Nature of the magnetic and structural phase transition in MnAs/GaAs(001)

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In the bulk the structural and magnetic phase transitions between α- and β-MnAs are coupled and proceed abruptly by first order. In heteroepitaxially constrained MnAs/GaAs(001) films, on the other hand, the two phases coexist at 10–40 °C and the magnetization decreases continuously with temperature. We present detailed magnetic measurements on MnAs/GaAs(001) in the phase transition region covering the ferromagnetic α phase, the paramagnetic β phase and the $\alpha+\beta$ coexistence region. The coexistence of two magnetically distinguishable types of α-MnAs around the onset of the coexistence region at 10 °C, the occurrence of metastable magnetic properties, and the absence of a Curie-Weiss peak in the susceptibility point to a first order of the magnetic phase transition also in thin films. The two types of α-MnAs are characterized by different coercivity and magnetic anisotropy, the latter due to a change in shape anisotropy of the striped phase.

Manganese arsenide was first studied by Heusler.[1] Its ferromagnetic α phase crystallizes in the hexagonal NiAs (B8$_1$) structure with alternating hexagonal planes of Mn and As atoms. At about 40 °C it transforms into the paramagnetic, orthorhombic β phase (B31).[2–4] The coupled magnetic and structural phase transition is of first order as confirmed by the appearance of latent heat.[5] The magnetic order discontinuously breaks down and the lattice spacing within the hexagonal plane (a axis) shrinks abruptly leading to a contraction in volume by $\sim 2\%$. Along the c axis the spacing remains unchanged.[6] As pointed out already by Guillaud, the α/β-phase transition seems to be no Curie point, since the extrapolation of the temperature dependence of the spontaneous magnetization would lead to a disappearance of the magnetization at about 130 °C.[2] At that temperature the orthorhombic β-MnAs is also transforming to the hexagonal, paramagnetic (B8$_1$) γ phase.[6] This fact and the anomalous behavior of the inverse susceptibility of the β phase, i.e., between 40 and 130 °C, led to the speculation that β-MnAs is antiferromagnetic;[2] however, no long range order was detected by means of neutron diffraction.[7] Within the γ phase, the inverse susceptibility is Curie-Weiss-like, i.e., linear.[2] In view of the preceding discussion, it seems to be plausible that the α/β-phase transition is fundamentally different from a Curie point behavior where the magnetic long range order disappears due to thermally activated fluctuations.

Recently, there is increasing interest in MnAs since it became possible to grow high quality epitaxial films on Si(001) and GaAs(001).[8–10] Epitaxial MnAs films are not only interesting for technological applications such as spin injection[11] and magnetologic,[12] but also from a fundamental point of view. The epitaxial constraints imposed by the substrate significantly alter the α/β-phase transition. For example, in the case of MnAs/GaAs(001) the phase transition no longer proceeds abruptly as in the bulk. Instead, a strain-stabilized pattern of coexisting α- and β-MnAs stripes along the c axis ("$\alpha+\beta$ region") is formed in the broad temperature range of 10–40 °C.[13,14] For a 60-nm-thick MnAs film it has been shown that the magnetization continuously decreases in the

coexistence region until the entire system is in the paramagnetic phase around 40 °C.[15] From comparison with x-ray diffraction data[16] it seems that the decrease in magnetization is mainly due to the decreasing amount of the ferromagnetic α phase, but an unambiguous correlation between the experimental quantities is not straightforward. Therefore it is not clear so far, whether the ferromagnetic transition is of first or second order, since the decrease of magnetization can either be due to the drop in α phase because of the involved variable stress conditions[15] or due to temperature dependent disorder.

In this study we focus on the clarification of the nature of the magnetic phase transition of heteroepitaxially constrained MnAs film on GaAs(001). Specifically, we investigated the magnetic anisotropy, coercivity and magnetic susceptibility, whose temperature and/or time dependence provide deeper insight into the order of the phase transition. Our experimental results reveal that the magnetic phase transition of MnAs films is also coupled to the structural one as in bulk and it proceeds by first order.

The MnAs films on GaAs(001) are prepared under As-rich growth conditions[10] yielding predominantly the so-called A orientation with MnAs($\bar{1}100$)$\|$GaAs(001) and MnAs[0001](c axis)$\|$GaAs[$1\bar{1}0$]. Accordingly, the easy axis of magnetization (MnAs[$11\bar{2}0$], a axis) lies in the film plane. The measurements were performed in a thickness range of 40–120 nm, and are exemplarily discussed by means of a 60 nm thick film. The temperature was ranged from 0 to 50 °C thus including the pure α and β phases of MnAs as well as the striped $\alpha+\beta$ region. The magnetic properties were investigated by ferromagnetic resonance (FMR) spectroscopy at a microwave frequency of 9 GHz and a commercial superconducting quantum interference device (SQUID) magnetometer. We also employed the SQUID magnetometer as well as a mutual inductance bridge[17] to measure the quasistatic zero-field susceptibility over a broad temperature range. The amplitude of the external oscillatory field ranged from 3.5 Oe down to 17 mOe.
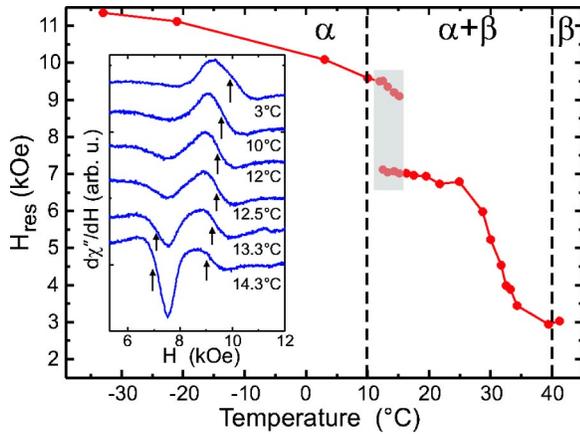
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FIG. 1. (Color online) FMR of 60 nm MnAs/GaAs(001): Resonance field (H_{res}) as function of temperature with an external field applied perpendicular to the film plane. The transition temperatures from the α to the striped $\alpha+\beta$ region and to the β phase are indicated by the dashed lines; the coexistence range of the two types of α-MnAs (see text) is shaded in gray. The inset shows the FMR spectra taken at different temperatures with the two resonance fields marked by arrows.

The presence of magnetic anisotropy and magnetic hysteresis are characteristics of ferromagnetism. With FMR spectroscopy, the magnetic anisotropy of α-MnAs can be determined. Figure 1 shows FMR spectra of 60 nm MnAs/GaAs(001) around 10 °C (inset) and the resulting resonance field H_{res} (marked by the arrows in the inset) as a function of temperature. The respective value of H_{res} is given by the FMR resonance condition relating H_{res} to the microwave frequency $\omega = 2\pi f$. In our experiments the external field $\vec{H}$ was applied perpendicular to the film plane. Under the assumption that $\vec{H}$ is large enough to align the magnetization $\vec{M}$ parallel to the film normal, the resonance condition is given by

$$\frac{\omega}{\gamma} = \{[H - (M_{\text{eff}}^{\perp} - M_{\text{eff}}^{\parallel})][H - M_{\text{eff}}^{\perp}]\}^{1/2}. \tag{1}$$

Here $\gamma = g \cdot \mu_B / \hbar$ is the gyromagnetic ratio, $M_{\text{eff}}^{\perp} = N_b M - 2K_{2\perp}/M$ and $M_{\text{eff}}^{\parallel} = N_a M - 2K_{2\parallel}/M$ are the effective anisotropy fields out of and in the film plane, respectively. They include the intrinsic anisotropy fields $2K_{2i}/M$ and a contribution due to the demagnetizing field ($N_i M$). $M_{\text{eff}}^{\parallel}$ is a measure of the anisotropy between the hexagonal c axis and the a axis, whereas $M_{\text{eff}}^{\perp}$ describes the anisotropy between the c axis and the film normal (b axis). For $M_{\text{eff}}^{\perp} < 0$ (>0) an in-plane (out-of-plane, b axis) magnetization is preferred, whereas $M_{\text{eff}}^{\parallel} < 0$ (>0) then favors the a axis (c axis). For our MnAs films it has been shown that both quantities are negative and $M_{\text{eff}}^{\parallel}$ is larger than $M_{\text{eff}}^{\perp}$ so that the a axis is the easy axis of magnetization.[18] Note that without magnetic anisotropy (i.e., $M_{\text{eff}}^{\perp} = M_{\text{eff}}^{\parallel} = 0$) Eq. (1) reduces to $\omega/\gamma = H$ which is the well-known condition for an isotropic system. For the given microwave frequency of $f = 9$ GHz and for a "spin-only" g factor of 2, H_{res} is 3.2 kOe, in the following referred to as the "isotropic value." From Eq. (1) it follows
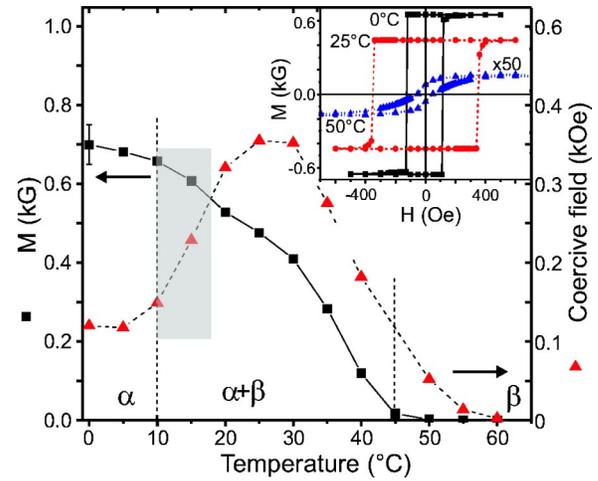

FIG. 2. (Color online) Magnetization (squares) and coercivity (triangles) of 60 nm MnAs/GaAs(001): The data are taken from complete hysteresis loops measured by SQUID as a function of the temperature (see inset). Whereas the magnetization decreases continuously with increasing the temperature, the coercive field is increased by a factor of three in the $\alpha+\beta$ region.

that for a given microwave frequency the M_{eff}^{i} shift the resonance field away from the isotropic value. In the case of negative M_{eff}^{i} the resonance field increases compared to the isotropic value. Thus, the resonance line below 10 °C at fields around 10 kOe (see Fig. 1) indicates that the out-of-plane direction is a magnetically hard axis. The resonance field shifts towards the isotropic value with increasing temperature revealing decreasing magnetic anisotropy. However, at about 10 °C, a second, coexisting line appears at a clearly decreased resonance field of 7 kOe. At this temperature, obviously two magnetically distinguishable types of ferromagnetic MnAs coexist which are characterized by different magnetic anisotropy. For the homogeneous α-MnAs film (termed α_F-MnAs) the demagnetizing factors are $N_a = N_c = 0$, and $N_b = 4\pi$ (indices refer to crystallographic axes). α-MnAs in the $\alpha+\beta$ region (termed α_S-MnAs), on the contrary, has a different demagnetizing factor of $N_a = 0.16 \cdot 4\pi$, $N_c = 0$, and $N_b = 0.84 \cdot 4\pi$ due to the finite width of the stripes.[18] Using the anisotropy values (K_{2i}) from Ref. 18 and the two different sets of demagnetizing factors, Eq. (1) yields indeed a change of H_{res} that quantitatively agrees with the observed difference of about 3 kOe. Accordingly, the two different anisotropies are the result of the different spatial distribution of α-MnAs within the film. We interpret this as a coexistence of α_F-MnAs which is magnetically identical to a homogeneous film and α_S-MnAs located in the striped $\alpha+\beta$ region. Note that α_F and α_S are not different phases or different crystallographic structures of MnAs, but merely exhibit different magnetic properties due to the changed spatial distribution. There is a small temperature range where α_F- and α_S-MnAs coexist (shaded in Fig. 1). At higher temperatures only the line of α_S-MnAs is observed, and the signal continuously decreases and approaches to that of paramagnetic β-MnAs at about 40 °C.

Figure 2 collects SQUID results of 60 nm thick MnAs/GaAs(001). It shows the temperature dependence of the
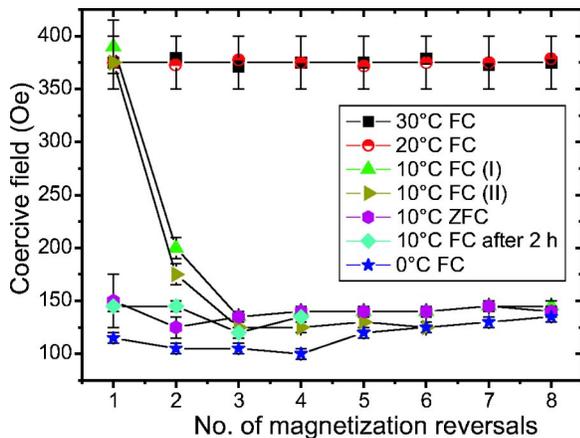
FIG. 3. (Color online) Metastable magnetic properties of 60 nm MnAs/GaAs(001): The coercivity at different temperatures is plotted as a function of the number of magnetization reversals, deduced from subsequently measured magnetic hysteresis loops. Prior to each sequence of hysteresis loops at a given temperature the sample was heated to 50 °C to establish the paramagnetic β phase as a reproducible initial state. Then the sample was cooled either in zero field (ZFC) or in an external field of 5 kOe (FC).

magnetization (squares) as well as of the coercivity (triangles), both quantities deduced from magnetic hysteresis loops along the easy a axis. The hysteresis loops included in the inset of Fig. 2 are taken at 0 °C, 25 °C, and 50 °C (data at 50 °C are enlarged by a factor of 50) and correspond to α_F-, α_S-MnAs, and to the almost completely formed β phase, respectively. Note that below 50 °C all loops are squarelike indicating strong magnetic interaction between α_F- and/or α_S-MnAs. The experimental magnetization at 0 °C is 0.70(5) kG [corresponding to an effective moment of 2.6(2) μ_B per Mn atom] in good agreement with the bulk[19] and continuously decreases with temperature. Surprisingly, the coercive field of α_S-MnAs between 20 and 30 °C is larger by a factor of three compared to α_F-MnAs at 0 °C, whereas usually the coercivity decreases with increasing temperature. Therefore the temperature dependence of the coercivity allows to distinguish between α_S- and α_F-MnAs. Upon approaching the β phase the magnetization drops to very small values, whereas the coercivity of the remaining α_S-MnAs is still relatively high (see also hysteresis at 50 °C in the inset). Obviously the vanishing magnetization is not accompanied by a comparable decrease of coercivity as usually observed when approaching the Curie temperature. The residual tiny hysteresis loops observable above 50 °C are more rounded than the one in the inset of Fig. 2. We attribute them to a small fraction of α-MnAs grains in an altered strain state, e.g., at defects or at the interface, which transform at even higher temperatures, however, this fraction is below 0.5% of the entire film.

Our time- and field-dependent SQUID investigations provide further clues on the phase transition. In Fig. 3 the coercive field measured at various temperatures is plotted as a function of the number of magnetization reversals. Prior to each sequence of hysteresis loops at a given temperature the sample was heated to 50 °C to establish the paramagnetic β

phase as a reproducible initial state. Then the sample was cooled down to temperatures between 30 and 0 °C in an applied external magnetic field of 5 kOe and four hysteresis loops were recorded in a row, corresponding to eight magnetization reversals. The coercivity of α_S-MnAs at 20 and 30 °C is about 375 Oe for each reversal (Fig. 3, squares, circles), whereas the coercivity of α_F-MnAs measured at 0 °C is about 100 Oe (Fig. 3, asterisks). Interestingly, the hysteresis recorded at 10 °C, i.e., in the region where the two ferromagnetic resonance lines are detected, reveals a coercive field that is initially as high as at 20 and 30 °C. However, it reduces to the value measured at 0 °C after a complete hysteresis cycle. The shaded area in Fig. 2 indicates the interval in which the measured coercivity ranges, whereas the respective data points represent the average value. The metastable behavior is reproducible, excluding irreversible structural changes due to the cooling and heating procedure (Fig. 3, triangles I and II). Note that the coercive field is reduced after the first reversal leading to an asymmetric hysteresis loop as in exchange biased systems. Subsequent loops then are symmetric. If the sample is cooled in zero field, the high coercivity value of α_S-MnAs is not observed (Fig. 3, hexagons) and each reversal has the same low coercivity of α_F-MnAs. From the measurements we conclude that the resulting asymmetric first hysteresis loop at 10 °C and the field-cooled (FC) vs zero-field-cooled (ZFC) behavior cannot be explained by exchange bias of the sample as suspected earlier[20] but represents a metastable magnetic behavior. This is further supported by the time dependence of the coercive field. Upon cooling the sample in applied field down to 10 °C and recording the first hysteresis after a two hours delay (Fig. 3, diamonds) only the low coercive field values are obtained. Thus, the transformation of the α_S- to the α_F-MnAs is metastable with respect to both time and field in a small temperature range around 10 °C.

Above 20 °C the continuous decrease of anisotropy (Fig. 1) and magnetization (Fig. 2) seems to suggest a Curie-point behavior for the disappearance of the ferromagnetic order. However, the unusually high coercivity of the remaining small fractions of α_S-MnAs at 50 °C and the observed metastability contradict a Curie-point behavior. To get further experimental support for this interpretation we measured also the quasistatic zero-field susceptibility χ both with SQUID and the mutual inductance bridge. At the Curie temperature T_C a clear Curie-Weiss peak of χ due to fluctuations can typically be expected. While a small susceptibility peak is visible around 40 °C using the largest modulation amplitude of 3.5 Oe (not shown), we were not able to detect any susceptibility peak at smaller oscillating external fields down to 17 mOe. Since reliable χ values are only obtained at small external oscillatory fields,[21] the χ signal observed at higher oscillatory field is an artifact originating from reversal of the magnetization of MnAs regions having a coercivity smaller than the oscillatory field, i.e., regions where the α-MnAs is close to the structural transition to the β phase, thus having vanishing coercivitiy. The absence of a Curie-Weiss peak therefore points towards the absence of a Curie-point behavior.

In view of our experimental findings we conclude that the

disappearance of ferromagnetic order in MnAs/GaAs(001) proceeds by a first order phase transition. FMR and SQUID reveal the occurrence of two magnetically distinguishable spatial distributions of ferromagnetic α-MnAs: On the one hand, below 10 °C α_F-MnAs with low coercivity, and on the other hand, above 20 °C striped α_S-MnAs with high coercivity and a decreased effective anisotropy due to the different spatial distribution. Note that the existence of striped α_S-MnAs is equivalent to the existence of β-MnAs. The coexistence of α_F- and α_S-MnAs observed by FMR therefore implies that a nucleation process is necessary for the formation of the β phase at 10 °C, which is characteristic of first order phase transitions. The metastability between α_F- and α_S-MnAs observed in the SQUID measurements provides further evidence for a nucleation step upon forming α-MnAs during cooling and corroborate a first order character of the phase transition between α- and β-MnAs. In addition, the FMR and SQUID results are consistent with the absence of a Curie-Weiss peak in the susceptibility. Although the magnetization and anisotropy have the appearance of a Curie-like behavior, the temperature where the magnetization vanishes does not have the specific properties of a Curie temperature (T_C). Therefore, it is merely a transition temperature (T_c) where a first order structural phase transition takes place, in the course of which the ferromagnetic order breaks down.

As discussed in Ref. 14 the broad temperature range for the coexistence of α- and β-MnAs can be understood by taking the strain state of the film into account. Combining the experimental results of Refs. 6 and 15 allows us to determine the strain state of our MnAs film quantitatively. The temperature dependence of the lattice constant along the a axis of bulk MnAs, measured in Ref. 6, shows that the lattice spacing of MnAs at the film preparation temperature of 250 °C is larger than in β-MnAs around 50 °C and smaller than in α-MnAs at about 10 °C. Assuming that the misfit strain is nearly relaxed at the preparation temperature—as presumed in Ref. 10—cooling of the sample leads to a tensile strain in β-MnAs because the thermal expansion coefficient of MnAs is by about one order of magnitude larger than that of the GaAs substrate.[22] In α-MnAs, on the contrary, the resulting thermal strain along the a axis is compressive due to the increase in lattice spacing. It is known for bulk MnAs that compressive strain—equivalent to external pressure—leads to a reduction of the phase transition temperature.[19] According to Menyuk *et al.*[19] the lower α/β-phase transition temperature of 10 °C observed in the film, compared to 40 °C of bulk, corresponds to compressive stress of -0.1 to -0.15 GPa. Recently we showed that the difference in stress between the α and the β phase is 0.59 GPa.[15] Therefore β-MnAs is under tensile strain and nucleation of the β phase at 10 °C is accompanied by a reduction of the net compressive stress. At about 20 °C the net stress becomes tensile. α_S-MnAs transforms into the β phase at the bulklike transition temperature of 40 °C indicating that net tensile stress obviously has no significant influence on the phase transition temperature.

In conclusion, although the temperature dependence of the magnetization of MnAs/GaAs(001) differs significantly from bulk, our detailed experimental study reveals that the nature of the phase transition is identical. The heteroepitaxial constraints imposed by the substrate are responsible for a change of various magnetic properties such as anisotropy, coercivity and a broadening of the phase transition region. However, despite the continuous decrease of the magnetization, the coupled phase transision proceeds by first order.

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