Surface Segregation-Induced Critical Phenomena at FeCo(001) Surfaces

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We present an x-ray scattering study of the continuous $B2$-$A2$ order-disorder transition in semi-infinite FeCo using synchrotron radiation, which gives access to the weak one-electron contrast associated with the $B2$ ordering phenomena in this alloy. The asymptotic (001) Bragg scattering profiles disclose an oscillating Fe-Co layering profile, which alters the surface critical phenomena in a characteristic way: The surface-related order parameter persists above the bulk critical temperature and exhibits a temperature dependence which provides unambiguous evidence for the existence of a surface field (h_1) which couples to the surface susceptibility. [S0031-9007(97)03171-2]

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The influence of the presence of a surface upon bulk critical behavior has been the focus of scientific interest during the last decade [1,2]. Since the free surface is the omnipresent natural break of the translational symmetry in any real system, the proper understanding of criticality in so-called semi-infinite matter is one current milestone in the attempt to master critical behavior in nonideal materials. Modern theories predict novel universality classes to emerge in the presence of a surface which depends on only one additional scaling field, the enhancement (g) of the surface interactions with respect to the bulk [3]: For $g < 0$ (i.e., reduced surface interactions) the *ordinary transition* occurs with the surface being less ordered than the bulk, for $g > 0$ (i.e., enhanced surface interactions) the *extraordinary transition* characterized by a surface that favors the ordered state. The latter case is particularly interesting for temperatures above the bulk critical temperature (T_c), since a mesoscopic surface layer with critical order (ψ_s) emerges which floats on a disordered bulk [4]. At a new surface critical temperature $T_s > T_c$ this surface layer undergoes a 2D phase transition to the disordered state, accordingly, $\psi_s = t^{\beta_s(2d)}$ with $t_s = (T_s - T)/T_s$ and $\beta^{(2d)} = 0.125$. In this Letter we present an x-ray scattering study of semi-infinite FeCo(001) and give, indeed, experimental evidence for a partially ordered surface layer above T_c. We demonstrate, however, that the critical behavior of this surface layer is not induced by enhanced surface couplings ("$g > 0$") but by surface segregation, which causes a completely different surface critical behavior.

The experimental search for surface segregation-induced critical phenomena has been inspired by the experimental findings from the (noncritical) $Cu_3Au(001)$ surface, which shows an oscillating Au surface segregation profile [5]. As a promising candidate appeared the binary alloy FeCo, which undergoes a continuous order disorder transition from the $B2$ (CsCl) structure to the $A2$ (bcc) structure in a wide composition range (40–60 at. % Co) [6] with critical temperatures around $T_c \approx 900$–1000 K [7]. Normal to the FeCo(001) surface the $B2$ structure is composed of alternating layers belonging to sublattice 1 or 2, which are occupied by turns with Fe and Co [Fig. 1(a)]. Consider now $T > T_c$ (bulk disorder): Since the internal interactions favor Fe-Co nearest neighbor pairs, any surface segregation of either Fe or Co at the topmost (001) layer should cause the subsequent layers to be alternatingly occupied by the other species and to generate by this a surface-bound oscillating sublattice profile which is just equivalent to a nonzero surface order [Fig. 1(b)]. Surface phenomena associated with the $B2$-$A2$ order-disorder transition have been considered recently by Monte Carlo simulations [8] and in a field-theoretical study [9]. Both theories consider, in particular, the (001) surface, which breaks the symmetry between the two sublattices, and conclude that surface segregation can give rise to a so-called surface field h_1, which stabilizes order parameter profiles as shown in Fig. 1(b) for the two cases $T < T_c$ (dashed line) and $T > T_c$ (full line). Note, in particular, that again a surface order ψ_s emerges above T_c as in the aforementioned case of enhanced surface couplings; however, it should exhibit a smeared temperature dependence in analogy to the familiar behavior of a bulk magnetization in the presence of an external bulk field [Fig. 1(c)], thus, in linear response, $\psi_s(t, h_1) = \psi_s(t) + (\partial\psi_1/\partial h_1)h_1$ with $\psi_1(t)$ as the spontaneous order and with $\partial\psi_1/\partial h_1 = \chi_{11} = t^{-\gamma_{11}}$ as the surface susceptibility [$t = (T_c - T)/T_c$] [1]. Consequently, the associated surface Bragg intensity should show the leading temperature dependence

$$S(0, t) = 1 - t^{-\gamma_{11}} \quad (1)$$

for $T > T_c$ with $\gamma_{11} = -0.33$ (in the ordinary case) [1,2,10]. This scenario is in clear contrast to the 2D behavior in the case of enhanced surface couplings (mentioned in the introduction), which implies

$$S(0, t_s) = t_s^{2\beta^{(2d)}}. \quad (2)$$

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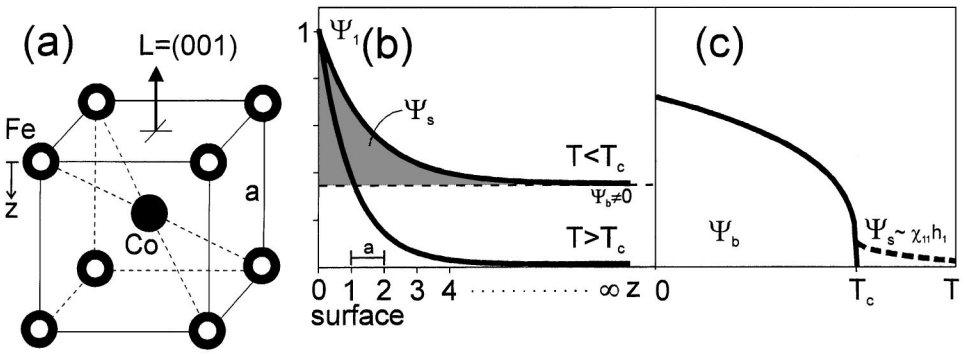

FIG. 1. (a) Structure of ordered FeCo and the (01) surface. (b) Order parameter profiles associated with surface-enhanced order for $T < T_c$ and $T > T_c$. (c) Schematic temperature dependence of the bulk and surface order in the presence of a surface field h_1,

Interestingly, there is a current theoretical controversy whether or not a nonzero h_1 field does evoke extraordinary critical behavior [8,11–14]; thus, it was also one of the aims of this x-ray study to shed light onto the role of the h_1 field onto critical behavior in semi-infinite matter.

Figure 2(a) shows the reciprocal lattice of semi-infinite FeCo(001) including bulk $A2$ ("bcc") reflections (full symbols) and bulk $B2$ ("CsCl") superlattice reflections (small open circles), which are absent in the disordered bcc phase. In the presence of the (001) surface asymptotic Bragg rods emerge (dashed lines) which contain the information on surface-related structures, as here on eventually present surface order profiles depicted in Fig. 1(b). The associated asymptotic (00L) Bragg rod is given by

$$S(L,t) \propto \left| \int_0^\infty dz\, \psi(z,t) e^{iLz} \right|^2 . \qquad (3)$$

Figure 2(b) shows numerical calculations of Eq. (3) along (00L) for the order parameter profiles in Fig. 1(b): For $T < T_c$ the Bragg scattering is dominated by the δ-function contribution from the nonzero bulk order parameter ψ_b, while for $T > T_c$ the remaining surface order ψ_s, which decays exponentially versus depth, generates a broad feature around $L = 1$, which should readily be observable in an x-ray scattering experiment as a direct evidence of surface order.

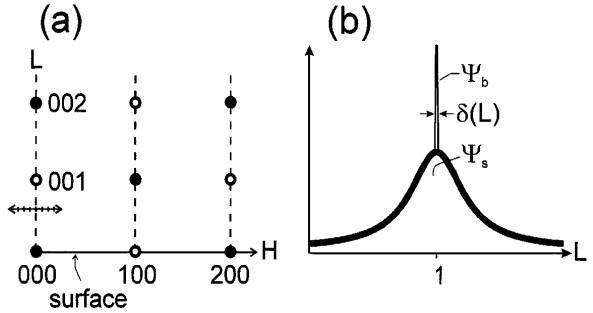

FIG. 2. (a) Reciprocal map of FeCo including bcc points (full symbols) and superlattice points (open symbols); the dashed vertical lines indicate the asymptotic Bragg scattering from the free (001) surface; (b) asymptotic Bragg intensity along $L = (001)$ in the case of surface-enhanced order [see Fig. 1(b) and main text].

When growing FeCo from the liquid phase it undergoes a martensitic fcc-bcc transition at $T = 1200$ K, thereby destroying any useful single crystal quality. In this study a 1 μm thick $Fe_{44}Co_{56}$ single crystal has been MBE-grown on a MgO(001) substrate kept at $T = 520$ K and then annealed at $T = 1050$ K (safely below the fcc-bcc transition) for 24 hours in UHV. Subsequent LEED and Auger analysis revealed a well-ordered and atomically clean single crystal surface. The fundamental Bragg reflections exhibited a small inplane and out-of-plane mosaicity of less than 0.04° and 0.06°, respectively. The surface roughness was $\sigma = (2.5 \pm 0.5)$ Å. For the x-ray studies the sample has been transferred into a portable UHV chamber which enables a 360° x-ray access through a Be window and a control of the sample temperature with a relative accuracy of ± 0.02 K by a W-Re thermocouple. The absolute surface temperature was measured in addition by a pyrometer (± 0.5 K). The x-ray scattering study has been performed at the TROIKA beamline of the ESRF. Note here that ordering phenomena in FeCo produce only very weak x-ray scattering signals associated with the one-electron x-ray contrast $|f_{\mathrm{Fe}} - f_{\mathrm{Co}}|^2$ between Fe and Co (f_{Fe} and f_{Co} being the atom form factors). The experiments have been carried out using a wavelength of $\lambda = 0.8$ Å (a 100 μm Al foil was used in front of the detector to remove the Fe and Co fluorescence background). We performed detailed H and L scans at the (001) and (100) reciprocal lattice points [see Fig. 2(a)] in a temperature range between $T = 870$ K ($= T_c - 45$ K) and $T = 940$ K ($= T_c + 25$ K).

Figure 3 shows some typical asymptotic Bragg profiles around (001) versus L for $T < T_c$ and $T > T_c$. At various L positions an H scan has been performed. The inset depicts by way of example a typical H scan as observed for $L = 0.98$ [$T = T_c + 0.7$ K; see arrows in Figs. 2(a) and 3], displaying the inplane δ function of the Bragg rod and diffuse scattering, which has been subtracted in order to obtain the shown L profiles. For $T < T_c$ the asymptotic Bragg profiles are composed of a Gaussian contribution generated by bulk long range order and a surface-related broader component, which does not disappear for $T > T_c$ but clearly persists above the order-disorder tran-

sition as direct evidence of the presence of an ordered surface sheet. The temperature dependence of the Gaussian contribution in Fig. 3 is shown in Fig. 4(a) (full symbols) and can be used as a reference for the critical behavior of the bulk superlattice intensity $I_{\text{bulk}} \propto t^{2\beta}$, providing the bulk critical temperature to be $T_c = 919.5 \pm 0.5$ K and the bulk critical exponent to be $\beta = 0.307 \pm 0.10$ [inset in Fig. 4(a)] in excellent agreement with theoretical expectation ($\beta = 0.315$) and with neutron diffraction work from FeCo powder ($\beta = 0.31 \pm 0.01$) [7].

The first key observation is the temperature dependence of the broad (surface-related) intensity component in Fig. 3, which is shown in Fig. 4(b) for $T > T_c$. It exhibits a smooth concave decay until it reaches a very small, temperature independent value at approximately $T_c + 4.5$ K. The dashed curve has been calculated under the assumption that the observed surface order undergoes a new surface (2D) phase transition located at $T_s = T_c + 4.0$ K [Eq. (2)] the predicted convex shape is clearly not in agreement with our observation. The dash-dotted line, on the other hand, which has been obtained using the h_1 field model [Eq. (1)] gives an almost perfect match with the data. The observed temperature dependence of the surface-related order for $T > T_c$ is, thus, in complete agreement with the presence for a nonzero h_1 field clearly excludes the possibility that enhanced surface couplings ($g > 0$) are the agents of the observed surface order. We argue in what follows that the driving surface field h_1 is mediated by a surface segregation of Fe at the (001) top layer.

The information on the surface segregation and on the depth profile of the associated surface-bound order results from a detailed analysis of the broad L components in Fig. 3. Interestingly, they exhibit an unusual double-peak structure which can be understood within the following model: We assume an exponentially decaying order parameter profile

$$\psi(z_n, t) = \psi_b(t) + \psi_1 e^{-z_n/\xi_s} \tag{4a}$$

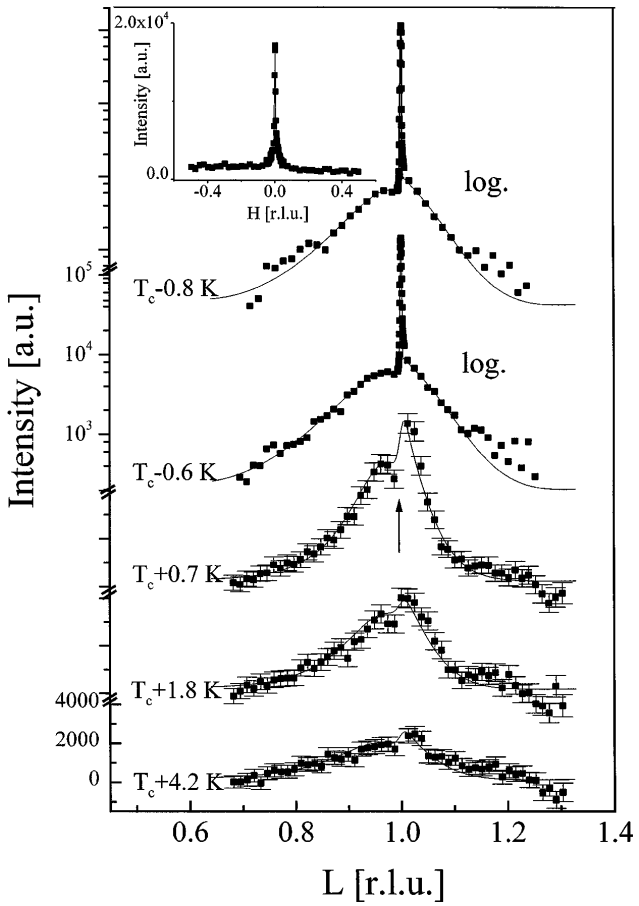

FIG. 3. Selected asymptotic Bragg profiles along $L = (001)$ as observed at various temperatures below and above T_c. The two upper curves ($T < T_c$) are shown on a logarithmic scale. The full lines are theoretical curves (see main text). The inset shows a typical H profile as obtained at $L = 0.98$ for $T = T_c + 0.7$ K (arrow). Within our experimental resolution the width of the H Gaussian is L independent.

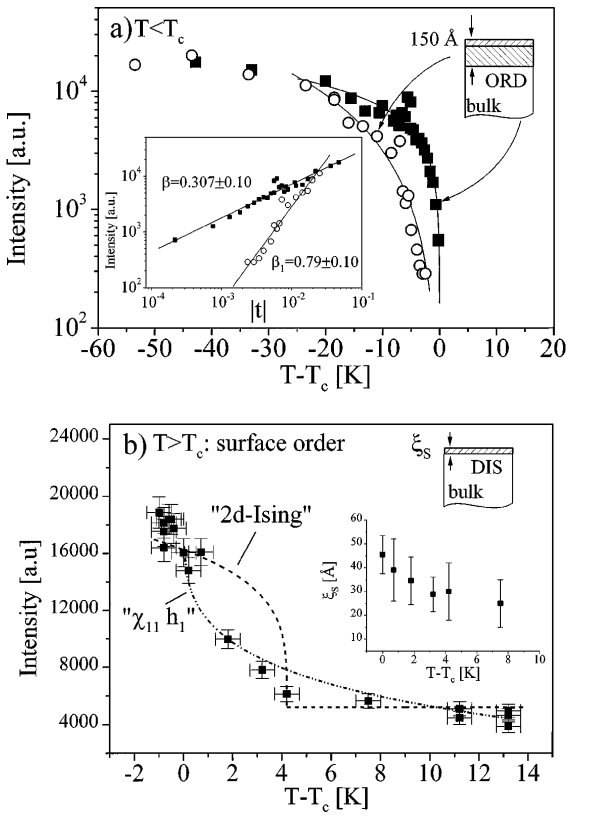

FIG. 4. (a) Temperature dependence of the order-related superlattice intensity for $T < T_c$: bulk intensity (full symbols), near-surface (evanescent) intensity (open symbols). The inset shows the associated double logarithimic plots versus reduced temperature t disclosing the power-law exponents $\beta = 0.307 \pm 0.10$ (bulk) and $\beta_1 = 0.79 \pm 0.10$ (near surface). (b) Temperature dependence of the asymptotic superlattice intensity for $T > T_c$: The dashed curve ("2D-Ising") calculated according Eq. (2), the dash-dotted curve ("$\chi_{11} h_1$") according Eq. (1). The inset shows the temperature dependence of decay length ξ_s within the ordered surface sheet close to T_c.

$(n = 0, 1, 2, \ldots)$ which is superimposed by an oscillating surface relaxation

$$z_n - z_{n-1} = a - \Delta a(-1)^n e^{-na/\xi_r} \qquad (4b)$$

with $2a = 2.86$ Å as the bulk lattice constant, Δa as the surface relaxation amplitude, and ξ_s and ξ_r as the decay lengths for the surface-bound order and surface relaxation, respectively. The resulting rod intensity follows by inserting (4) into (3) using Δa, ξ_s, and ξ_r as free fitting parameters. The full lines in Fig. 3 are least square fits to the data implying that Fe is enriched at the FeCo(001) surface (in agreement with complementary AUGER spectroscopy measurements) accompanied by a surface contraction of the first layer (with $\xi_2 \approx a$) [15]. The decay length ξ_s [see inset Fig. 4(b)] turns out to be strongly temperature dependent close to T_c with a mesosocopic size around 30–50 Å, which is typical for critical phenomena in the investigated temperature range.

A further key observation is the temperature dependence of the near-surface order for $T < T_c$: The associated Bragg scattering is directly accessible by evanescent x-ray diffraction [2], since it eliminates the strong bulk contribution for $T < T_c$ which dominates the scattering in Fig. 3 and allows us to integrate over a large surface regime. We investigated the temperature dependence of the inplane (100) superlattice reflection at an incidence angle $\alpha_i = 0.8\alpha_c$ (α_c is the critical angle for total external reflection) and exit angles $\alpha_f = 1.2\alpha_c$ resulting in an escape depth of the evanescent wave field of 150 Å [2]. The open symbols in Fig. 4(a) show the observed integrated intensity of this evanescent one-electron Bragg scattering versus temperature after correction for diffusion scattering background. For $T > T_c - 20$ K we find that the critical order parameter in the mesosocopic surface layer (150 Å depth) is well described by a power-law behavior $S \propto t^{2\beta_1}$ governed by a critical exponent $\beta_1 = 0.79 \pm 0.10$ which is well known in semi-infinite critical matter and characteristic for the ordinary universality class. Apparently the surface-segregation phenomena, which dominate a surface layer of thickness $\xi_s = 30$–40 Å and give rise to surface ordering above T_c are not strong enough to change the ordinary behavior in larger depth range and within the temperature range of this study. These findings are, in fact, in good agreement with the Monte Carlo simulations [8] and with the ideas developed in [9] and [13]. The asymptotic extraordinary behavior, however, which is predicted for semi-infinite alloys exposed to h_1 fields [9], has so far not been found in this study, thus, we think it can only occur at FeCo(001) within a narrow temperature window of 0.5 K around T_c.

In summary, we have performed a bulk and surface-sensitive x-ray scattering study of the order-disorder transition a FeCo(001) and showed that surface segregation evokes a mesoscopically thick surface sheet with critical order which persists above the bulk critical temperature. The temperature dependence of this surface order resembles the behavior of a magnet exposed to an external field in support of recent theoretical suggestions that surface segregation at alloy surfaces which break the sublattice symmetry [as here the (001) surface] should evoke a surface field h_1 which alters critical phenomena in semi-infinite matter. From the critical temperature dependence of the evanescent (100) superlattice diffraction it is concluded that the local order parameter within a 150 Å surface sheet belongs to the ordinary universality class. One may speculate whether a crossover to extraordinary behavior may occur very close to T_c. For a further experimental test of these ideas we are currently preparing experiments at FeCo(011) surfaces, which should, be symmetry, not allow surface order above T_c [9], and at $Fe_{0.5}Al_{0.5}$(001) surfaces, which should exhibit strong Al surface segregation.

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