperature. A data set taken after annealing at about 1200 K was effectively indistinguishable from another taken after annealing at about 1300 K. It covers seven symmetrically inequivalent beams between 20 and 500 eV, yielding a total data base width of 1890 eV.

For the structural-chemical evaluation of the spectra two possible surface terminations (or mixtures of them) must be considered, as, in (100) orientation, an ideal $B2$ CoAl crystal consists of alternating planes of Co and Al. Yet, also for a single type termination one has to check for off-stoichiometry, e.g., for Co antisite atoms in an Al layer which might cause the diffuse intensities observed. Next, atomic vibrations must be taken into account as they modify the elemental scattering strength and characteristics (the features by which quantitative LEED differentiates between Al and Co). Finally, the intensity analysis has to allow for the relaxation of interlayer spacings off the bulk value ($d_0 = 1.43$ Å [20]). So, on the chemical side, the structural search included the basic surface termination and the chemical composition of the top four layers via their Al content x_i $(i = 1, \ldots, 4)$, modeled as laterally randomly distributed if not 0% or 100%. Isotropic vibrational amplitudes were treated as independent parameters for Al and Co in the top layer but assumed to have a common value in the second. In the bulk, the amplitude was kept fixed at $u_b = 0.09$ Å at 100 K as found in an earlier analysis of CoAl(110) [21]. On the geometry side, the top four interlayer spacings $d_{i,i+1}$ were varied. In the very first layer, the vertical coordinates of Al and Co were allowed to differ, described by the parameter $\Delta h_1^{\text{Co-Al}}$.

Using this total of 12 model parameters, an outstandingly good best fit between calculated and experimental data resulted, reflected by an R-factor $R_P = 0.075$ with var(P) $= 0.011$. A Co-type termination can be clearly ruled out. The result of the LEED analysis, visualized in Fig. 1(a), is summarized in Table I. Its key feature is a large amount of Co atoms (30 ± 7%) on the nominal Al sublattice in the topmost plane—a substantial concentration of Co "antisite defects." Evidently, they are confined to the outermost planes; i.e., they must be due to a generic surface effect: the second and third layers show much less disorder, and no deviation from bulk order and geometry is detectable below (reperforming the LEED fit with the fifth layer included shows its composition and position to be bulklike).

We emphasize that allowing for this stoichiometric variation of the surface layers is essential to reach the above fit quality. With the layerwise Al concentrations fixed at the ideal bulk values (100% or 0%), the R factor nearly doubles ($R_P = 0.129$). Even more disturbingly, the vibrational amplitude in the top layer then results at an unreasonably high value (0.23 Å), much higher than for the full fit (0.17 Å/0.16 Å for Co/Al), and above the bulk value (0.09 Å) by a factor > 2.5, a relation to our knowledge never observed in a surface. Instead, the factor <2 for the actual best fit seems much more plausible—it is within the usual range [22], and possibly accounts also for some static displacements typical for chemically disordered layers.

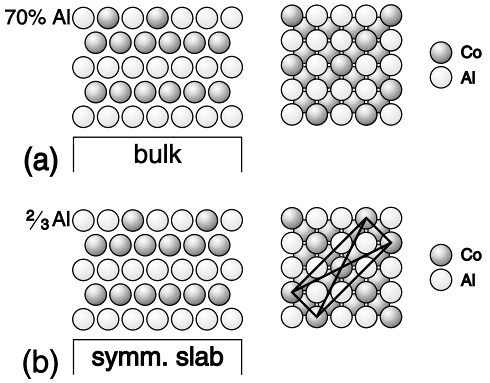

FIG. 1. Side and top views of (a) the best fit structure and composition of CoAl(100) assuming random distributions of atoms within layers, and (b) the ordered model slab used to simulate top layer antisites in first-principles calculations.

Our result is further supported by comparing the LEED best-fit geometry of Table I with first-principles calculations. Since the latter is restricted to ordered atomic arrangements, a structure as close as possible to the actual composition and short-range order of the surface must be assumed for a meaningful comparison to LEED. Regarding short-range order, the observed centered diffuse intensities are compatible with both $c(2 \times 2)$- or $c(\sqrt{2} \times 3\sqrt{2})$-like top layer site occupations. With

TABLE I. Results of the LEED and DFT analysis of CoAl(100). The concentration weighted average is given for d_{12}. LEED error limits are at the parameter values for which the variance level [R_P + var(P)] is crossed [14]. No significant subsurface rippling (technically allowed due to the assumed order) was found in DFT.

	LEED	DFT-GGA
d_0 [Å]	1.43 (fix)	1.427
d_{12} [Å]	1.38 ± 0.02	1.385
d_{23} [Å]	1.46 ± 0.02	1.424
d_{34} [Å]	1.42 ± 0.01	1.438
d_{45} [Å]	1.43 ± 0.01	1.424
$\Delta h_1^{\text{Co-Al}}$ [Å]	0.08 ± 0.02	0.027
x_1 [at.% Al]	70 ± 5	67 (fix)
x_2 [at.% Al]	10 ± 8	0 (fix)
x_3 [at.% Al]	85 ± 5	100 (fix)
x_4 [at.% Al]	0 ± 7	0 (fix)

2:1 stoichiometry, the latter order type is better suited, and a layer of this type atop a $B2$-ordered stacking sequence was chosen as the DFT model [Fig. 1(b)]. Bearing this approximation in mind, the DFT geometry (Table I, right column) agrees quite well with LEED. The relaxation is the same within 2% of the bulk spacing d_0 (which is quantitatively reproduced by DFT), and both methods find an outward displacement of top layer Co with respect to Al atoms ($\Delta h_1^{\text{Co-Al}} > 0$).

In total, the available evidence forces us to accept a substitutionally disordered surface plane in CoAl(100). At a first glance, it might appear that this is simply an artificial nonequilibrium residuum of the initial sputtering process in which such antisite atoms were created. However, the comparison to a FeAl(100) surface, which had undergone the same treatment with respect to sputtering and subsequent annealing, tells a different story [2,23]: There, the initially created defects disappeared at much lower annealing temperatures, obviously dissolving into an extended region below the surface (or the bulk). The very surface consisted of a *pure* Al layer even though the bulk itself was significantly Fe enriched (6% Fe antisites). Moreover, Refs. [2,23] show that there is always local equilibrium between the very top layer and the near-surface region below during the annealing process of FeAl. In other words, the transition-metal (TM) enriched surface slab is structurally well ordered long before full compositional equilibrium with the bulk is attained, with its structure strictly dictated by the phase diagram for its momentary average stoichiometry.

From this we conclude that the detected significant defect accumulation in the top layer of CoAl(100) must also be in equilibrium with the underlying, extended near-surface region—even if this contains only a tiny concentration of antisite atoms $0 < \epsilon \ll 0.5$, corresponding to an alloy $\text{Co}_{0.5+\epsilon}\text{Al}_{0.5-\epsilon}$. In equilibrium, there are two possible explanations for the top layer enrichment with Co antisite defects: their creation right there, or their segregation from a slightly Co-enriched region below. However, in bulk CoAl, the creation of a Co antisite atom is known to cost approximately 1.29 eV [24]. Even for the significantly modified environment of a surface atom, a drastic change of this balance seems quite improbable (indeed, we shall prove this below). However, the segregation of *existing* Co antisite atoms to the Al surface plane could indeed be favorable. Since a (100) surface site lacks four nearest neighbors (nn) compared to the bulk, antisite atom segregation would effectively replace four unfavorable Co-Co nn pairs with four favorable Co-Al ones. If this is more favorable than any potentially opposing surface energetics, antisite atoms must indeed segregate to the surface in thermal equilibrium. In total, our structural result can be understood naturally as the equilibrium termination of a slightly Co-enriched $B2$ $\text{Co}_{0.5+\epsilon}\text{Al}_{0.5-\epsilon}(100)$ region below the very surface. Of course, the same arguments also hold for the case that the slightly Co-enriched subsurface region is the sample's bulk. Indeed, we have no knowledge about a slight off-stoichiometry in the bulk of our CoAl sample, and cannot exclude that segregation from the bulk adds to that from the subsurface region.

Although the argument above is made for the case of CoAl(100), its scope is probably more general, in line with recent theoretical work by Ruban [1]. Obviously, no real ordered alloy will ever be *exactly* stoichiometric—characteristic "constitutional defects" must always exist (here Co antisite defects for Co-rich, and Co vacancies for Al-rich CoAl samples). However, the stronger an alloy's ordering tendency, the less favorable is the placement of structural defects in the bulk—their segregation could result. As a consequence, *the surface termination of an ordered alloy is not necessarily defined by the ideally ordered compound, but can be dominated by minor subsurface or bulk deviations from its ideal composition.* In a way, the topmost layer acts as a "magnifying glass" for subsurface or bulk defects.

For further support, a look at the closely related system NiAl(100) is quite rewarding. This surface has been the subject of numerous studies [4–9], all claiming to investigate the nominally stoichiometric compound, and finding a complex development of the surface composition with annealing. However, different groups arrive at contradictory and mutually exclusive results for the high-temperature annealed surface. These include a complete Al termination [5], a termination by a mixed Al-rich layer [4,6], and even a bulklike Ni termination without [7] or with [9] vacancies. Obviously, an interpretation analogous to ours for CoAl(100) offers a convenient resolution for this situation: If antisite atoms showed a tendency to segregate in NiAl(100), different authors might not actually have been looking at a state characteristic for the exactly stoichiometric NiAl(100) surface. Indeed, as noted above, such a state might not even be strictly well defined at all. The contradictory observations are then the result of slightly different levels of off-stoichiometry in the near-surface region or bulk, being below the detection limit of the techniques used.

It can be only the above-described energetics which set CoAl and NiAl apart from FeAl with respect to defect accumulation at their (100) surfaces. Even in $\text{Fe}_{0.53}\text{Al}_{0.47}(100)$, with a substantial amount of antisite atoms in the bulk, the surface is terminated by a pure Al layer [2,3]. One may handwavingly interpret this difference between three outwardly so similar surfaces as already outlined for CoAl(100), by separating the segregation energetics into two qualitatively different terms. First, there is the bond energy change between nearest and possible higher neighbors: The segregation of a TM antisite replaces four TM-TM nn pairs by four TM-Al ones, which must be a favorable process in any $B2$-ordering material. Second, a persistent trend of TM-Al surfaces to terminate with Al is observed in many systems. The responsible energy contribution need not depend on any bonds, but primarily on the atoms' location in the topmost plane. As given above, the formation of bulk FeAl, CoAl, and NiAl is clearly exothermic with enthalpies $\Delta H_f < 0$, but while the values for CoAl and NiAl are similar, they are approximately twice as large as that for FeAl. Assuming that ΔH_f is roughly proportional to the nn bond energy in these systems, it follows that the driving force for ordering in FeAl is weaker than in CoAl or NiAl (also, off-stoichiometric $B2$ Fe-Al shows a $B2$-$A2$ order-disorder transition, while $B2$ CoAl and NiAl do not [20]). Thus, the inherent Al termination term may win over antisite atom segregation in FeAl(100), but succumb in the stronger ordering cases CoAl(100) and NiAl(100).

So far, we have presented a consistent but qualitative model to explain the behavior of CoAl(100) and NiAl(100) vs that of FeAl(100). In order to definitely prove its validity, we have calculated the segregation energy $E_{\mathrm{seg}}^{\mathrm{TM-AS}}$ of a bulk TM antisite to an Al-terminated (100) surface plane for the three materials from first principles. Here $E_{\mathrm{seg}}^{\mathrm{TM\text{-}AS}}$ is the energy difference when exchanging a surface Al atom with a bulk TM antisite atom. As before, surface TM antisites were modeled by the ordered slab of Fig. 1(b). The bulk TM antisite atom energy was calculated for an isolated defect in a 54-atom supercell, analogous to Ref. [24]. The agreement of the results with our postulate above is convincing: For CoAl(100) [NiAl(100)], $E_{\mathrm{seg}}^{\mathrm{TM\text{-}AS}} = -0.85$ eV (-0.61 eV) shows that defect segregation is accompanied by an energy gain so much larger than thermal energy (also for the annealing temperatures used) that even a TM excess well below 1% should drastically influence the surface's stoichiometry when equilibrium is achieved. In contrast, $E_{\mathrm{seg}}^{\mathrm{TM\text{-}AS}} = +0.05$ eV results for FeAl(100), i.e., Fe antisite segregation *costs* energy and is hence prohibited. A pure Al termination must therefore prevail even for $\mathrm{Fe}_{0.5+x}\mathrm{Al}_{0.5-x}(100)$, i.e., in the presence of a noticeable Fe excess ($x > 0$), in reassuring unison with the experimental situation [2,3].

As a side effect, the calulated segregation energy definitely proves our interpretation of the LEED result for CoAl(100): Not only *could* the observed surface termination exist on a slightly Co-enriched region below, but there is, in fact, *no other way* to explain its appearance. For even though $E_{\mathrm{seg}}^{\mathrm{TM\text{-}AS}}$ is large, it is not large enough to initiate the *creation* of a TM antisite in a fully stoichiometric bulk ($E_{\mathrm{bulk}}^{\mathrm{AS}} = 1.29$ eV for CoAl according to Ref. [24]), or even an Al-rich sample.

In conclusion, we have shown that it is the presence of even only slight subsurface or bulk off-stoichiometries, and not the ideal stoichiometric properties of the ordered material, which determines the surface composition of CoAl(100). This realization naturally explains the pronounced Co antisite atom population localized in the topmost plane of this strongly ordering compound. The concept of *antisite atom segregation* allows us to place the three related systems FeAl(100), CoAl(100), and NiAl(100) in one consistent picture, and offers a resolution for the contradictory observations for NiAl(100) in the literature. The latter now appears as a consequence of different and very slight off-stoichiometries in the samples used by the various authors. At least for strongly ordering alloys, the surface composition may hinge on ever so slight deviations from the ideal stoichiometry, where it may be least well-defined as the dominant defect type changes sharply. Although it depends on the exact balance of bulk and surface ordering forces, this scenario could affect many related systems.

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