Two-dimensional Ising behavior in $c(2\times2)$ antiferromagnetic Mn and Cr monolayers on Ag(001)

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The magnetic order $M_S(T)$ is determined as a function of temperature for the $c(2\times2)$ antiferromagnetic monolayers of Mn and Cr on Ag(001), using the intensity of the coherent superlattice $(\frac{1}{2},\frac{1}{2})$ reflections in low-energy electron diffraction to obtain the sublattice magnetization M_S. The data fit the Onsager-Yang theoretical result rather well for the spontaneous magnetization of the plane square lattice in the Ising model with critical temperatures $T_C \approx 198$ and 462 K for Mn and Cr, respectively. Near T_C a fit to a universal power law $M_S(T)\sim(1-T/T_C)^{\beta}$ confirms the two-dimensional Ising class with β close to $\frac{1}{8}$ and indicates the importance of second-order magnetic anisotropy in these two-dimensional antiferromagnets.

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I. INTRODUCTION

The reduction of dimensionality for metallic films often results in new and exciting magnetic properties. Within the Heisenberg model, which is the most general way to describe the magnetic moments of an ideal two-dimensional (2D) film, no long-range order can exist at finite temperature.[1] However, in the presence of uniaxial anisotropy as expected in real samples, the system is predicted to become Ising-like near the transition temperature.[2] The transition between the ferromagnetic and paramagnetic state has been studied for many ultrathin layers such as Co/Cu(111),[3] Fe/W(110),[4,5] Fe/Pd(100),[6] Fe/Ag(100),[7] or V/Ag(001),[6] and by means of different techniques such as electron capture microscopy,[6] spin-polarized low-energy electron diffraction,[4] or magneto-optic Kerr measurements.[7] For these films, the magnetization $M(T)$ is properly described by the asymptotic power law $M(T)\sim(T_C-T)^{\beta}$ with a critical exponent β close to $\frac{1}{8}$.

In contrast, very few works have been devoted to the antiferromagnetic-paramagnetic transition for thin layers. As for these systems the net magnetization is equal to zero, and techniques generally used for ferromagnetic layers are not suitable. Nevertheless, linear polarized x-ray-absorption spectroscopy (XAS) has allowed investigation of the temperature and thickness dependence of the magnetic moments for NiO epitaxial films (5–20 monolayers) grown on MgO(100).[8] Low-energy electron diffraction (LEED) can be used as well to study the surface of antiferromagnetic (AF) systems or 2D AF layers. Indeed the small difference between scattering amplitudes at spin-up and spin-down atoms due to exchange scattering produces additional spots on the LEED diagram, whose intensity is proportional to $\langle M_S\rangle^2$, the square of the thermal average of the spin moment component of the scattering atom.[9] For example, the temperature dependence of the sublattice magnetization in a NiO(001) crystal has been recorded by measuring the intensity of the $(\frac{1}{2},0)$ LEED spots.[10,11] Note that later a 2D surface spin-ordering transition has been observed on the NiO(001) surface by means of metastable helium atom diffraction.[12]

Now we have shown recently that monolayer Cr domains can be grown on Ag(001), which are characterized by a $c(2\times2)$ LEED superstructure. This superstructure is identical to that obtained for a flat Mn monolayer grown on Ag(001).[13] The $(\frac{1}{2},\frac{1}{2})$ spots are remarkably sharp, and their intensity is very weak, $\approx$4% and $\approx$6% of the (1,0) integer spots at 40 eV and at 100 K for Cr and Mn films, respectively. According to a dynamical LEED analysis, the Mn magnetic moments in the Mn overlayer present an antiferromagnetic arrangement.[14] As the properties of the $c(2\times2)$ superstructure induced by the Cr overlayer are quite close to those of the half-order spots obtained on 1 monolayer (ML) Mn/Ag(001), we concluded that the Cr atomic moments are also antiferromagnetically ordered.[13] Thus the challenge was to investigate, for both Cr and Mn, the temperature dependence of this magnetic order, and to seek a possible transition between the antiferromagnetic and the paramagnetic state. In this paper we show that the $c(2\times2)$ superstructure fades away with increasing temperature and that a transition temperature can be seen for both systems. Comparing our data with the exact solution of the Ising model, we also conclude that these systems belong to the 2D Ising universality class.

II. EXPERIMENT

The experiments were performed in an uhv chamber equipped with a four-grid LEED apparatus and a charge-coupled-device (CCD) camera for spot intensity measurements. The Ag(001) crystal was cleaned *in situ* by cycles of Ar-ion sputtering and annealing at 800 K until a sharp LEED structure was obtained. The substrate temperature during deposition was controlled by a thermocouple located besides the sample. Cr and Mn were evaporated from a homemade source operating at a rate of $\approx$0.2 ML/min and a base pressure of 3×10^{-10} Torr. One monolayer corresponds to the Ag(001) surface atomic density. The coverages were determined by means of a quartz balance, which had been previously calibrated by mounting a second balance in the sample position, in order to estimate the geometric correction factor. In the monolayer range the accuracy is about 10%. The temperature of the substrate was kept at 100 K for Mn deposition and 430 K for Cr. When 0.9 ML of Mn is deposited at 100 K, a flat Mn 2D monoatomic layer is formed on Ag(001). In contrast, for a coverage of 1 ML Cr at 430 K, a heterogeneous film grows, constituted by 2D Cr domains and by

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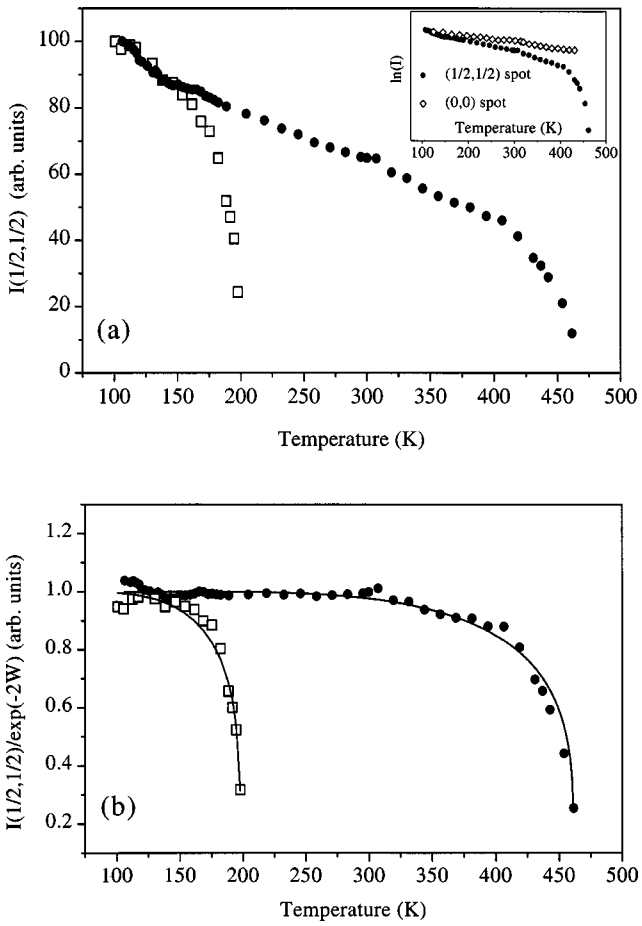

FIG. 1. Intensity of the $(\frac{1}{2},\frac{1}{2})$ LEED spot as a function of temperature for 1 ML Cr (●) deposited at 430 K (incident energy $E=25$ eV; incidence angle $\theta=0°$) and 0.9 ML of Mn (□) deposited at 100 K (incident energy $E=22$ eV; incidence angle $\theta=7.5°$): (a) raw data; (b) data divided by the Debye-Waller factor $\exp(-2W)$. Solid line: best fit with the Onsager-Yang solution (see text). Inset: logarithm of the $(\frac{1}{2},\frac{1}{2})$ (●, incident energy $E=25$ eV; incidence angle $\theta=0°$) and (0,0) (◇, incident energy $E=22$ eV; incidence angle $\theta=7.5°$) reflections intensities vs temperature for 1 ML Cr deposited at 430 K. The incidence angle did not influence the thermal behavior of the spot intensities.

multilayer islands made of $p(1\times1)$ Ag patches on top of a mixed Cr-Ag phase. According to x-ray photoelectron diffraction (XPD) and valence-band photoemission data, the $c(2\times2)$ LEED pattern originates in these Cr domains only, which are located on top of defect-free Ag terraces or of the $p(1\times1)$ Ag patches. Detailed structural studies of the films can be found in Refs. 14 and 15 for Mn/Ag(001) and Ref. 13 for Cr/Ag(001).

III. RESULTS AND DISCUSSION

In Fig. 1(a) the intensity of the $(\frac{1}{2},\frac{1}{2})$ spots at 25 eV (Cr) and 22 eV (Mn) has been recorded as a function of temperature. Raw data are presented, and both curves have been normalized to their highest value. As we are interested in a purely temperature effect, we first checked that the Cr and Mn domains are stable upon annealing. For Cr, the film was

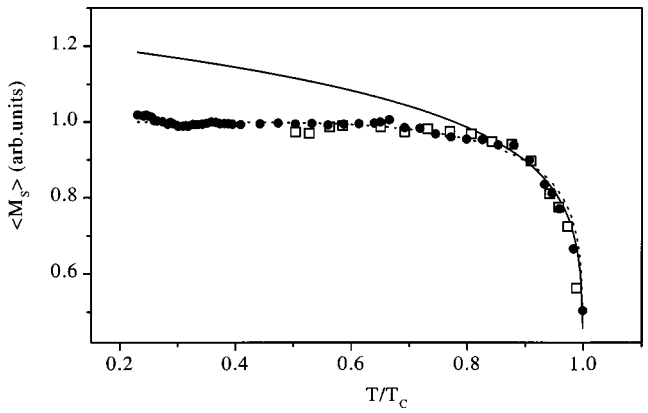

FIG. 2. Sublattice magnetization as a function of reduced temperature T/T_C, where T_C is the transition temperature, for 1 ML Cr (●) deposited at 430 K and 0.9 ML of Mn (□) deposited at 100 K. The incidence energies and angles are the same as in Fig. 1. Dashed line: best fit of the exact solution of the 2D Ising model. Solid line: best fit of power law approximation for $T\rightarrow T_C$ in the $0.826<T/T_C<0.999$ (Cr) and $0.895<T/T_C<0.998$ (Mn) range ($\beta=0.136$).

first immediately cooled to 100 K after deposition at 430 K. Then the sample temperature was slowly ramped, measurements were taken during annealing, and the film was cooled back rapidly to 100 K after experiment. When the annealing temperature is higher than ≈470 K, no $c(2\times2)$ superstructure can be observed indicating an irreversible destruction of the Cr monolayer domains and, according to photoemission data, formation of 3D Cr islands.[16] However, when the temperature does not exceed 470 K, we observe that the superstructure intensity has regained ≈96% of its initial value, i.e., the total area of the antiferromagnetic domains is the same as before annealing. Moreover, XPD and valence-band photoemission measurements indicate that no structural modifications are induced by the annealing cycle. So we can conclude that the diminution of the Cr $(\frac{1}{2},\frac{1}{2})$ intensity in Fig. 2(a) (provided that $T<470$ K) is purely a reversible temperature effect.

Things are different for Mn, as annealing the film grown at 100 K at a temperature higher than 150 K systematically results in a partial destruction (≈30% of the total area) of the Mn monolayer. Therefore, to obtain the data of Fig. 1(a), we quickly heated the sample up to 200 K and measured the $(\frac{1}{2},\frac{1}{2})$ spot intensity during cooling, so the area of the 2D Mn domain remains constant. Clearly the LEED intensity decreases drastically with increasing temperature for both systems. More precisely, the initial slope is similar for the Cr and the Mn film, about 15% of the initial intensity is lost from 100 to 150 K. Then the Mn signal keeps diminishing quickly and the $c(2\times2)$ superstructure vanishes around 200 K. For Cr, the slope is not so steep from 150 to ≈400 K, and finally transition occurs above 450 K. Generally LEED spots intensity are known to decrease with increasing temperature because of the thermal motion of atoms. In single scattering theory, the beam intensity is reduced by the Debye-Waller factor $\exp(-2W)$, where W is proportional to temperature T.[17]

The contribution of multiple scattering events is certainly

strong in our present case, as data are taken at low incident energy, where the superstructure is the most visible. However, the experiment has amply shown that even in the presence of multiple scattering, LEED spot intensities usually closely follow a simple temperature dependence in the form $I=I_0\exp(-\alpha T)$, but the dependence of α on spot indices and incident energy is not the one expected from simple Debye-Waller theory.[18] In this respect, let us have a look at the inset of Fig. 1(a), which presents the logarithm of $(\frac{1}{2},\frac{1}{2})$ and (0,0) spot intensities for a Cr overlayer. Clearly, for the integer spot, the decreasing $\ln(I)$ is linear over the whole temperature range, indicating that the diminution of the diffracted intensity is the result of thermal vibrations. In contrast, for the fractional order spot, $\ln(I)$ is proportional to T only between $\approx$150 and 300 K, so both atomic vibration and the decrease of sublattice magnetization must contribute to the temperature dependence of the LEED half-order spots.

One may wonder if the $c(2\times2)$ intensity evolution could be related to the formation of an ordered Cr-Ag surface alloy, as can be found in the case of Mn films deposited on Ag(001) at room temperature.[14] However, during the annealing procedure, the LEED superstructure intensity would be expected initially to grow with temperature, then reach a maximum, and finally decrease because of the destruction of the ordered domains. Indeed at 100 K the mobility of the atoms is limited, so surface ordering, which is a thermally activated phenomenon, is very low. At higher temperature surface diffusion is favored, thus allowing the formation of ordered surface alloy domains, as in the case of the Mn-Ag surface alloy.[19] In fact, as shown in Fig. 1(a), the $(\frac{1}{2},\frac{1}{2})$ spots decrease continuously with increasing temperature, so the data cannot interpreted in terms of formation of a $c(2\times2)$ Cr-Ag surface alloy. Conversely, destruction of a $c(2\times2)$ Cr-Ag surface alloy upon heating might explain the half-order spot intensity decrease with temperature, but this would be an irreversible and not a reversible process as observed.

Figure 1(b) displays the ratio between the $(\frac{1}{2},\frac{1}{2})$ LEED intensity and the Debye-Waller factor $\exp(-2W)$ as a function of temperature T for 1 ML Cr (circles) and 0.9 ML Mn (squares). The Debye-Waller factor has been extracted using the linear part of the $\ln[I(\frac{1}{2},\frac{1}{2})]=f(T)$ curve, i.e., between 150 and 300 K for Cr [see inset of Fig. 1(a)], and from 100 to 154 K for Mn. These curves now reflect the temperature dependence of $\langle M_S\rangle^2$ only. Let us first discuss the data for Cr/Ag(001). It can be seen that after a rapid initial diminution, the $(\frac{1}{2},\frac{1}{2})$ spot intensity remains nearly constant up to $\approx$300 K. Then it decreases slowly and afterwards very abruptly above 400 K. As our structural investigations indicate that the $c(2\times2)$ Cr domains are two-dimensional, we fitted the data with the exact solution of the 2D Ising model for the sublattice magnetization given by Onsager[20] and Yang,[21]

$$\langle M_S\rangle=\left\{1-1\Big/\left[\sinh\left(\ln(1+\sqrt{2})\,\frac{T_C}{T}\right)\right]^4\right\}^{0.125},$$

and we obtained a transition temperature $T_C=462$ K. It can be seen [Fig. 1(b)] that the 2D Ising model provides a good description of the magnetic order of the Cr 2D islands for $150\text{ K}<T<461$ K, i.e., for T/T_C ranging between 0.33 and 0.998. Note that for $100\text{ K}<T<150$ K, the temperature dependence of M_S is quasilinear, which has been already observed for 2D magnetic thin films when $T\ll T_C$.[7] The quality of the fit can be readily compared to that obtained on ferromagnetic layers such as Fe/Pd(001) and V/Ag(001).[6] For Mn/Ag(001), a similar fit lead to $T_C=198$ K [see Fig. 2(b)].

Figure 2 presents the sublattice magnetization $\langle M_S\rangle$ as a function of reduced temperature T/T_C for the Cr and the Mn monolayer. The modulations of the $c(2\times2)$ superstructure intensity can be superimposed on each other, which suggests that the phase transition for both systems belongs indeed to the same universality class. We also fitted the data around the transition temperature with the universal power law $M_S(T)\sim(1-T/T_C)^{\beta}$. However, we must keep in mind the fact that the power law corresponds to the asymptotic approximation of the exact Onsager-Yang solution for T near T_C; therefore the value obtained for β depends on the temperature range ΔT taken for the fit. For Cr/Ag(001), we obtain $\beta=0.138$ for $\Delta T/T_C=17\%$ and $\beta=0.145$ for $\Delta T/T_C=12\%$. For Mn/Ag(001), β increases from 0.126 to 0.133 for $18\%<\Delta T/T_C<11\%$. Clearly the value for β is close to that expected for a perfect 2D Ising system (0.125), especially for the Mn monolayer. In fact, as discussed by Qiu, Pearson, and Bader,[7] two factors counterbalance each other. On the one hand, from a mathematical point of view, β tends to be underestimated when the temperature domain ΔT taken to fit the Onsager-Yang function is too large. On the other hand, finite-size effects have to be taken into account as our films are formed of monolayer islands, whose diameter, according to a rough estimation using the $(\frac{1}{2},\frac{1}{2})$ spot width, does not exceed 2.5 nm. Landau has shown that a diminution of the size of the ordered domains tends to lower the sharpness of the transition and to increase the apparent value of the critical exponent β.[22] These two effects may result in a value for β quite close to the theoretical one expected for a 2D Ising system. In this respect the value obtained for the critical exponent is higher for the Cr monolayer islands than for Mn/Ag(001), which would indicate that the Cr antiferromagnetic domains are smaller than the Mn ones. This is in agreement with our structural studies, which have shown that the Cr film is more heterogeneous than the Mn monolayer;[13,14] in particular, the proportion of Mn in second-layer position is negligible, while the Cr film is made both of 2D $c(2\times2)$ Cr domains and mixed Cr-Ag islands. However, these observations must be taken with care considering the limited accuracy in the half-order spot intensity measurements near transition temperature.

IV. CONCLUSION

In summary, we have investigated the temperature dependence of the LEED superstructure observed on two-dimensional Cr and Mn antiferromagnetic domains grown on Ag(001). We find a transition temperature of 462 K for Cr and 198 K for Mn. Moreover, a fit of the data indicates that both antiferromagnetic systems belong to the 2D Ising universality class. It is noteworthy that the transition tempera-

ture for Cr is much higher than that of bulk antiferromagnetic Cr (312 K), in contrast to what is usually observed for ferromagnetic ultrathin films, where the Curie temperature is lower for thin films than for their bulk counterpart.[7] However, in the case of the Cr 2D domains on Ag(001), the interatomic distance is much larger (2.88 Å) than in bulk bcc Cr (2.49 Å), and the magnetic moment is much higher ($\approx 4\mu_B$ instead of $0.49\mu_B$), i.e., close to the moment corresponding to Cr impurities in an Ag matrix.[16,23] Moreover, bcc Cr is made of ferromagnetic planes that are antiferromagnetically coupled, whereas a Cr monolayer is characterized by in-plane antiferromagnetism. In other words, the magnetism is quite different for bulk Cr and flat Cr domains, and involves apparently a much larger effective exchange coupling constant J in the 2D phase. This in turn might not be too surprising if one recalls that drastic changes in the d-state electronic structure are observed in the Cr monolayer with respect to bulk Cr. In particular, at E_F a very large gap ($\geqslant 2$ eV) exists between majority- and minority-spin $3d$ states in the Cr monolayer.[16,24]

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