Biaxial Strain in the Hexagonal Plane of MnAs Thin Films: The Key to Stabilize Ferromagnetism to Higher Temperature

V. Garcia,[1,*] Y. Sidis,[2] M. Marangolo,[1] F. Vidal,[1] M. Eddrief,[1] P. Bourges,[2] F. Maccherozzi,[3] F. Ott,[2] G. Panaccione,[3] and V. H. Etgens[1]

[1]*Institut des NanoSciences de Paris, INSP, Université Pierre et Marie Curie-Paris 6, Université Denis Diderot-Paris 7, CNRS UMR 7588, Campus Boucicaut, 140 rue de Lourmel, 75015 Paris, France*

[2]*Laboratoire Léon Brillouin, CEA/CNRS, F-91191 Gif-sur-Yvette Cedex, France*

[3]*TASC Laboratory, INFM-CNR, in Area Science Park, S.S. 14, Km 163.5, I-34012 Trieste, Italy*

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The α-β magnetostructural phase transition in MnAs/GaAs(111) epilayers is investigated by elastic neutron scattering. The in-plane parameter of MnAs remains almost constant with temperature from 100 to 420 K, following the thermal evolution of the GaAs substrate. This induces a temperature dependent biaxial strain that is responsible for an α-β phase coexistence and, more importantly, for the stabilization of the ferromagnetic α phase at a higher temperature than in the bulk. We explain the premature appearance of the β phase at 275 K and the persistence of the ferromagnetic α phase up to 350 K with thermodynamical arguments based on the MnAs phase diagram. It results that the biaxial strain in the hexagonal plane is the key parameter to extend the ferromagnetic phase well over room temperature.

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The first-order phase transition near room temperature and the magnetic properties of bulk manganese arsenide (MnAs) have been intensely investigated in the last century [1–3]. Recently, the possibility of epitaxial growth of MnAs thin films on standard semiconductors such as GaAs has renewed interest in MnAs for spintronics related research [4]. Indeed, high quality epilayers of MnAs can be grown on GaAs substrates with a very low reactivity between the ferromagnet and the semiconductor [4–7]. Also, electrical spin injection in GaAs has been recently demonstrated with MnAs [8] and spin-polarized tunneling performed with MnAs/GaAs/MnAs junctions [9]. Even if MnAs has a great advantage over common transition metals in terms of reactivity with GaAs, its Curie temperature, associated with the first-order ferromagnetic-paramagnetic phase transition, is only slightly above room temperature. A great challenge is to understand this phase transition to maintain ferromagnetism in MnAs to higher temperature.

Bulk MnAs is a room temperature ferromagnetic and metallic compound up to $T_C = 313$ K where the first-order phase transition from hexagonal (α phase, NiAs type) to orthorhombic (β phase, MnP type) is accompanied by a ferromagnetic-paramagnetic transition [2,10]. A large volume contraction of about 2% is observed at T_C and this contraction occurs mainly in the hexagonal basal plane. A hydrostatic pressure of a few kilobars can however stabilize the β phase over the α phase below T_C [2] [see Fig. 3(a)].

Interestingly, in the case of MnAs epilayers grown on GaAs substrates, the epitaxial strain disturbs the first-order phase transition. MnAs epilayers grown on GaAs(100) substrates have been deeply investigated. The epitaxy is sketched in Fig. 1(b) with the hexagonal c axis aligned in the film plane. Kaganer *et al.* [11] have shown that the epitaxial strain leads to the α-β phase coexistence to minimize the elastic energy. Strain dependent magnetic properties were analyzed by Das *et al.* [12] and Iikawa *et al.* [13] in the case of MnAs epitaxied on GaAs(001). The unit cell of the ferromagnetic α phase was found to be orthorhombically distorted, as the hexagonal plane of MnAs lies out of the substrate surface. This temperature dependent structural modification induces the early appearance of the paramagnetic β phase at $T_C^{(1)} = 273$ K [14]. Minimization of elastic energy makes the two phases coexist up to $T_C^{(2)} = 315$ K, which is almost the same transition temperature as for the bulk material.

In order to probe the effect of a biaxial strain on this transition, we have grown 100 nm thick MnAs(001) thin films on GaAs(111)B substrates. The films display a single epitaxy with the hexagonal c axis along the growth direction and the hexagonal plane over the hexagonal (111) surface of the GaAs substrate [Fig. 1(a)] [6]. Magnetic measurements reveal a bulklike saturation magnetization (900–950 emu/cm^3) at low temperature with high remanence and low coercive fields [6]. The critical temperature is significantly enhanced with a Curie point (deduced from $\partial M/\partial T$ curve) of 335 K and a magnetization that is detected up to 350 K. X-ray magnetic circular dichroism (XMCD) spectra collected at the APE beam line (Elettra synchrotron, Trieste) attest that ferromagnetism is stable up to 340 K. No significant modification of the α-pure XMCD line shape is detected from 100 to 340 K [Fig. 1(c)]: this implies that persistent ferromagnetism can be ascribed to the α phase. A detailed discussion about absorption spectra is beyond the scope of this Letter and will be published elsewhere.

In this Letter, we show magnetostructural characterizations of MnAs(001) thin films by neutron diffraction experiments in a wide range of temperature (100–420 K).

The decisive advantage of neutron scattering is that it enables us to transmit through the substrate and measure directly the in-plane and growth-axis lattice parameters from selected Bragg reflections. The films display large in-plane deformations compared to the bulk, inducing an α-β phase coexistence from 275 to 350 K. The mean in-plane parameter [15] is almost constant from 100 to 420 K and follows the expansion coefficient of the GaAs substrate. We estimated the strain induced in each phase from the measured deformations in the plane. Considering the biaxial stress equivalent to a hydrostatic pressure, we have succeeded in explaining the early appearance of the β phase ($T_C^{(1)} = 275$ K) and the high temperature preservation of the α phase ($T_C^{(2)} = 350$ K). Finally, we conclude that the stability of the ferromagnetic phase is strongly dependent on the epitaxial strain in the basal plane.

Elastic neutron scattering measurements were performed on the triple-axis spectrometer 4F1, installed on a cold neutron beam at the reactor Orphée in Saclay, France. A monochromatic neutron beam was obtained with a double monochromator, made of pyrolytic graphite in (002) reflection [PG(002)], and filtered by cold beryllium to eliminate higher-order contamination. The diffracted beam was analyzed by a PG(002) crystal, with 40′ collimators on each side. The initial neutron wave vector was set to $k_i = 1.2$ Å^{-1}. A 100 nm thick MnAs thin film was grown by molecular beam epitaxy on a GaAs(111)B substrate as described elsewhere [7] and capped *in situ* with a thin gold layer (5 nm) to prevent oxidation. The sample with a surface of about 2 cm^2 was mounted in an aluminum can containing helium exchange gas and fixed on the cold finger of a closed cycle refrigerator, operating from 100 to 420 K. The sample was aligned so that (100), (101), and (002) Bragg reflections of the hexagonal phase were accessible. We monitored the temperature dependence of the in-plane and out-of-plane parameters, from 100 to 420 K; each temperature point was preceded, after temperature stabilization ($\approx$30 min), by a rocking scan on GaAs(111) reflection.

The triple-axis spectrometer resolution [16] was adjusted from the (111) and (1$\bar{1}$0) reflections of the GaAs substrate which we assume to be a perfect crystal. We find that in both in-plane and out-of-plane directions the experimental resolution is defined by a Gaussian function with a full width at half maximum (FWHM) of $\sim$0.01 Å^{-1}. The analysis of the neutron data was performed self-consistently around three different wave vectors: (100), (101), and (002) of the hexagonal phase. Bragg peaks were fitted with Gaussian functions convoluted with the experimental resolution function. The intensities, widths, and positions of the Gaussian functions are free parameters in our analysis. Out-of-plane measurements were performed along α-(002) [and β-(200)] peaks. They show an almost constant intrinsic width from 100 to 420 K, corresponding to a correlation length of 80 nm perpendicular to the film, in good agreement with the film thickness (100 nm). In-plane measurements reveal an in-plane correlation length of 70 to 80 nm. Three temperature cycles (100 K $\rightarrow$ 420 K $\rightarrow$ 100 K) were performed showing very reproducible structural parameters without any hysteresis between heating and cooling.

Figure 1(d) displays the temperature dependence of the radial scan along α (100) including the β-(011)(002) doublet. The β phase is found to nucleate around 275 K and the α phase is present up to 350 K. In this temperature range, the neutron data cannot be described by a single peak anymore. Owing to their intrinsic widths, the two Gaussian functions associated with the Bragg peaks of the α and β phases heavily overlap, but the peak positions can still be determined accurately [see magnifications in Fig. 1(d)].

The temperature evolution of the lattice parameters of MnAs epitaxied on GaAs(111)B are compared to bulk MnAs values [17] in Fig. 2. Strong epitaxy-induced modifications of MnAs thin films parameters are observed. At low temperatures the in-plane α phase MnAs unit cell is compressed as compared to the bulk; the strain remains

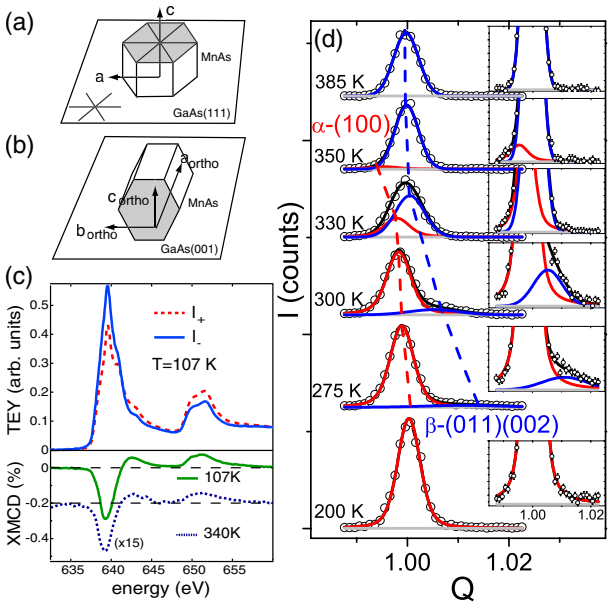

FIG. 1 (color online). Schemes of MnAs epitaxy (a) on GaAs(111)B and (b) on GaAs(001) with an orthorhombically distorted unit cell. (c) Mn $L_{2,3}$ x-ray-absorption spectroscopy spectra for antiparallel (dotted line) and parallel (continuous line) helicity and magnetization, at 107 K; difference spectrum (XMCD) ($I_+ + I_-$) normalized to the L_3 peak of the summed spectra ($I_+ - I_-$) and scaled for photon polarization (70%) and incidence angle (45°), at 107 K (solid line) and 340 K (dotted line). Sample magnetization lies in plane. The 340 K spectrum is multiplied by 15 for clarity. The line shape remains unchanged at high temperature. (d) Temperature dependence of the neutron diffraction patterns of MnAs (100 nm)/GaAs(111)B for in-plane (100)-α and corresponding (011)-(002)-β reflections. The dashed lines following the maxima of each Bragg peak are only guides for the eyes. Magnifications of the patterns are shown in the insets.

stable up to the appearance of the β phase at 275 K [Fig. 2(a)]. As already observed by Mattoso *et al.* [6], the β phase displays a strong temperature dependence of its lattice parameter in the coexistence temperature range. The nucleation of the β phase allows the α phase in-plane parameter to relax towards its bulk value. A tensile strain is observed in the film plane for the pure β phase and it progressively disappears at higher temperature [Fig. 2(a)].

Around each of the three different wave vectors of the hexagonal phase (100), (101), and (002) we further computed the neutron scattering cross section associated with Bragg reflections of the paramagnetic β phase and ferromagnetic α phase, assuming a temperature independent magnetization of $3.6\mu_B$ per Mn [18]. This intensity is proportional to the volume fraction of each phase in the film. Thus for any wave vector, the temperature dependence of the total norm of the measured α and β peaks allows us to determine the volume fraction of each phase. Figure 2(c) shows the temperature dependence of the volume fraction of the α phase, deduced from the temperature dependencies of the total norm of the peak(s) measured around three different wave vectors of the hexagonal phase (100), (101) and (002) [Fig. 2(d)].

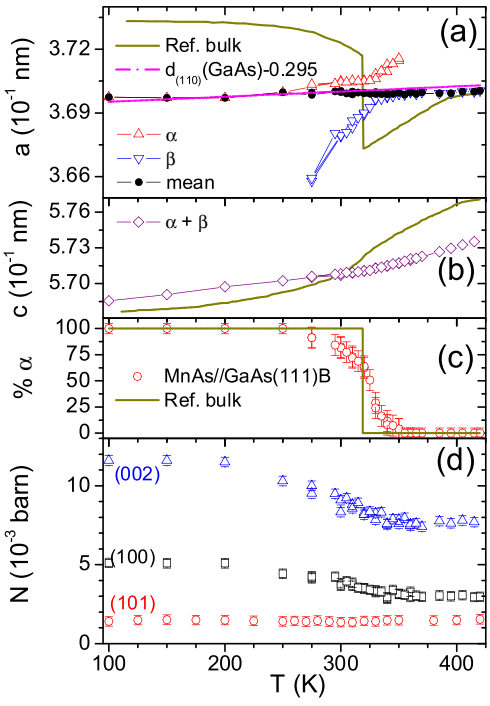

FIG. 2 (color online). Temperature dependence of structural parameters of a 100 nm thin film of MnAs grown on GaAs(111)B substrate: (a) in-plane parameter for both phases deduced from neutron diffraction experiments on MnAs(100), (b) out-of-plane parameter deduced from scans along MnAs(002). The in-plane and out-of-plane parameters of bulk MnAs (adapted from Ref. [17]) are added. (c) α phase fraction deduced from (d) the integrated intensity of the spectra along MnAs(100), (101), and (002). The mean in-plane parameter calculated from this α phase fraction is added in (a) together with the evolution of GaAs parameter.

The conservation of the thin film lateral size leads to a thermal evolution that is not as free as it is possible for a bulk single crystal. Since our films are continuous and epitaxied, the temperature evolution of the mean lateral lattice spacing in the film should follow the thermal lattice expansion coefficient of the GaAs substrate. This condition is fulfilled as shown in Fig. 2(a), where we compare the measured in-plane thermal evolution of GaAs (d_{110}) with the mean lateral lattice spacing of MnAs, obtained by considering the evaluated volumic fraction of each phase at a given temperature [Fig. 2(c)]. In other words, MnAs thin films are almost fully relaxed at the growth temperature ($T \cong 500$ K) because the large lattice mismatch (7%–8%) is released by dislocations, but when temperature is reduced, no more dislocations can be generated and the ''frozen'' films undergo two lateral size preserving phase transitions.

The out-of-plane parameter increases continuously with temperature, similarly to bulk MnAs [see Fig. 2(b)]. The temperature evolution of the in-plane parameters of the thin films can be quantitatively compared to those of bulk MnAs to evaluate the strain incorporated in the material. Cooling the sample from growth temperature, an in-plane progressive tensile strain is introduced in MnAs. In the following, we put forth the hypothesis that the biaxial strain in the hexagonal plane of MnAs is the leading parameter for the pressure dependencies of $T_C^{(1)}$ and $T_C^{(2)}$ reported by Menyuk *et al.* [Fig. 3(a)] [2].

Consequently, the persistence of the α phase at higher temperature ($T_C^{(2)}$) in MnAs/GaAs(111)B thin films and the early nucleation of the β phase at lower temperature ($T_C^{(1)}$) can be understood by thermodynamical considerations. For example, at 360 K an in-plane lattice expansion of $+0.36\%$ is observed in the β phase corresponding to a tensile stress of 1.7 kbar. On the contrary, at 250 K an in-plane lattice compression of -0.82% is observed in the α phase that corresponds to a compressive stress of 3.8 kbar [19]. From Fig. 3(a), the negative slope of $T_C^{(2)}$ with pressure ($\partial T_C^{(2)}/\partial P = -20$ K/kbar with $T_{C,0}^{(2)} = 307$ K, [2]) is coherent with the enhancement of $T_C^{(2)}$ with tensile strain (negative pressure). In parallel, the compressive strain in the α phase lowers $T_C^{(1)}$ ($\partial T_C^{(1)}/\partial P = -15$ K/kbar with $T_{C,0}^{(1)} = 313$ K, [2]).

On the other hand, since MnAs thin films grown on GaAs(001) are virtually strain free in the basal plane of the β phase above the phase transition [12], the critical temperature ($T_C^{(2)}$) is not enhanced compared to the bulk material.

Going through details, we can estimate the two critical points where the phase transition should proceed given the strain incorporated by calculating the in-plane stress in both phases for each experimental point [Fig. 3(b)]. We deduced a first critical point at $T_C^{(1)} = 265$ K corresponding to the onset of the α to β phase transition and a second one at $T_C^{(2)} = 347$ K corresponding to the onset of the β to

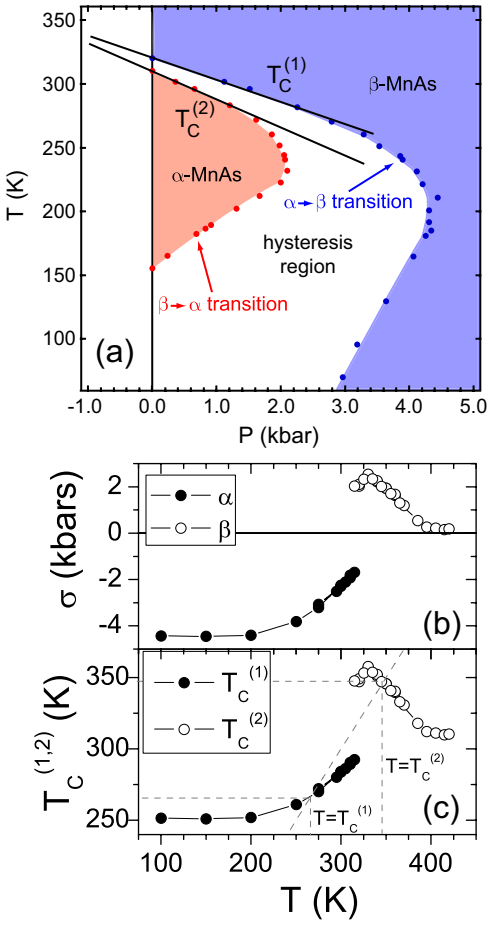

FIG. 3 (color online). (a) Temperature-pressure phase diagram of bulk MnAs adapted from Ref. [2]. Pressure dependencies of the transition temperatures of -15 K/kbar and -20 K/kbar are deduced for $T_C^{(1)}$ and $T_C^{(2)}$, respectively. (b) Calculated in-plane stress deduced from the lattice deformation compared to bulk values in Fig. 2(a). (c) Calculated critical temperature considering the in-plane stress equivalent to pressure: the critical points are deduced from the intersection between the experimental points and the straight line $T = T_C$.

α phase transition [Fig. 3(c)]. We observe a very good agreement between the calculated critical point and the experimental α-β phase coexistence observed between 275 and 350 K. When the sample is heated, from the first critical point $T_C^{(1)} = 265$ K, the β phase nucleation induces a partial relaxation of the compressive strain in the ferromagnetic phase and the transition temperature is increased [Fig. 3(c)]. This behavior explains why, in the epitaxial system, a phase coexistence is observed instead of a total α-β phase transition.

The general agreement between the phase diagram of bulk MnAs and the pressure induced by the biaxial strain in MnAs(001) thin films leads to the conclusion that this strain is the key parameter for the α-β phase transition. We demonstrate that biaxial strain in the hexagonal plane of MnAs thin films can significantly enhance the stability of the ferromagnetic phase with temperature. We anticipate that larger $T_C^{(2)}$ critical temperature may be obtained by increasing the tensile strain in the film plane. This could be achieved by applying external strain to the substrate similarly to the experiments performed by Iikawa *et al.* [13]. For example, if we apply a tensile strain of 0.5% in the film plane, it would be possible to increase the critical temperature to $T_C^{(2)} = 373$ K [20]. Another way to enhance ferromagnetism to higher temperature is to grow nonrelaxed MnAs(001) thin films on a small mismatched (111) cubic substrate where the MnAs hexagonal basal plane would remain under tensile strain.

*Present address: Department of Materials Science, University of Cambridge, Cambridge, CB2 3QZ, UK. vg253@cam.ac.uk

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