Surface magnetism in the strongly correlated Hubbard model

M. Potthoff and W. Nolting
Humboldt-Universität zu Berlin, Institut für Physik, Invalidenstrasse 110, 10115 Berlin, Germany
(Received 5 September 1996)

A generalization of a self-consistent moment method is applied to the semi-infinite Hubbard model for the (100) surface of a bcc crystal. Using this method, surface magnetism in the strongly correlated Hubbard model is investigated. We find the top-layer magnetization to be always strongly enhanced. Varying the average band occupation, a phase transition between ferromagnetic and antiferromagnetic order is observed which is confined to the very surface. Below a critical occupation, an antiferromagnetic surface can coexist with a paramagnetic bulk.

Collective magnetism of itinerant valence electrons poses a long-standing problem in solid-state physics. Although much is known about three-dimensional systems, many aspects remain to be understood in systems of low dimensionality. Among them the effects of surfaces on magnetic phase transitions have attracted considerable attention in the recent past. Experimental investigations have confirmed the prediction that a magnetically ordered surface can coexist with a paramagnetic bulk. The conditions for the existence of such a phase have been studied in detail within the semi-infinite Ising and Heisenberg model of free surfaces. The different approximation schemes applied all yield the same qualitative behavior: The coexistence of a magnetic surface with a paramagnetic bulk can only be obtained if the surface exchange interaction \( J_S \) is assumed to be different from the bulk coupling constant \( J \). Provided that \( J_S \) exceeds a certain critical value \( J_{S,c} \) in which turn is larger than \( J \), the moments at the surface order magnetically at temperatures \( T \) above the bulk Curie temperature.

While there is extensive work on these localized spin models, little is known about surface magnetism in the context of itinerant-electron models. This paper presents an investigation of itinerant surface magnetism within the strongly correlated Hubbard model.

The Ising and Heisenberg models have to be interpreted as effective models of magnetism where a ferromagnetic ground state is implemented by an ansatz. The models thus cannot contribute to the question of whether collective magnetic order confined to the surface of a single crystal is possible at temperature \( T=0 \). Within the Hubbard model, even at \( T=0 \), the possibility of spontaneous magnetism depends on a complex interplay between the on-site Coulomb interaction \( U \), the Pauli principle, the band-filling, and the local geometry. If at all, spontaneous magnetism should be likely in the strong-correlation regime \( U \gg W \) (\( W \) is the Bloch-band width). We thus intend a solution of the semi-infinite Hubbard model that is clearly beyond a mean-field approximation, which has been applied previously.

A change of the on-site Coulomb interaction at the surface \( U_S \) with respect to the bulk value \( U \) may be possible in any real system. In analogy with the localized spin models and guided by the simple Stoner criterion, an enhanced \( U_S>U \) in the semi-infinite Hubbard model is expected to imply a stronger tendency towards a magnetic surface. For the present study we tentatively assume \( U_S=U \). It turns out that even in this case a magnetically ordered surface can coexist with a nonmagnetic bulk.

For the semi-infinite Hubbard model we require an approximation scheme that on the one hand is simple enough to allow for a systematic study of magnetic phase transitions at surfaces and on the other hand still gives reliable results. The recent generalization of the standard spectral-density approach (SDA) to systems with reduced symmetry fulfills these requirements rather well. The main features of the approach are sketched briefly in the following; details can be found in Ref. 8.

Using standard notation, the Hubbard model for the semi-infinite crystal reads

\[
H = \sum_{ij\sigma} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \frac{1}{2} U \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}}.
\]

\( i \) and \( j \) refer to the sites of a semi-infinite lattice. The hopping integrals \( T_{ij} \) are assumed to be unchanged at the surface and nonzero up to nearest-neighbor distances. The energy zero will be chosen to coincide with the Fermi energy. The basic quantity to be calculated is the retarded one-electron Green function \( G_{ij\sigma}(E) = \langle \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle \rangle \). Its diagonal elements determine the spin-dependent local quasiparticle density of states (LDOS) \( \rho_{ij\sigma}(E) = -\text{Im} G_{ij\sigma}(E)/\pi \hbar \). The Green function fulfills the following equation of motion:

\[
\sum_k [E_{ik} - T_{ik} - M_{i\sigma}(E)] G_{kj\sigma}(E) = \hbar \delta_{ij}.
\]

Hereby, we have introduced the electronic self-energy \( M \) which incorporates all effects of electron correlations.

Our moment method essentially consists of two steps. Guided by the exactly solvable atomic limit of vanishing Bloch-band width \( W \) and by rigorous results for \( U/W \rightarrow \infty \) (cf. Ref. 9), a general local one-pole ansatz for the self-energy \( M_{ij\sigma}(E) \) can be motivated in the first step. Hereby, we restrict ourselves to the strong-correlation regime \( U/W \gg 1 \). In the second step all \( a \) priori unknown parameters in the ansatz are fixed by exploiting the equality between two alternative but exact representations for the moments of the LDOS:
\[
\frac{1}{\hbar} \int_{-\infty}^{\infty} E^n \rho_{12}(E) dE = \langle [L^n c_{1\sigma}, c_{1\sigma}^+ \rangle \rangle.
\]

Here, \([O, H]_m\) denotes the \(m\)-fold commutator of an operator \(O\) with \(H\) and \([\cdots, \cdots, \cdots]_+\) the anti-commutator. Taking into account the first four moments at each site, the tedious but straightforward calculation finally results in

\[
M_{ij\sigma}(E) = \frac{\delta_{ij} U \langle n_{i\sigma} \rangle (E - B_{ii\sigma})}{E - B_{ii\sigma} - U(1 - \langle n_{i\sigma} \rangle)}.
\]

It is decisive that the spin- and layer-dependent occupation numbers \(\langle n_{i\sigma} \rangle\) and the spin- and layer-dependent higher-order equal-time correlation functions \(B_{ii\sigma}\) can be calculated exactly from the LDOS in turn and can thus be determined self-consistently.\(^8\)

The advantages of the SDA rest on its clear concept and its nonperturbative character. On the other hand, a serious drawback consists in the neglect of lifetime effects. The SDA turns out to be essentially equivalent to the Roth method\(^{10,11}\) and the Mori-Zwanzig projection technique.\(^{12,13}\) For the usual three-dimensional Hubbard model the methods have proved their usefulness in a number of previous applications.\(^6,7\) Recently, comparisons have been performed\(^{11,13}\) with the results of an exact-diagonalization study\(^14\) and with quantum Monte Carlo simulations\(^15\) for the two- and one-dimensional Hubbard models. They prove that the \(\delta\)-like quasiparticle peaks as resulting from the SDA almost exactly recover the average density of the lower and upper Hubbard bands. Furthermore, the local ansatz for the self-energy has been justified for a band filling not too close to half-filling.\(^5,13\)

The energy dependence of the self-energy and the reduced translational symmetry of the system represent the main difficulties when solving the equation of motion (2). Here, we apply a straightforward generalization\(^8\) of the conventional real-space recursion method\(^16\) which is able to deal with the additional energy dependence in a computationally efficient way.

The numerical calculations have been performed for the \((100)\) surface of a bcc crystal which exhibits a comparatively small ratio between the coordination numbers of atoms at the very surface and in the bulk: \(z_{1}^{(S)}/z_{1}^{(B)} = 4/8\). Relatively strong surface effects can thus be expected.

The LDOS is calculated within the recursion scheme at the central atoms out of a finite cluster of sites which simulates the actual surface (cf. Ref. 4). The cluster LDOS is broadened by convoluting with a Lorentzian [full width at half maximum (FWHM) \(\Gamma = W/200\)] and a Gaussian profile (FWHM \(\alpha = W/20\)). For this choice \(N \approx 8000\) sites turn out to be sufficient for convergence of the results. The slight broadening has only minor effects on integral quantities such as the occupation numbers. This has been verified by varying \(\Gamma\) and \(\alpha\) and controlling the resulting self-consistent values for \(\langle n_{i\sigma} \rangle\) and \(B_{ii\sigma}\).

For the determination of the expectation values \(\langle n_{i\sigma} \rangle\) and \(B_{ii\sigma}\), we assume perfect translational symmetry within layers parallel to the surface. Up to \(L = 12\) inequivalent surface layers are necessary to ensure that \(\langle n_{i\sigma} \rangle\) and \(B_{ii\sigma}\) approach their bulk values smoothly.

**FIG. 1.** Spin-dependent local quasiparticle density of states (LDOS) and magnetizations \(m_i = \langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle\) for the first four layers from the surface and for the bulk. Layer 1 means the topmost surface layer. The energy zero is the Fermi energy.

Taking \(U = 3 W\) we consider a strongly correlated electron system. It turns out that the results only weakly depend on \(U\) as soon as \(U\) exceeds a critical value of about \(2W - 3W\). Therefore, the bulk band filling \(\langle n \rangle = \langle n_{\uparrow} \rangle + \langle n_{\downarrow} \rangle\) essentially remains as the only parameter to be varied.

Figure 1 shows the LDOS corresponding to a ferromagnetic solution at \(\langle n \rangle = 0.65\). For each surface layer and for the bulk the LDOS shows up a Hubbard satellite at energies around \(U\) above the Fermi level. The band shift \(B_{ii\sigma}\) is recognized to be decisive for the possibility of spontaneous magnetism: \(B_{ii\uparrow} \neq B_{ii\downarrow}\) induces an additional spin splitting of the respective lower and upper Hubbard parts for each LDOS. For the topmost layer, for example, we find \(B_{ii\uparrow} - B_{ii\downarrow} = 0.071 W\), while \(B_{ii\downarrow} - B_{ii\uparrow} = 0.018 W\) in the bulk. Generally, the LDOS of a certain surface layer is the more distorted compared with the bulk LDOS the nearer the layer is located to the surface. The LDOS of the 12th layer from the surface can no longer be distinguished from the bulk LDOS within numerical accuracy. A strong effective narrowing is seen in Fig. 1 for the LDOS of the topmost layer which is a consequence of the reduction of the coordination number of the top-layer sites. This results in a strongly enhanced magnetization of the top layer. Layer magnetizations different from the bulk magnetization are found for all surface layers shown in Fig. 1. We notice that the differences are not due to Stoner-like shifts of the respective spin-dependent LDOS, but due to a rearrangement of spectral weight.

The dependence of the layer magnetizations on the band occupation \(\langle n \rangle\) is consequently derived from the respective LDOS (see Fig. 2). We recognize that for the bulk there is a critical band occupation, \(\langle n \rangle_c = 0.57,17\) below which magnetic order is impossible. For \(\langle n \rangle > \langle n \rangle_c\) a ferromagnetic (FM) solution appears. The bulk magnetization \(m(\langle n \rangle)\)
FIG. 2. Layer magnetizations \( m_i = \langle n_{i \uparrow} \rangle - \langle n_{i \downarrow} \rangle \) for the first nine layers from the surface (solid lines) and bulk magnetization (dashed line) as functions of the bulk band occupation \( \langle n \rangle \). For comparison the bulk magnetization curve is shown in each panel. The thin solid lines for \( \langle n \rangle > 0.65 \) show the layer-dependent charge densities \( \langle n_i \rangle = \langle n_{i \uparrow} \rangle + \langle n_{i \downarrow} \rangle \) as functions of \( \langle n \rangle \). The horizontal lines indicate \( m_i = 0 \),

steeply increases with increasing \( \langle n \rangle \) and finally becomes saturated \((m=\langle n \rangle)\). This bulk FM solution turns out to be always stable compared with the ever-existing paramagnetic (PM) solution.18

In Fig. 2 the magnetizations of layers near the surface are compared with the bulk magnetization. The overall dependence of all layer magnetizations and the bulk magnetization on the band occupation is similar; yet there are important differences. First, there is an apparent enhancement of the top-layer magnetization in the whole \( \langle n \rangle \) range considered. On the other hand, the magnetization of the second layer is found to be smaller than the bulk magnetization for almost all \( \langle n \rangle \). Generally, we observe a damped oscillation of the magnetization around and finally convergence to its bulk value when passing from the very surface to the crystal volume. The oscillations are caused by the presence of the surface which can be interpreted as a perturbation of the infinitely extended, periodic lattice. Similar but considerably weaker oscillations with increasing distance to the surface can be found for the layer-dependent charge density \( \langle n_i \rangle = \langle n_{i \uparrow} \rangle + \langle n_{i \downarrow} \rangle \). The charge transfer between the different layers is necessary to ensure a common Fermi level in the self-consistent calculation (even at \( U = 0 \)). The topmost surface layer exhibits a clear charge excess compared with the bulk \((\langle n_i \rangle > \langle n \rangle)\). This explains the higher saturation magnetization of the top layer which can be seen in Fig. 2.

Let us now turn over from the saturation regime to lower band occupations. Just as the bulk magnetization, the magnetization of each surface layer shown in Fig. 2 is decreasing with decreasing \( \langle n \rangle \). In the vicinity of \( \langle n \rangle = 0.57 \), however, the layer magnetizations are discontinuous (e.g., third layer) or show up discontinuous derivatives (e.g., first layer). These mark a first-order phase transition from the ferromagnetic to a layerwise antiferromagnetic (AFM) order. Comparing the magnetization curve for the ninth layer with the bulk magnetization curve, we notice that hardly any differences can be seen. The transition is thus confined to the near-surface region only.19 Despite the fact that the transition is found for a band occupation \( \langle n \rangle_{tr} \) which is quite close to the critical occupation \( \langle n \rangle_c \) for the bulk FM-PM phase transition, the surface FM-AFM transition is not directly provoked by the transition of the bulk.20 Indeed, we find \( \langle n \rangle_{tr} = 0.578 \) different from \( \langle n \rangle_c \) as can be seen in Fig. 3 from the zero crossing of the magnetizations of the third and fifth layers, for example. At \( \langle n \rangle = \langle n \rangle_c \) all layer magnetizations and their derivatives are continuous. This result is also found for different (but small) values of the broadening parameters \( \Gamma \) and \( \alpha \). Below \( \langle n \rangle \), a ferromagnetic solution could not be found. In the very small range between \( \langle n \rangle_{tr} \) and \( \langle n \rangle_c \) a layerwise AFM magnetic order near the surface (up to the sixth layer) is coexisting with a FM order in the bulk. Below \( \langle n \rangle_c \) the bulk is paramagnetic while the surface shows AFM order. An exception is the somehow irregular behavior of the second layer (Fig. 3). The absolute values of the layer magnetizations rapidly decrease with increasing distance to the surface and finally converge to the vanishing bulk magnetization. With decreasing \( \langle n \rangle \) the AFM order persists up to a critical value \( \langle n \rangle_{S,c} = 0.52 \) where the surface undergoes a second-order transition to the paramagnetic state.

Since we have assumed that the magnetic moments within a layer parallel to the surface if at all order ferromagneti-
cally, our present investigations are limited to layerwise AFM order. While layerwise antiferromagnetism, being consistent with the reduction of translational symmetry perpendicular to the surface, is most plausible, a different AFM order at the surface cannot be strictly excluded. In any case, however, we can conclude that below $\langle n \rangle_c$, the surface is antiferromagnetic. Furthermore, calculations within the SDA for the infinitely extended three-dimensional bcc lattice show\(^\text{21}\) that below $\langle n \rangle_c$, the bulk is paramagnetic. Different types of bulk AFM order can be excluded.

Finally, we state the main result of our study once more: Depending on the average band occupation, the strongly correlated Hubbard model predicts quasi-two-dimensional magnetism at the surface of a single crystal. Within the framework of a standard moment method, an antiferromagnetically ordered (100) surface of a bcc lattice has been observed co-existing with a paramagnetically bulk.

This work was supported by the Deutsche Forschungsgemeinschaft within the SFB 290.

---

17. The critical $\langle n \rangle_c=0.57$ is different from the one found in Ref. 7: $\langle n \rangle_c=0.54$ for $U \rightarrow \infty$. This is not only due to the finite $U$ considered here, but also due to the slight broadening of the LDOS.
18. It is known (Ref. 7) that for $\langle n \rangle >0.79$ a second FM solution for the bulk can be found. However, in any case it shows up a higher internal energy $\langle H \rangle$ compared with the first FM solution. Since the bulk internal energy is also decisive for the stability of solutions for the semi-infinite system (the surface contribution is infinitesimal), the second FM solution can be ignored here.
19. This result is qualitatively quite different from the result of the mean-field study in Ref. 4, where (varying $U$) a FM-AFM transition was observed which also starts from the very surface but then penetrates into the the crystal volume until the whole system shows AFM order.