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

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The first-order phase transition near room temperature and the magnetic properties of bulk manganese arsenide (MnAs) have been intensively investigated in the last century [1, 2, 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, 5, 6, 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 temperatures.

Bulk manganese arsenide (MnAs) is a room temperature ferromagnetic and metallic compound up to $T_C=313$ K where the first-order phase transition from hexagonal ($\alpha$-phase, NiAs type) to orthorhombic (\(\beta\)-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. An hydrostatic pressure of a few kbars can however stabilize the $\beta$-phase over the $\alpha$-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 Figure 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 $\alpha-\beta$ phase coexistence to minimize the elastic energy. Strain dependent magnetic properties were analyzed by Das et al. [12] and Ikawa et al. [13] in the case of MnAs epitaxied on GaAs(001). The unit cell of the ferromagnetic $\alpha$-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 $\beta$-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 bulk like 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 is detected up to 350 K. X-ray magnetic circular dichroism (XMCD) spectra collected at the APE beamline (Elettra synchrotron, Trieste) attest that ferromagnetism is stable up to 340 K. No significant modification of the $\alpha$-pure XMCD lineshape is detected from 100 K to 340 K [Fig. 1(c)]: this implies that persistent ferromagnetism can be maintained ferromagnetism in MnAs to higher temperature.

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ascribed to the $\alpha$-phase. A detailed discussion about absorption spectra is beyond the scope of this letter and will be published elsewhere.

In this letter, we show magneto-structural characterizations of MnAs(001) thin films by neutron diffraction experiments in a wide range of temperature (100 K - 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 $\alpha \rightarrow \beta$ phase coexistence from 275 K to 350 K. The out-of-plane parameter has an almost bulk-like behavior. The mean in-plane parameter is almost constant from 100 K 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 strain equivalent to an hydrostatic pressure, we have succeeded to explain the early appearance of the $\beta$-phase ($T_C(1) = 275$ K) and the high temperature preservation of the $\alpha$-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 K 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 [15] was adjusted from the (111) and (110) 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 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 $\alpha$-(002) and $\beta$-(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 → 420 K → 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 $\alpha$-(100) including the $\beta$-(011)(002) doublet. The $\beta$-phase is found to nucleate around 275 K and the $\alpha$-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 $\alpha$- and $\beta$-phases heavily overlap, but the peak positions can still be determined accurately (see zooms in

![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$_{2,3}$ XAS spectra for antiparallel (dotted) and parallel (continuous) 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 (line) and 340 K (dot). Sample magnetization lies in plane. The 340 K spectrum is multiplied by 15 for clarity. The lineshape remains unchanged at high temperature. (d) Temperature dependence of the neutron diffraction patterns of MnAs (100 nm)/GaAs(111)B for in-plane (100)-$\alpha$ and corresponding (011)-(002)-$\beta$ reflections. The dashed lines following the maxima of each Bragg peak are only guides for the eyes. Zooms of the patterns are shown in inset.]
Thus for any wave vector, the temperature sensitivity is proportional to the volume fraction of each phase. 

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ture is close to that of 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 forward 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 temperatures ($T_C^{(1)}$) 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 strain of 1.7 kbars. Also, at 250 K an in-plane lattice compression of -0.82% in the α-phase corresponds to a compressive strain of 3.8 kbars [18]. From Fig. 3(a), the negative slope of $T_C^{(2)}$ with pressure ($\partial T_C^{(2)}/\partial P = -20$ K/kbar with $T_C^{(2)}_{C,0}=307$ 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 $T_C^{(1)}_{C,0}=313$ K, [2]).

On the other hand, since MnAs thin films grown on GaAs(001) are virtually strain-free in the basal plane of the epitaxial system, a phase coexistence is observed in- stead 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 Ikawa 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 [19]. Another way to enhance ferromagnetism to higher temperature is to grow non-relaxed MnAs(001) thin films on a small mismatched (111) cubic substrate where the MnAs hexagonal basal plane would remain under tensile strain.

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19. The in-plane strain $\sigma_2$ is calculated from the lattice expansion $\epsilon_1$ along [110] axis of MnAs considering planar constraints ($\sigma_2=0$ along [001] axis of MnAs): $\sigma_1 = (\epsilon_{11} + \epsilon_{12} - 2\epsilon_{13}/c_{13})\epsilon_1$. The elastic constants $c_{ij}$ were taken from M. Dörfler and K. Bärner, Phys. Status Solidi (a) 17, 141 (1973).
20. Applying biaxial tensile strain to the substrate will induce a positive shift of the mean in-plane parameter in Fig. 2(a). $T_C^{(2)}$ is calculated from the strain induced in the β-phase using Fig. 3(a) and Ref. 18.