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# Thickness-dependent Curie temperature of Gd(0001)/W(110) and its dependence on the growth conditions

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The Curie temperature $T_C$ of 5–100 monolayers Gd is determined by *in situ* ac-susceptibility ($\chi_{ac}$) measurements. $T_C$ of properly annealed layer-by-layer-grown Gd films decreases as a function of film thickness in the same way as is usually found from finite-size effects in other ferromagnets. Sharp cusps in the susceptibility as a function of temperature are measured. The shape of the $\chi_{ac}$ signal and the Curie temperature is strongly dependent on the growth mode and on the annealing procedure after deposition at room temperature. These results are compared to our earlier experiments on Gd films grown at elevated substrate temperatures.

Ultrathin magnetic films exhibit a rich variety of magnetic properties, which depend critically on deposition conditions and substrate choice. Dramatic changes of magnetic anisotropies as a function of substrate conditions during deposition have been reported in the literature.[1] The thickness-dependent Curie temperature $T_C(d)$ has been measured for some films.[2–7] However, the influence of growth conditions on $T_C$ for a particular film was not studied in great detail. In some cases (Co, Fe) only a very narrow range of thickness was measured. In recent years, there have been numerous reports on the magnetism of gadolinium in ultrathin films and of the surface layer measured under ultrahigh vacuum (UHV) conditions. In comparison to transition-metal ferromagnets only a very small decrease of $T_C(d)$ was observed for Gd monolayers (ML) on W(110) by magnetic resonance, i.e., $T_C(1\ \text{ML})=0.9\ T_C$ (bulk).[8] Other thin-film and surface magnetic properties of Gd have been measured by spin-resolved photoemission[9–11] and spin-polarized low-energy-electron diffraction.[12] Surface-enhanced magnetic order of up to 350 K,[13] i.e., 58 K above bulk $T_C$, was found and an antiferromagnetic coupling of the surface magnetic moment to the bulk moment was measured[12] and calculated.[14,15] Recent experiments, however, contradict the later result and indicate a ferromagnetic coupling.[13,16] For Gd on Cu(100), synchrotron-radiation photoemission results reveal a local magnetization component along the surface normal of the film.[17] All these studies have been performed at the highest standards possible. This unusual and contradictory behavior of the well-localized rare-earth ferromagnet Gd, however, may indicate a special sensitivity to growth parameters, which could not be resolved in those experiments, but needs to be clarified before theoretical analysis can be applied to the experiments.

Recently, it was shown[18] that the classical ac-susceptibility technique is applicable in UHV to investigate magnetism with monolayer sensitivity. $\chi_{ac}$ measurements may be superior to some other magnetic characterization techniques cited above, because the analysis of the data is straightforward and is best understood from bulk measurements. Its signal is absolutely calibrated within 20% in magnetic units. With the same precision the number of atoms carrying a magnetic moment can be determined. Therefore we can eliminate the hypothetical presence of nonmagnetic Gd layers in our films. The technique is not surface sensitive and measures truly the ground state of a magnetic system in quasizero applied magnetic field. In the present investigation we applied this technique to film thicknesses of a few atomic layers only. We focus on the dramatic changes of the *magnetic* properties as observed quantitatively by $\chi_{ac}$. A detailed structural analysis will be given elsewhere. Data for 5 to 100 ML thick epitaxially grown Gd(0001) films on W(110) are presented. The Curie temperature of carefully prepared layer-by-layer-grown Gd(0001) films varies from $T_C$ (bulk)=292.5 K to $T_C$ (5 ML)=120 K. It is also demonstrated that different growth conditions change the film's Curie temperature dramatically.

The ac-susceptibility data are shown in Fig. 1 for different film thicknesses. A very sharp—almost divergent—peak is recorded at the magnetic phase transition. This is theoretically expected from the well-known critical behavior of the susceptibility at $T_C$ (Ref. 19) and indicates high quality, magnetically homogeneous films. A detailed discussion of the complete behavior in the ferro- and paramagnetic phase is given elsewhere.[20] Here we will focus on the determination of $T_C$, which is directly obtained from the maximum of $\chi_{ac}$. The peak width is only a few degrees which has never been achieved in metallic ferromagnets before.[21,22] As a result the determination of the Curie temperature for these high-quality films is very precise and unambiguous. Figure 1 shows $\chi(T)$ for various optimally prepared films, which we define as films which show the sharpest and largest peak. First, we discuss $T_C(d)$, however note that the signal depends sensitively on the history of the film as described in the second part of this communication. Within $\pm 1$ K the maximum of $\chi(T)$ determines $T_C$.[18,20] These values are plotted in Fig. 2 (squares). Here the vertical error bar is

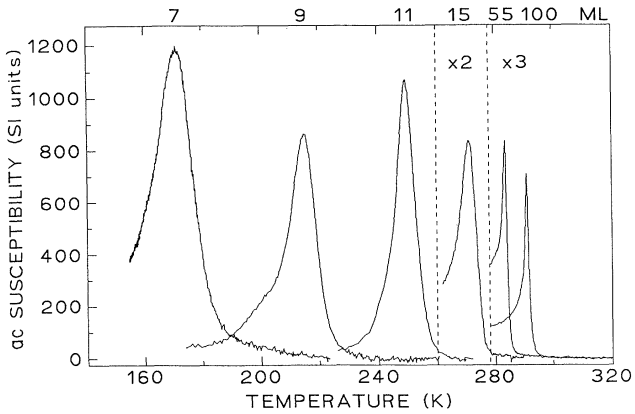


FIG. 1. ac-susceptibility data as function of temperature of Gd(0001)/W(110) for different film thicknesses.

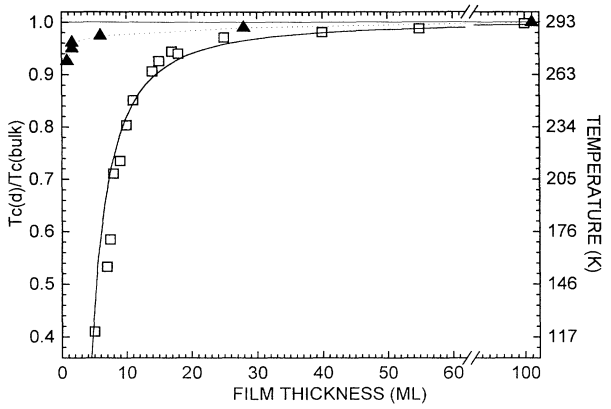


FIG. 2. Reduced Curie temperature [$T_C$(bulk)=292.5 K] as function of film thickness $d$. Squares: $T_C(d)$ of optimally prepared samples (see text). Solid line: Fit according to Eq. (1). Triangles: $T_C(d)$ of Refs. 8 and 25 grown at a substrate temperature of 720 K. The dotted line is a guide to the eye.

very small, while horizontal relative error bars become large, in particular for small $d$. The finite-size effect determines $T_C(d)$ according to

$$\frac{\Delta T_C(d)}{T_C(\text{bulk})} \equiv \frac{T_C(\text{bulk}) - T_C(d)}{T_C(\text{bulk})} = C_0 \times d^{-1/\nu} . \quad (1)$$

Equation (1) may be questionable by itself. At present we will discuss our results assuming the validity of Eq. (1) for a better comparison to other work. For an arbitrary factor $C_0$ (variation over orders of magnitude) power law fits through many data sets have been made. However, theory predicts a physically meaningful value of $C_0 \approx 2$ to 10. The solid line in Fig. 2 uses $C_0 = 7.0$ and $1/\nu = 1/0.63$, the three-dimensional (3D) Ising critical exponent of the correlation length. The monotonic shift of $T_C(d)$, and the consistency of $\chi(T)$ give very strong evidence that the layer-by-layer growth indeed takes place which is also found by Auger spectroscopy. In Fig. 1 the signal is calibrated in the international system of units (SI). This enables us to determine the absolute value of the magnetic moment, provided the number of atoms is known.[20] Our total error bar is 20% typically. The absolute value of $\chi_{\max}$, normalized to the mass, scales even more closely. The $\chi_{\max}$ values of the thinner films range up to 1200, whereas $\chi_{\max}$ of 15 and 100 ML is 400 and 200 (note the change in gain in Fig. 1). At first glance this seems to be contradictory. As the signal in SI is normalized to the mass (the number of atoms), one would expect a constant $\chi_{\max}$. We have shown[18,23] how to analyze $\chi_{ac}(T > T_C)$, including a small distribution of Curie temperatures in the macroscopic sample and including small, but finite, demagnetizing factors $N_\parallel$ for the in-plane susceptibility. It is demonstrated[23] that the shape of the cusp can be simulated quantitatively, and changes of the demagnetizing factor of $\Delta N_\parallel < 10^{-3}$ can be easily distinguished in the films. For a flat disk $N_\parallel$ can be approximated by

$$N_\parallel \cong \pi g/4 - g^2 \quad (2)$$

with $g$ being the thickness-to-diameter ratio of a disk. Equation (2) is rewritten for Gd as $N_\parallel \cong 4.5 \times 10^{-8} d$ ($d$=number of layers),[23] if one assumes films with a diameter of a few mm yielding $N_\parallel \cong 5 \times 10^{-7}$ for an ideally flat 10-ML film. Smaller values have no physical meaning, and in real films $N_\parallel$ can only increase. With the lower limit of $N_\parallel$ fixed one can estimate the area under the paramagnetic side.[18,20] The result is that $\chi(T)$ for the 15–100-ML films can be simulated consistently using Eq. (2) and the critical exponent $\gamma = 1.24$.[18,20] For the 7–11-ML films, however, the area calculated with the previous $\gamma$ and $N_\parallel$ is about 10 times smaller than the experimental one leading to $\gamma > 1.24$. A detailed analysis of the quantitative fitting[23] will be given elsewhere.

Here we focus on the variation of $T_C$, that is to say of $T_{\max}$. The data points down to 5 ML in Fig. 2 show an almost perfect finite-size dependent $T_C(d) \sim d^{-1/\nu}$, which is in fair agreement with Eq. (1) with a reasonable parameter $C_0$. Another interesting point is that the widths $\delta T_C$ of the susceptibility peaks shown in Fig. 1 are larger for the very thin films than for the 40–100-ML films, even after the proper annealing cycle was used. As discussed later, this can be attributed to a larger strain distribution in the thin films. In Fig. 2 we also show the result (triangles) of our earlier study.[8] With the present improved analysis and the differences in deposition conditions discussed later on, we conclude that the old 0.8 and 1.6-ML films with a $T_C$ of approximately 270 K did not grow layer by layer, and that the stated thickness is a measure for the deposited mass only. These former $T_C(d)$ data can be explained if we assume the formation of islands of about 15 ML thickness and lateral dimensions of $\mu$m scale. The old data point for $d = 28$ ML ($\approx 90$ Å) is in agreement with the present result.

Gd films were grown on W(110), which was chosen as a substrate because of its excellent wetting characteristics and the nonexistence of Gd-W alloys.[24] The W(110) substrate is prepared Auger clean, that is no C or O signal is detected, with sharp low-energy electron-diffraction (LEED) spots for the W(110) surface.[8,12,25,26] Films were grown from a precleaned Ta crucible in a pressure of $< 2 \times 10^{-10}$ mbar during evaporation (base pressure $2 \times 10^{-11}$ mbar) at rates of 0.05 Å/s. No contamination of the Gd films was detectable by Auger spectroscopy before and after the measurements performed at $2 \times 10^{-11}$

mbar. The low pressure was mandatory to produce the high-quality films reported here. Evaporation at higher pressure, i.e., $1\times10^{-9}$ mbar did not yield the magnetic response reported here. Films were deposited at two different substrate temperatures of 300 and 720 K resulting in a completely different growth mode. Films deposited at 300 K grew layer by layer as well as could be determined by Auger spectroscopy.[26,27] The Gd(138 eV) Auger amplitude increases linearly as function of deposition time with characteristic slope changes at the completion of each monolayer.[27] A diffuse hexagonal LEED pattern of the as-deposited Gd(0001) films is seen for all thicknesses. Based on our Auger characterization island growth as the reason for broader LEED spots can be excluded as we discuss later on. After annealing to approximately 600 K the spots sharpen considerably. For films thicker than 100 Å a sharp hexagonal LEED pattern appears only after annealing at 800 K. For films less than 11 ML thickness, however, annealing above 600 K produces a LEED pattern consisting of a superposition of a good Gd(0001) and a weak diffuse W(110) pattern. Accordingly, the W Auger signal reappears and increases with respect to the Gd Auger signal upon further annealing at higher temperatures. Since alloying of Gd and W can be excluded, this indicates the breakup of the continuous film into islands. A quantitatively similar annealing dependence has been observed for Pt on W(110).[28] No Auger signal of W is observed for films thicker than 100 Å for all annealing steps. Auger analysis of the film growth at a substrate temperature of 720 K suggests a Stransky-Krastanov growth mode as described elsewhere.[8,12] Sharp LEED patterns of the Gd film are observed.[25] Annealing of these films to 900 K did not change the LEED patterns nor the Auger signal ratios. Before we turn to the description of the $\chi_{ac}$ signal changes caused by the annealing procedure, we need to point out that the susceptibility signal of films $\leq 10$ ML vanished after 24 h in a vacuum of $2\times10^{-11}$ mbar.[23] This may be of relevance to some other experiments in which only the surface layer is measured.

The annealing procedure yields dramatic changes in the ac susceptibility. In Fig. 3, we show the evolution of the $\chi_{ac}$ signal of an 11-ML film as it is annealed consecutively for 1 min at increasing temperatures. The as-deposited film shows a broad maximum, which is not shown here (for comparison see Fig. 1 in Ref. 18). Upon annealing to approximately 530 K the maximum shifts slightly, sharpens considerably and one obtains the largest peak shown in Fig. 3. As described earlier, no changes in the Auger spectrum are observed up to this temperature. Annealing up to 710 K decreases the $\chi_{ac}$ peak height, the maximum shifts by as much as 34 K and only a shallow peak at 283 K remains. This type of behavior is observed for all film thicknesses. Parallel monitoring of Auger showed the reappearance of the W signals, when films were annealed between 530 and 710 K.

The interpretation of these magnetic results is straightforward. Up to an annealing temperature of 530 K locally varying strains caused by misfit dislocations in the Gd(0001) film are relaxed.[18] This narrows the distribution of Curie temperatures,[18] which are caused by a variation in the local strains. One obtains a magnetically more homogeneous film with a sharper $\chi_{ac}(T)$ cusp. The sharpening of LEED spots in this temperature range confirms the idea that the film's homogeneity and coherence increases (to at least $\geq 100$ Å for the lateral length scale). Annealing above 530 K promotes cluster formation and at 710 K the film is believed to be broken up into large three-dimensional Gd islands with wide open areas in between. Such a film is also produced by deposition at a substrate temperature of 720 K. On the basis of our LEED and Auger analysis it cannot be decided, if these "open" areas are truly Gd free or if they are covered with at most 4 Gd monolayers. This limit is given by the mean free path of the W Auger electrons, which are seen for this type of film. Comparing our observations to scanning-tunneling-microscope studies of Pt on W(110),[28] it seems possible that uncovered W areas may exist. Above 530 K the change in the film geometry, i.e., island formation, increases the demagnetizing factor [Eq. (2)]. This reduces the experimentally observed susceptibility $\chi_{ac}(T)$ (Fig. 3) according to $\chi_{ac}(T)=\chi_{int}(1-N\chi_{int})$, in which $\chi_{int}$ is the true susceptibility.[18,20]

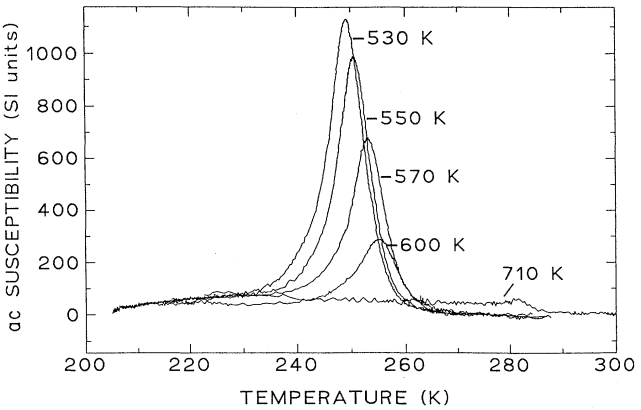


FIG. 3. $\chi_{ac}$ for 11 ML Gd(0001)/W(110) as function of temperature. The dependence on annealing between 530 and 710 K is shown. The sample was annealed in $5\times10^{-11}$ mbar for 1 min at each indicated temperature, cooled down, and measured.

The discussion of the changes in width and position of the susceptibility signal, that is the distribution of local $T_C$ values and the average $T_C$ of the film, involves two aspects. The finite-size effect reduces $T_C$ according to Eq. (1). It easily explains the large reductions of $T_C(d)$ as function of film thickness shown in Fig. 2. We would like to turn the argument around and propose in general: *if $T_C(d)$ does not follow Eq. (1)* (at least qualitatively) *one does not have layer-by-layer growth.* Consequently, the $T_C=283$ K of the 11-ML film annealed at 710 K (Fig. 3) is used to determine the mean height of the islands. The result is a reasonable height of 20–25 ML. In the same way our early data (triangles in Fig. 2) must be interpreted as a mass deposition equivalent, such that a nominally 1.6-ML film consists of islands about 15 ML thick. An additional aspect is the strain of the films as shown for example in the case of Ce.[29] The Curie temperature of Gd is reduced at a rate of $-1.4$ to $-1.8$ K/kbar,[30,31] if the crystal is compressed. A pressure of 5 kbar corre-

sponds to $\Delta T_C \approx -8$ K and a 1% compression. This offers an explanation for the measured behavior upon annealing to 530 K. Existing strains on the order of $\varepsilon = 1$–$2\%$ in the as-deposited film are relaxed and the width of the peak narrows to about 1 K for the thicker films. This corresponds to a realistic strain distribution of approximately 0.1%. Also the shift of the maximum by about 20 K ($\Delta\varepsilon \approx 2\%$) is possibly the result of the *accomodation of misfit dislocations,* which reduces the average compression and shifts the peak. However, the overall large shift of $T_C(d)$ as shown in Fig. 2 cannot be attributed to the pressure dependence of $T_C$. The larger signal width of the thinner films (Fig. 1) most likely arises from the presence of large inhomogeneous strains caused by steps and other defects at the interface. Due to the small thickness of the film these strains cannot relax when annealed to 530 K only.

In conclusion, this investigation shows a potential application for future work: It may be possible that from a finite-size scaling of $T_C(d)$ the layer growth and the number of layers will be detectable. In the present report 5–10-ML, Gd films grown layer by layer (no substrate Auger detectable) show a remarkable depression of $T_C$ following finite-size scaling. If the same films are annealed between 530 and 710 K afterwards, the W Auger signal reappears (cluster formation) at the same time as $T_C$ shifts to higher values (thicker films). We also show how sensitive the magnetic response is to moderate annealing (300–530 K) which induces the accommodation of misfit dislocations. As $\chi_{ac}$ is absolutely calibrated,[32] no free-fit parameters are left and we can deduce from the lower limits of $N_{\parallel}$ the average dimension of islands. Finally it is worthwhile to mention that to date only a few cases, namely Ni/Re,[7] Ni/W,[6] and Gd/W, have been published where $T_C(d)$ was determined over a large range of thicknesses (5–100 ML as reported here). In most of the other cases Co/Cu, Fe/Pd, Ni/Cu, etc., the experiments are limited to narrow temperature and thickness ranges because of interdiffusion problems.

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[32]With absolute calibration we mean that the susceptibility is not measured uncalibrated in arbitrary units. In more general context $\chi$ is the relative susceptibility defined as $\mu = 1 + \chi$.