Magnetically Driven Buckling and Stability of Ordered Surface Alloys: Cu(100)c(2 × 2)Mn

M. Wuttig and Y. Gauthier[a]

Institut für Grenzflächenforschung und Vakuumphysik, Forschungszentrum Jülich,
Postfach 1913, W-5170 Jülich, Federal Republic of Germany

S. Blügel

Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, W-5170 Jülich, Federal Republic of Germany

We present evidence for a new class of magnetic materials, namely two-dimensional, ordered surface alloys. Structure and composition of the prototype Cu(100)c(2 × 2)Mn were determined by a quantitative low energy electron diffraction analysis, which shows an unusually large buckling in the surface alloy layer. By comparing our results with *ab initio* total energy calculations we identified the magnetism of Mn as the driving force for the buckling and moreover for the stability of the alloy. Possible additional members of this new class of materials are suggested.

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In the last decade, we witnessed an unprecedented progress in the growth of ultrathin films. In particular, in the field of magnetism possibilities opened up to grow materials which approach two-dimensional (2D) itinerant magnetism and show novel properties in phase transitions and magnetic anisotropies. The forefront of the investigations has been dominated by studies of ultrathin magnetic layers on nonmagnetic substrates, such as Co/Cu(100) [1], Fe/Cu(100) [2], Mn/Ag(100) [3], and Cr/Ag(100) [4]. Theoretical predictions including greatly enhanced magnetic moments [5], new magnetic phases such as the 2D, $c(2 \times 2)$ antiferromagnetic phase [6], and new magnetic materials such as Ru/Ag(100) or Rh/Au(100) [7] have been put forward. All of these predictions are strictly true only for one monolayer thick pseudomorphic overlayers, and some of them are certainly invalid for thicker films [8]. However, the preparation of pseudomorphic films in the one monolayer range is particularly difficult. Most of the systems mentioned above are thermodynamically unstable. Stress, double-layer growth, island formation, interdiffusion, and incomplete wetting can, for example, impede the preparation of monolayer samples. This, together with a frequently incomplete structural characterization, often results in lengthy discussions about the quality and reliability of the prepared samples. Therefore it is difficult to perform experiments which can be analyzed directly to verify or invalidate the theoretical predictions.

In this paper, we present unequivocal experimental evidence for a 2D, one monolayer thick epitaxial $c(2 \times 2)$ MnCu surface alloy film on Cu(100) (Fig. 1). This surface alloy is thermodynamically stable over a wide temperature range of 400 K and shows an unusual buckling relaxation of the Mn atoms. Complementarily, we have performed a structural optimization by *ab initio* total energy calculations. The theoretical results are in agreement with the experimental findings and show that the

unusual buckling of Mn and moreover the stability of this unexpected alloy are directly related to the magnetic properties of the surface alloy. This system can therefore be regarded as a prototype of a new class of magnetic films, namely magnetic surface alloys.

Growth, structure, and composition of the films were characterized by a variety of techniques including low energy electron diffraction (LEED) and Auger electron spectroscopy [9]. The $c(2 \times 2)$ structure is observed after deposition of approximately 0.5 ML (monolayer) Mn on the Cu(100) surface held above 270 K [9,10]. This phase is stable upon cooling to 80 K and annealing to 470 K. To establish the structural model and to determine atomic positions, LEED I-V curves for seven nonequivalent beams were measured from 40 to around 350 eV. In these experiments, the $c(2 \times 2)$ structure was produced by deposition of 0.50 ± 0.05 ML Mn at 375 K. The coverage calibration was performed using the LEED intensity maximum of the (1/2,1/2) beam as described in [9].

Full dynamical LEED calculations utilizing the layer doubling scheme to describe the interlayer multiple scattering were used [11]. The electron scattering at the ion cores was described by up to 9 phase shifts derived from band structure calculations [12]. Thermal vibra-
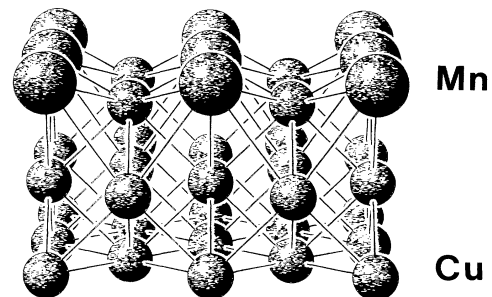

FIG. 1. Structural model for the $c(2 \times 2)$ surface alloy.

tions were included using a Debye temperature of 440 K for Mn and 460 K for Cu. The fit between theory and experiment and the error bar in the structure determination were evaluated by the Pendry R factor (R_p) [13].

In the initial step of the analysis, two completely different models were considered: the first was a Mn overlayer in which Mn atoms are located in every other four-fold hollow site on the Cu(100) surface and the second, a surface alloy in which Mn atoms replace every other Cu atom in the topmost plane of the substrate (Fig. 1). Both models were tested extensively. In the overlayer model, the distance between the Mn overlayer and the topmost atomic plane of the Cu(100) substrate was varied between 1.4 Å and 2.5 Å in steps of 0.1 Å. In the alloy model, the corrugation in the first layer was varied from +0.5 Å (Mn displaced outwards) to −0.5 Å in steps of 0.1 Å (see Fig. 1). Additionally, the first interlayer distance was optimized between 1.6 Å and 2.0 Å in steps of 0.05 Å. From this initial analysis, the hollow site model with a best fit Pendry R factor of $R_p = 0.72$ could be clearly discarded. The surface alloy model had a comparatively low R factor of $R_p = 0.31$ and was therefore considered for further refinement.

In the next step of the analysis, the first three interlayer distances (d_i) and the corrugations in the first three layers (Δz_i) were optimized. Table I gives the best fit structure. The most surprising result is the considerable corrugation of $\Delta z_1 = 0.30 \pm 0.02$ Å in the surface alloy layer. Practically no corrugation is found in the second and third layers and all interlayer distances are close to the bulk value. An investigation of the composition profile in the near surface region [14] shows that the top layer is an almost perfectly ordered alloy above a copper layer, which contains at most a few percent Mn, if any.

In Fig. 2, the spectra calculated for the best fit $c(2 \times 2)$ Mn structure are compared with the measured I-V curves. Both the peak positions and the intensities are fairly well reproduced as expected from the low R factor. Furthermore, the R factor shows one deep minimum for all beams with an average value of 0.287 upon a variation of structural parameters around the best fit structure [14]. This leads to a small error bar of 0.02 Å for the first interlayer spacing and the first layer corrugation.

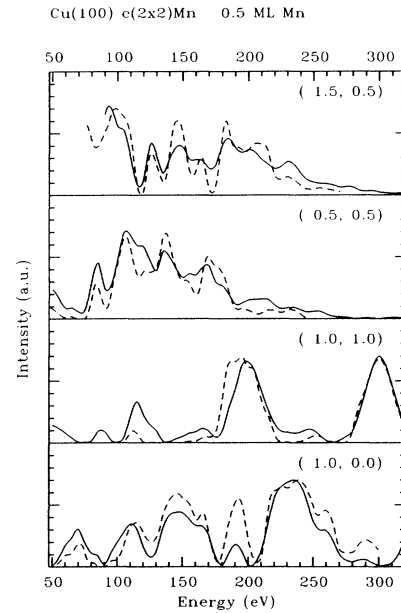In Table I, the best fit structure for the Cu(100)$c(2 \times$

FIG. 2. Experimental spectra (broken line) for the Cu(100)$c(2 \times 2)$Mn structure compared to the best fit spectra for the surface alloy (solid line).

2)Mn phase is compared with two other ordered surface alloys, namely the Cu(100)$c(2 \times 2)$Au phase [15] and the Cu(100)$c(2 \times 2)$Pd phase [16]. For all three systems, the interlayer distances found are close to the bulk interlayer spacing. On the other hand, the corrugation of the alloy layer shows considerable differences. While the corrugation Δz_1 is only 0.03 Å for Pd [16], and 0.1 Å for Au [15], a corrugation of 0.3 Å is found for the Cu(100)$c(2 \times 2)$Mn phase. It has been suggested [16] that the corrugation of ordered surface alloys increases with increasing difference in atomic diameters of the constituing elements. While this explains the trend for Au and Pd, it fails miserably for Mn. Since the Mn radius (1.365 Å) is similar to the Cu radius (1.276 Å) and smaller than Pd (1.375 Å) and Au (1.442 Å), one would expect only a marginal corrugation contrary to the experimental observation. Another seeming mystery regarding the stability of the Cu(100)$c(2 \times 2)$Mn phase is posed by the bulk phase diagram. While the bulk phases of CuAu and CuPd show a pronounced tendency towards ordering, the heat of formation of CuMn bulk alloys is negative, indicating that the formation of ordered bulk alloys is energetically unfavorable [17]. This is consistent with the experimental observation that it was impossible to grow ordered alloy films with larger thickness. Instead even after deposition of 4 ML Mn at temperatures above 440 K, ordered alloy formation was only observed for the surface layer while the excess Mn dissolved in the bulk.

To understand the large corrugation of Mn and in particular to shine more light onto the structural stability of this surface alloy, we performed a structural op-

TABLE I. Structural results obtained by LEED analyses for different ordered surface alloys. Ellipses or the symbol d_b indicate that the corresponding value has not been optimized. The bulk interlayer distance d_b is 1.807 Å.

Structure (Å)	Cu(100) $c(2 \times 2)$Au [15]	Cu(100) $c(2 \times 2)$Pd [16]	Cu(100) $c(2 \times 2)$Mn
Δz_1	0.1	0.02 ± 0.03	0.30 ± 0.02
Δz_2	...	...	0.02 ± 0.03
d_{12}	1.88	1.81 ± 0.03	1.79 ± 0.02
d_{23}	d_b	d_b	1.80 ± 0.03

timization of paramagnetic (P) and ferromagnetic (F) $Cu(100)c(2 \times 2)Mn$ surface alloy (S) by *ab initio* electronic structure calculations. These calculations are based on the density functional theory in the local spin density approximation [18]. The equations are solved using the full-potential linearized augmented plane-wave method (FLAPW) for thin film geometry [19]. As a structural model, we have chosen a 7 layer film consisting of 5 layers of Cu with 2 Cu atoms per layer simulating the $c(2 \times 2)Cu(100)$ substrate and at each surface, one Mn and one Cu atom simulating the (2×2) surface alloy according to Fig. 1. In the structural optimization, which is based on minimizing the total energy $E_S\{P/F; \Delta z_{Mn,F/P}; \Delta z_{Cu,F/P}\}$, we included for the paramagnetic as well as the ferromagnetic case 2 degrees of freedom. These were the relaxations Δz of Mn and the top Cu atom along the surface normal. This is sufficient as it is shown by our LEED analysis. Prior to this study, the bulk Cu lattice constant $(a_{Cu} = 3.52 \text{ Å})$ and the interlayer spacing $(d_{Cu} = a_{Cu}/2 = 1.76 \text{ Å})$, respectively, had also been determined by a FLAPW method [20] to avoid any incompatibilities due to different band structure methods. To study the structural stability of the surface alloy against the formation of a similar Cu_3Mn bulk alloy, we repeated the calculation treating the two $c(2 \times 2)$ MnCu layers as interlayers (I) separated by a Cu layer and covered by two layers of Cu in an otherwise unchanged environment of a 7 layer slab. Since the direct overlap of the Mn d electrons is of minor importance, this interlayer calculation serves also as a first approximation on the energetic stability of single Mn atoms against interdiffusion.

Two important points are to be seen upon comparing the results of the paramagnetic with the ferromagnetic surface alloys (see Fig. 3): (i) the ferromagnetic solution is lower than the paramagnetic one by about 1.4 eV/Mn atom; and (ii) in the paramagnetic case, the position of the Mn atom remains nearly at the ideally terminated Cu site $(\Delta z_{Mn,P} = -0.5\% d_{Cu})$, whereas the ground state solution was found for magnetic Mn showing a large outwards buckling of $\Delta z_{Mn,F} = +11.5\% d_{Cu}$ and Cu showing a small inwards buckling of $\Delta z_{Cu,F} = -2.5\% d_{Cu}$. This large buckling is in agreement with the experiment, and we can therefore conclude at this point that (i) the CuMn surface alloy is magnetic and (ii) the buckling motion of Mn is caused by its magnetism. On the other hand, the small corrugation found for the paramagnetic solution is in line with the corrugation observed for the CuAu and CuPd surface alloy.

These findings can be understood considering the bonding behavior of the Mn d electrons. In the paramagnetic case, the d bands are half filled. Therefore, all bonding states are occupied and Mn favors an environment with a lot of bonding neighbors. In fact, when we calculate the paramagnetic $c(2 \times 2)$ MnCu layer as an interlayer in Cu, we find that due to the increased number of Cu neighbors the total energy is reduced by
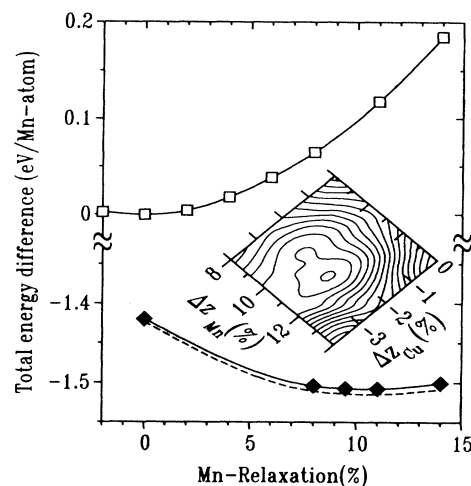

FIG. 3. Theoretical total energy difference per Mn atom of $Cu(100)c(2 \times 2)Mn$ vs the buckling relaxation Δz_{Mn} of Mn in relative units with respect to the theoretical interlayer spacing of Cu, $d_{Cu} = 1.76 \text{ Å}$. The open squares represent the paramagnetic and the solid diamonds the ferromagnetic results. The solid lines (for Cu atoms fixed at the ideally terminated position $\Delta z_{Cu} = 0$) and dashed line (the top Cu atom is always at its optimally relaxed position) are the fitting polynomials. The inset shows the contour plot of the ferromagnetic total energy difference with respect to the buckling of Mn and Cu. The minimum, which determines the optimal structure, is found in the inner circle. The contour interval is 1 meV.

0.56 eV/Mn atom. This means that a paramagnetic MnCu surface alloy would be highly unstable against interdiffusion. When we remove the constraint of paramagnetism, the system becomes magnetic and the Mn atom at the surface alloy obtains a magnetic moment of $M_S(\Delta z_{Mn} = \Delta z_{Cu} = 0) = 3.64\mu_B$, which is accompanied by the large gain of magnetic energy. In fact, a magnetic moment of that size means that the majority Mn d orbitals are nearly completely occupied and the minority d bands are nearly empty. As a consequence, there are nearly as many Mn d bondings states occupied as d antibondings states and as a result, the d cohesion becomes less important and is energetically more than compensated by the gain of magnetic energy. In the language of atomic radii used above to explain the buckling, it means that the ferromagnetic Mn atom is much bigger than the paramagnetic one and its size depends on the magnetic moment itself. The minor importance of the Mn d cohesion becomes also evident by comparing the energy of the ferromagnetic interlayer system $E_I(F, 0) = E_I(F, \Delta z_{CuMn} = 0)$ with that of the ferromagnetic surface layer $E_S(F, 0) = E_S(F, \Delta z_{Mn} = \Delta z_{Cu} = 0)$. Although the environment of the Mn atom is very different the energy is nearly degenerate $[E_S(F, 0) - E_I(F, 0) = -0.04 \text{ eV/Mn}]$. The magnetic moment of the Mn overlayer atom is larger than that of the interlayers, $M_I(\Delta z_{CuMn} = 0) = 3.23\mu_B$, and it is this ad-

ditional gain of magnetic energy which stabilizes the surface alloy. The buckling motion of the Mn surface atom is very efficient to release the pressure on the Mn atom. As a result of the relaxation, the magnetic moment increases to $M_S(\Delta z_{Mn} = +11.5\%, \Delta z_{Cu} = -2.5\%) = 3.75\mu_B$ and the total energy is further reduced by 0.1 eV/Mn atom, stabilizing the surface alloy. This relaxational release of compression cannot be matched by a Mn interface atom. The theoretically determined ground state buckling of $\Delta z_{Mn} = 11.5\%$ and $\Delta z_{Cu} = -2.5\%$, which adds up to the total buckling of $\Delta z_1 = \Delta z_{Mn} - \Delta z_{Cu} = 14\%$ ($\cong 0.24$ Å), is in fairly good agreement with the experimentally determined value of 16.6% ($\cong 0.3 \pm 0.02$ Å). The theoretical data given in absolute units are smaller than the experimental results, typical for *ab initio* calculations in the local spin density approximation.

In this paper, we did not make any theoretical effort to determine the long range magnetic order, which we assumed here to be ferromagnetic. At this point we cannot exclude the possibility of an antiferromagnetic order. It is known that for Mn monolayers on various substrates, the $c(2 \times 2)$ antiferromagnetic order is favored [6] due to a direct in plane Mn d-d hybridization. However, in the case of the CuMn surface alloy, the magnetic order is determined by an indirect, in-plane RKKY-type interaction due to the hybridization of the Mn d with the Cu sp electrons. In such a case (i) the long range magnetic order has practically no influence on the structural properties, and (ii) from the exchange coupling of Mn dimers on next nearest neighbor sites in Cu [21] we expect the ferromagnetic spin arrangement as the magnetic ground state. In fact we have carefully looked for an antiferromagnetic order by LEED. As is known, antiferromagnetism leads to extra LEED spots due to the reduced symmetry of the magnetic lattice [22]. We found, however, no evidence for their existence at temperatures above 100 K.

At the end we would like to speculate on the possibility of additional magnetic surface alloys, by relating our work to the attraction or repulsion of a vacancy and a $3d$ impurity as nearest neighbors in bulk Cu and Ni. *Ab initio* results [23] show that the interaction energy of a vacancy with Cr or Mn in Cu or of a vacancy with V, Cr, Mn, Fe, or Co in Ni is nearly degenerate between attraction and repulsion. If we take into account, as compared to atoms close to the vacancy, the reduction of the number of nearest neighbor atoms at the surface, which enhances magnetism, and the additional structural degrees of freedom at the surface, the magnetic energy can be gained and alloys may be stabilized on the surface. Since the buckling relaxation depends on the size of the magnetic moment, we expect on the basis of results on single magnetic impurities in Cu [21] and Ni [24] the largest buckling for Cu based surface alloys with Cr and Mn and a larger buckling for Cu based surface alloys than for Ni based alloys. This is in line with our experimental results for the $Ni(100)c(2 \times 2)Mn$ surface alloy, where a corrugation of 0.25 ± 0.02 Å has been found [14]. We

conclude that $Cu(100)c(2 \times 2)Mn$ is just a prototype of a much wider class of new magnetic material, namely the 2D ordered surface alloy.

(a) Permanent address: Laboratoire de Spectrometrie Physique, associe du CNRS, BP 87, Universite Joseph Fourier, 38402 Saint Martin d'Heres Cedex, France.

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