MnP films and MnP nanocrystals embedded in GaP epilayers grown on GaP(001): Magnetic properties and local bonding structure

A. de Andrés, A. Espinosa, C. Prieto, M. García-Hernández, R. Ramírez-Jiménez et al.

Citation: *J. Appl. Phys.* **109**, 113910 (2011); doi: 10.1063/1.3580270

View online: <http://dx.doi.org/10.1063/1.3580270>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v109/i11>

Published by the [American Institute of Physics](#).

Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT

The advertisement banner features a green and yellow background with abstract wavy lines. On the left, the text 'AIPAdvances' is displayed in a stylized font, with 'AIP' in blue and 'Advances' in green, followed by a series of orange dots. On the right, a circular seal contains the text 'Now Indexed in Thomson Reuters Databases'. Below this, a blue horizontal bar contains the text 'Explore AIP's open access journal:'. To the right of this bar, a list of three bullet points is shown: '• Rapid publication', '• Article-level metrics', and '• Post-publication rating and commenting'.

AIPAdvances

Now Indexed in
Thomson Reuters
Databases

Explore AIP's open access journal:

- Rapid publication
- Article-level metrics
- Post-publication rating and commenting

MnP films and MnP nanocrystals embedded in GaP epilayers grown on GaP(001): Magnetic properties and local bonding structure

A. de Andrés,^{1,a)} A. Espinosa,¹ C. Prieto,¹ M. García-Hernández,¹ R. Ramírez-Jiménez,² S. Lambert-Milot,³ and R. A. Masut³

¹*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain*

²*Departamento de Física, Escuela Politécnica Superior, Universidad Carlos III de Madrid, Avenida Universidad 30, 28911 Madrid, Spain*

³*Regroupement québécois sur les matériaux de pointe (RQMP) and Département de génie physique, École Polytechnique de Montréal, CP 6079 Succ. Centre-ville, Montreal, Quebec H3C 3A7, Canada*

(Received 8 November 2010; accepted 16 March 2011; published online 6 June 2011)

MnP nanostructures embedded in GaP epilayers, and MnP polycrystalline films, grown from the vapor phase on GaP(001) substrates using metalorganic precursors are compared with bulk MnP. We observe a large increase of the low transition temperature from the ferromagnetic to the antiferromagnetic screw phase, from $T_N = 47$ K for bulk to 82 K for nanocrystals in MnP:GaP films, while the Curie temperature T_C , close to room temperature, varies only slightly. A net magnetic moment is measured in the nanocrystals and films at 5 K, as well as large coercive fields, contrary to bulk MnP. X-ray absorption spectroscopy and diffraction show that epilayers and films contain MnP grains in the nanometric range with average Mn–P bond lengths very close to those of bulk MnP. The MnP film lattice parameters are almost identical to bulk values (within 0.5%) and the main crystallographic preferential orientations are those also present in the epilayers but with different relative populations. Overall the local structures of all MnP forms are very similar, except for indications of more disorder in the nanocrystals. Such combined changes of T_N and T_C are in apparent contradiction with the known response of bulk MnP to strains induced by hydrostatic, uniaxial or chemical pressure. We conclude that the differences in the low temperature magnetic behavior are most probably originated by local structural disorder at the surface of the nanostructures and by finite size effects. © 2011 American Institute of Physics. [doi:10.1063/1.3580270]

I. INTRODUCTION

Mn-based submicron ferromagnets embedded in III–V semiconductor host epilayers offer novel interesting properties suitable for magnetoelectronic devices. Interest in these granular structures has increased because they can be epitaxially grown on semiconductor substrates and their properties can in principle be tailored to exhibit room-temperature ferromagnetic behavior, as well as giant magneto-optical Kerr and Faraday effects.^{1,2}

In spite of promising advances with the GaAs:MnAs system for magneto-optical devices, the relatively small bandgap energy of GaAs (1.43 eV at 300 K) limits the use of this material to applications in the near-infrared spectral region. In order to obtain new magneto-optic functionalities and devices operating in a broader wavelength range, we focus on gallium phosphide (GaP), which is a wide indirect gap semiconductor (2.27 eV at 300 K) nearly lattice matched to Si. Previous structural characterization has established that GaP:Mn epilayers grown by metalorganic vapor phase epitaxy (MOVPE) on GaP(001) substrates are coherent with the substrate and under tensile strain. Transmission electron microscopy and parallel electron energy loss spectroscopy (PEELS) studies revealed the presence of small faceted MnP nanocrystals embedded in the single-crystal GaP film. The distribution of nanocrystals with diameters between 15 and 30 nm is found

to be uniform across the film thickness (~ 300 nm). The nanocrystals are slightly elongated in the in-plane directions whose facets are predominantly aligned along preferential planes of the GaP film matrix.³ The angular dependence of ferromagnetic resonance experiments indicated that the dominant populations of MnP nanocrystals have their c (easy) axis along GaP $\langle 110 \rangle$ directions.^{4,5}

The MnP crystallographic structure is orthorhombic, with the $Pnma$ space group.⁶ Mn is surrounded by six P at four different Mn–P distances forming a distorted octahedron, and its second coordination sphere contains 6 Mn ions with three Mn–Mn distances. Here, we will use the same space group setting as in Refs. 7–10, where the room temperature lattice parameters are $a > b > c$ ($Pbnm$), $a = 5.918$ Å, $b = 5.258$ Å, and $c = 3.172$ Å. The (H – T) magnetic phase diagram of MnP single crystals is complex, presenting different magnetic structures as a function of temperature and applied field (Fig. 1). MnP presents a strong biaxial magnetocrystalline anisotropy with its longer axis (a) as the harder magnetic axis, and the shorter (c), the softer.⁸ In the absence of external magnetic fields, MnP orders ferromagnetically around room temperature, $T_C = 291.5$ K, and at low temperatures presents a transition to a screw antiferromagnetic structure (helimagnetic) at $T_N = 47$ K. External magnetic fields induce different magnetic phases, at different values of the fields, depending on the field orientation relative to the MnP structure. The richness of the magnetic phase diagram of MnP (Fig. 1) is due to the competition between ferromagnetic and antiferromagnetic interactions in

^{a)}Electronic mail: ada@icmm.csic.es.

FIG. 1. (Color online) Magnetic phase diagram of MnP single crystals [adapted from Reis *et al.* (Ref. 7)] for applied magnetic fields along hard axis a , intermediate axis b , and easy axis c of the MnP structure ($Pbnm$). SCR = screw phase. The vertical lines indicate the different transition temperatures. T_{LP} : Lifshitz point temperature.

the system¹¹ and to the strong magnetocrystalline anisotropy. A detailed description of the different magnetic phases may be found in Refs. 7 and 10. Here we will only point out that in the screw phase (SCR) the macroscopic magnetic moment is zero.

In the present work we will present magnetic and structural measurements of polycrystalline MnP films and of hybrid GaP:MnP epilayers both grown on GaP(001) substrates by MOVPE and compare them to polycrystalline ($\sim 150 \mu\text{m}$ grains) commercial MnP powders and with single-crystal MnP data from the literature. The magnetic measurements of MnP commercial powder, thin film, and embedded nanoclusters will be shown to have an overall similar behavior, and yet they will also reveal several important differences, particularly at low temperatures. The most remarkable difference is the large increase, from 47 K (bulk value) to 82 K, of the low transition temperature T_N , while the Curie temperature T_C varies only slightly. We also report on and discuss the difference in coercive fields between bulk and MnP nanostructures.

In order to understand the origin of the observed magnetic differences we performed a structural study of polycrystalline MnP thin films and MnP embedded nanocrystals by means of x-ray diffraction (for the MnP film) and x-ray absorption spectroscopy (XAS) for both. Thus, we provide a comparison of the structure of the MnP nanocrystals in GaP:MnP epilayers and MnP polycrystalline thin films, also grown on GaP, to bulk MnP (polycrystalline powder measurements and single-crystal values extracted from the literature). No significant differences in the structural parameters between the different MnP samples (from nanoclusters to

bulk) are found. Moreover, the strain effects on bulk MnP, as reported in the literature, seem incompatible with our observed variations of the transitions temperatures T_C and T_N , therefore we argue that the relevant parameters to explain the observed differences in the magnetic properties are related to nanometric size and surface effects of clusters.

II. EXPERIMENTAL DETAILS

The GaP:MnP films were grown on n - and p -type GaP (001) substrates in a low-pressure cold-wall MOVPE reactor equipped with a fast-switching run-vent manifold with minimized dead volume³ using trimethylgallium, tertiarybutylphosphine, methyl cyclopentadienyl manganese tricarbonyl (MCTMn), and Pd-purified hydrogen as the carrier gas. The nominal growth rate was in the range of 16 nm/min for GaP(001) at a growth temperature of 650 or 600 °C. The MCTMn gas flow was varied in the range from 0.065 to 1.18 $\mu\text{mol min}^{-1}$, the V/III flow ratio was kept near 80, and film thickness is around 300 nm. MnP films were grown under similar conditions, also on GaP (001). The MnP powder was commercially obtained from Alfa Aesar, whose average grain size is 150 μm .

The magnetic characterization of the films as a function of temperature (2–350 K) and magnetic field (up to 5 T) was carried out with a superconducting quantum interference device magnetometer from Quantum Design. The magnetic in-plane measurements were performed by applying the external field along the sample surface parallel to each of the edges of the substrate: parallel to the $[110]$ and to the $[-110]$ directions of GaP. The diamagnetic signal corresponding to the GaP substrates was subtracted.

The structure was determined by a variety of characterization techniques, including transmission electron microscopy and LEED,³ x-ray diffraction (XRD), and XAS. The XRD study of MnP films was performed in a 4 circles Bruker D8 diffractometer with a $\text{Cu K}\alpha$ source. XAS was carried out at the Mn K edge in fluorescence yield detection mode at 30 K on the BM08 (GILDA) beamline of the ERSF synchrotron, Grenoble. The experimental geometry was chosen to minimize the strong elastic signal due to Bragg peaks from the substrate. Standard EXAFS analysis was performed by using the VIPER software¹² Oscillations were obtained after removing the background by a cubic spline polynomial fitting and the EXAFS signal, $\chi(k)$, was obtained by normalizing the magnitude of the oscillations to the edge jump. The corresponding pseudoradial distribution function around Mn atoms has been obtained by weighting the EXAFS signals by the wave number, k $\chi(k)$, multiplying by a Hanning window and Fourier transforming. For comparative study, the Fourier transform of EXAFS signal was performed within the same k range. Backscattering amplitude and phase functions to fit EXAFS signals were generated using the FEFF code.¹³

III. RESULTS AND DISCUSSION

A. Magnetic data

The magnetization (M) versus temperature was measured for several GaP:MnP films grown at 650 °C with the

FIG. 2. (Color online) Field cooled magnetization at 1000 Oe vs temperature of a GaP:MnP epilayer (red dots), a MnP film (blue open circles), and powder MnP (gray line, scale on the right). Lower panel: derivatives of the magnetization curves. The dashed lines signal the transition temperatures.

highest MCTMn gas flows (0.8 and $1.18 \mu\text{mol min}^{-1}$), as well as for a MnP thin film and for MnP commercial powder as reference compound (Fig. 2). From the minima of the derivatives (Fig. 2, lower panel) we obtain an estimation of the Curie temperatures, $T_C = 294$ K, for the GaP:MnP films that is slightly higher than those corresponding to MnP powder (291 K) and to the MnP film (290 K). The almost identical T_C 's as well as the similarities in the magnetization curves of powder and thin film forms of MnP, compared to single crystal,^{7–10} indicate that the magnetic signal is mainly due to MnP nanocrystals. The small decrease of the magnetization at the lowest temperatures, which is better seen as a steep increase of the derivative (Fig. 2, lower panel), may be due to a small fraction of diluted paramagnetic Mn in the GaP film, whose contribution varies as $1/T$ and is only detectable at very low temperatures.

Figure 2 also reveals several important differences in the magnetic behavior of MnP nanocrystals in GaP:MnP when compared to MnP bulk or film, such as: (i) a large variation of the magnetic transition temperature to the screw phase T_N (defined as the derivative maxima): 47 K for bulk, 67 K for film, and 82 K for nanocrystals (see the dashed vertical lines), (ii) a different temperature dependence of the magnetization in the low temperature regimes (compare curves and derivatives in Fig. 2) of the MnP nanocrystals and film compared to powder MnP, and (iii) while the magnetization in the screw phase is almost zero in bulk MnP (either powder or single crystal), in the MnP film and nanocrystals the magnetization is not far from its maximum value.

Figure 3 compares the field dependence of the magnetization for the powder, the polycrystalline film on GaP, and a representative GaP:MnP epilayer at several temperatures. A remarkable difference is the presence of large coercive fields detected for both MnP film and MnP nanocrystals, at any temperature, compared to the absence of coercive field in the powder, as it occurs in single crystals.⁸

FIG. 3. (Color online) Magnetization cycles of MnP powder (a), MnP film (b), and GaP:MnP (c), at four temperatures. Continuous lines correspond to 5 K. The arrows indicate field induced magnetic transitions.

For MnP powder, the different values of the magnetization when decreasing or increasing the positive field in the cycles below 130 K [Fig. 3(a)] are due to cooling of the sample under a high magnetic field (50 kOe) where the situation at higher temperatures remains frozen. For $T_N < T < T_C$ the cycles correspond to a ferromagnet with negligible coercive field and, at 5 K, two transitions induced by the external field are indicated by arrows (and vertical dashed lines) at slightly above 2000 and 8000 Oe. These features, labeled as *c* and *b* in the figure, correspond to the transition from the screw (SCR) to the ferromagnetic (FM) and to the fan (FAN) magnetic phases for grains with their easy axis *c* and intermediate axis *b*, respectively, along the direction of the external field (see the horizontal arrows in phase diagram in Fig. 1). No indications of the transition from the FAN to the collinear ferromagnetic phase (FM//*b*) at around 35 kOe (Fig. 1, horizontal arrow), are detected at 5 K.

MnP film and nanocrystals in GaP:MnP [Figs. 3(b) and 3(c)] show high coercive fields (up to 2700 Oe) at all measured temperatures below T_C . The remanence (M at zero field) is large even below the transition to the screw phase contrary to what happens in bulk MnP. The cycles are complex and also present indications of a field induced transition at around 20 kOe in Figs. 3(b) and 3(c).

Figure 4 presents the magnetization cycles of MnP and GaP:MnP films for two temperatures (5 and 130 K) and two

perpendicular directions of the magnetic field, both in the plane of the samples; it clearly evidences the in-plane anisotropy in both samples.

It is important to take into account the possible differences in the demagnetization effects related to the shape of the samples and to that of the grains inside the sample. The grains in the film are close to spheres, according to the diffraction data (as will be shown in Sec. III B, while discussing Fig. 6), and the shape of the MnP nanocrystals are only slightly elongated.³ The demagnetizing coefficients (N_d), however, may be very different in these two cases. For non-interacting dispersed MnP nanocrystals in the GaP:MnP films, because of their almost spherical shape, these coefficients are similar for any of the three measurement configurations: external field along two perpendicular axes in the film plane and H perpendicular to it. On the contrary, in the continuous MnP thin film the demagnetization effects related to the sample shape are much more important perpendicular to the sample surface ($N_d \sim 1$) than in plane ($N_d \sim 0$) due to the large difference between the thickness (at most 200 nm) and the lateral dimensions of the film ($6 \times 6 \text{ mm}^2$). Therefore, the demagnetizing effects are only relevant for measurements of the MnP film with the external field perpendicular to the sample surface, a configuration which we have not measured for this sample. We can conclude that the observed anisotropy (Fig. 4) is not originated by grain shape or sample shape.

We present in Fig. 5 the obtained coercive fields $H_C(T)$ (as the field at which the magnetization is reversed) for both type of samples (GaP:MnP epilayer and MnP polycrystalline film) as a function of temperature for the three configurations. The observed coercive fields corresponding to MnP nanoclusters in GaP are indicated by circles in Fig. 5(a) for

FIG. 4. (Color online) Comparison of the magnetization cycles of MnP and GaP:MnP films for two temperatures (5 and 130 K) and two perpendicular directions of the magnetic field, both in the plane of the samples showing the in-plane anisotropy.

FIG. 5. (Color online) (a) Coercive fields of two GaP:MnP epilayers grown at 650°C for the three orientations schematized: magnetic field (H) in the film plane in two perpendicular directions (circles) and H perpendicular to the film plane (horizontal segment). The values for the MnP (poly-c) film (Film) for both in-plane directions are also shown (stars). Continuous lines are guides to the eye. (b) GaP:MnP epilayer magnetization derivatives (FC, 1000 Oe) with the critical temperatures indicated as dashed vertical lines.

configurations where the magnetic field is parallel to any in-plane direction and with a horizontal segment when the applied field is perpendicular to the sample surface. The values for the MnP polycrystalline film grown on GaP are represented by stars. Note the two different $H_C(T)$ curves corresponding to two mutually perpendicular directions in the plane of the films indicating an in-plane magnetocrystalline anisotropy. The angular dependence of ferromagnetic resonance experiments evidenced a magnetocrystalline anisotropy in the GaP:MnP epilayers related to the preferred crystallographic orientations of the MnP nanocrystals embedded in GaP.^{4,5}

The obtained coercive fields are quite similar for both types of samples, GaP nanoclusters embedded in GaP and MnP films. The difference between the coercive fields for both in-plane directions is similar at 5 K while smaller at 130 K for the MnP film. On the other hand, the variation of the coercive fields with temperature does not correspond to a standard collinear ferromagnet. It rather seems to be correlated to the magnetic phase transitions occurring in the T - H plane for both types of samples as indicated by the correlation between the temperature dependence of coercive fields [Fig. 5(a)] and the derivative of the magnetization that reflects the temperature induced magnetic phase transitions [Fig. 5(b)]. In fact, the higher values coincide with the temperature of the Lifshitz point at 121 K (Fig. 1, vertical dashed line). On the contrary, bulk MnP samples (single crystal or powder) do not show coercivity at any temperature.

The influence of the preferred crystallographic orientations of the MnP clusters embedded in the GaP epilayers is readily revealed in the angular dependence of both the remanence and the coercive fields obtained from the hysteresis

TABLE I. Distances (d_i) and number of neighbors (N_i) in MnP thin film and in MnP nanocrystals from three GaP:MnP films obtained from EXAFS fits. $S_0^2 = 0.8$ for the whole series, is determined by the MnP film taken as reference. The estimated errors in d_i are between 1% and 2%. Φ indicates the MCTMn gas flow rate measured in $\mu\text{mol min}^{-1}$.

Sample		d_i (Å)	N_i	σ_i^2 (Å ²)	Growth conditions
MnP	Mn–P	2.35	3 ^a	0.004	$T_S = 650^\circ\text{C}$
		2.38	3 ^a	0.004	
Film	Mn–Mn	2.79	4 ^a	0.004	$\Phi = 0.3$
		3.01	2 ^a	0.004	
GaP:MnP	Mn–P	2.35	3.0	0.008	$T_S = 650^\circ\text{C}$
		2.43	3.0	0.008	
(A)	Mn–Mn	2.80	4.0	0.007	$\Phi = 0.412$
		3.10	2.0	0.007	
GaP:MnP	Mn–P	2.35	3.0	0.008	$T_S = 650^\circ\text{C}$
		2.41	3.0	0.008	
(B)	Mn–Mn	2.80	4.0	0.007	$\Phi = 0.6$
		3.08	2.0	0.007	
GaP:MnP	Mn–P	2.30	3.0	0.009	$T_S = 600^\circ\text{C}$
		2.42	3.0	0.009	
(C)	Mn–Mn	2.80	4.0	0.010	$\Phi = 0.065$
		3.08	2.0	0.010	

^aFixed from crystallographic data.

cycles. Based on the comparison of the angular dependence of the spectra obtained from ferromagnetic resonance (FMR) experiments it was possible to conclude that there are a limited number of crystallographic orientations of the nanoclusters with respect to the GaP matrix.⁴ From FMR and the angular dependence of the remanence it was also determined that the statistical weights of these orientations vary depending on the growth temperature of the samples, which was also reported (see Table I of Ref. 5). As for the MnP polycrystalline film, we will show later that a majority of the grains have their “ b ” axis (the intermediate magnetic axis) out of the film plane and the hard (a) and soft (c) axes are contained in plane, while the orientation of the axes of the grains in the plane of the substrate is a subject presently under study. The fact that we observe a similar in-plane anisotropy for both systems (embedded MnP nanocrystals in GaP matrix and MnP nanocrystals on the GaP substrate) indicates that the [110] and $[-110]$ axes of GaP are not equivalent (a well-known fact in III–V compounds). Thus the nanocrystals, in both systems, are not randomly distributed in these two crystallographic directions, which also points to the origin of the anisotropy observed in Fig. 5 for the coercive fields.

If we now focus on the differences observed in the magnetic data of the films when compared to bulk MnP several factors (other than nanocrystal orientations) have to be considered: (i) the local structure of the nanocrystals and the film (symmetry and interatomic distances) compared to bulk, (ii) effects related to the nanometric size, and (iii) the surface/interface nanocrystal/matrix in the case of clusters embedded in the GaP film.

B. Structure of GaP:MnP epilayers and MnP thin film

To characterize the MnP film and compare its growth on GaP to those of MnP nanocrystals embedded in the GaP epi-

FIG. 6. (Color online) (a) Diffraction intensity of a MnP film grown on GaP (001) (dotted line) and fitted pattern for polycrystalline MnP (blue line). The intensity of the (220) peak in the fit has been normalized to that of the film. GaP (200) and (400) diffraction peaks are indicated. (b) Zoom of the region of the main MnP peaks showing the different intensities compared to powder samples ($Pbnm$ setting with $a > b > c$). Three preferential orientations are labeled: (010) with an asterisk, (111) with A, and (110) with B. (c) Image of the diffracted intensity (in logarithmic scale) of a region of the reciprocal space.

layers (see Ref. 3), θ – 2θ diffraction patterns of this film were recorded. The obtained lattice parameters of the orthorhombic MnP structure ($a = 5.910$ Å, $b = 5.245$ Å, $c = 3.168$ Å) give a unit cell volume 0.5% smaller than bulk (with $a = 5.918$ Å, $b = 5.258$ Å, and $c = 3.172$ Å). The pattern [Figs. 6(a) and 6(b)] also shows that the film presents several preferential orientations. The MnP powder pattern has been scaled so that the (220) intensity matches that measured for the MnP film. It is clear that the preferential crystallographic orientations have the MnP [010] [asterisk (*)], [111] (A), and [110] (B) directions parallel to [001] axis of the GaP substrate. From the relative intensities of the different families of planes we can estimate that above 60% of the crystallites in the film have their b axes parallel to GaP [001] axis. The preferential orientations in the MnP film coincide with those found for the MnP nanocrystals in GaP ([111] and [010]),⁴ but with different weights. It is surprising that such large lattice mismatch between GaP and MnP lattices ($a_{\text{GaP}} = 5.465$ Å) and different interatomic distances can allow a coherent stacking, but the observed reduction of the lattice parameters of MnP films grown on GaP indicates that the substrate is effectively straining the film.

Also, the in-plane order of the MnP crystals was obtained by mapping the in-plane component of the transferred

moment $\Delta Q = \pm 0.2$ in reciprocal unit vectors of cubic GaP (corresponding to $0.2 \times 2\pi/a_{\text{GaP}} = 0.23 \text{ \AA}^{-1}$) [Fig. 6(c)]. The round spots in the L - H plane observed for almost all peaks indicate a unique in-plane orientation of the grains, nevertheless, (220) and (121) grains show weak rings characteristic of polycrystalline powder, indicating that a small fraction of these grains has a random distribution of their in-plane axes. The almost circular shape also indicates the same size of the grains for directions perpendicular and parallel to the sample plane which is estimated, from the width of the diffraction peaks, to be about 40 nm.

To obtain information of the local structure of the nanocrystals we have analyzed the x-ray absorption spectra at the Mn K edge, which were obtained for several GaP:MnP epilayers grown under different conditions as well as a MnP film. The edge energy and near edge shape are related to the oxidation state and symmetry of Mn in the solid. The x-ray appearance near-edge structure (XANES) spectra [Fig. 7(a)] of several GaP:MnP epilayers are almost identical to the MnP film while metallic Mn and Mn_3O_4 references, also shown, are clearly different. So we can conclude that Mn in the nanocrystals has the same kind of environment as in the MnP film.

The fit of the higher energy region (EXAFS) [Figs. 7(b)–7(d)], in principle, allows one to obtain the type and number of Mn neighbors as well as interatomic distances. However, the presence of seven different distances (within a range between 2.29 and 3.17 Å) around Mn in the MnP

structure is a drawback for EXAFS analysis since the number of fitting parameters increases dramatically and, in this case, the EXAFS signal is strongly reduced by interferences between the different contributions. According to the Nyquist criterion ($N_{\text{idp}} = 2\Delta k \Delta R / \pi$), the simulations of these data should be carried out with a maximum of nine independent parameters.

Table I collects the parameters obtained from the fits. First, we have fitted the MnP film data considering as input parameters a proper average of the crystallographic distances¹⁴ and fixing the number of neighbors. The free EXAFS parameters are therefore: two Mn–P and two Mn–Mn distances (d_i), the inelastic loss factor S_0^2 , two Debye–Waller factors (σ_i), and two energy shift values corresponding to the different atomic pairs, Mn–P and Mn–Mn, which makes a total of nine and is a reasonable assumption for the implicit constraints.

In a second step, the data from the MnP nanocrystals in GaP:MnP epilayers have been fitted. Due to the fact that no appreciable differences are observed in the XANES region, we have assumed the same ratio between the considered neighbor numbers in the nanocrystals as in bulk. In this way, the free EXAFS parameters allow one to obtain the considered four Mn–P and Mn–Mn average distances, the two Debye–Waller factors, and a possible reduction in the neighbor number (which together with the two energy shifts, also give nine independent parameters). In all GaP:MnP samples studied, the best fit was obtained with no reduction of the whole number of neighbors. In summary, this EXAFS analysis of MnP and GaP:MnP films gives reasonable fits with averaged interatomic distances within the range of crystallographic values of bulk MnP from the literature.

In Fig. 8, both Mn–P fitted distances have been plotted and compared to the four Mn–P crystallographic distances

FIG. 7. (Color online) (a) Mn K edge absorption spectra of a metallic Mn foil, Mn_3O_4 oxide, and several GaP:MnP epilayers (A, B, and C) compared to the MnP film. (b) Weighted Fourier transform of the data. (c) Filtered EXAFS signals (symbols) and fits (lines), and (d) modulus and imaginary parts of the filtered Fourier transform of the data (symbols) and fits (lines) (fitted window: 1–3 Å).

FIG. 8. (Color online) Right side: bottom, two Mn–P distances (circles and squares) and their mean value (triangles) and the difference between both Mn–P distances (top) obtained from the EXAFS fits as a function of the samples ordered according to their Debye–Waller factors. Left side: equivalent averaged distances obtained from diffraction for bulk and MnP film. The dashed horizontal lines correspond to the four Mn–P crystallographic distances and the numbers on the extreme left side indicate the number of pairs at each distance.

(dashed horizontal lines, the numbers on the left of Fig. 8 indicate the number of P atoms at each distance) and to the averaged crystallographic values (symbols): $d(\text{Mn-P}) = 2.323$ and 2.392 Å,¹⁴ deduced from the structural data. The samples are ordered following their increasing Debye–Waller factors from Table I. It can be seen that the distances obtained from EXAFS are similar in all films, but it appears that the distortion of Mn–P octahedron, reflected by the larger spread of Mn–P distances (Δd) (Fig. 8, top), seems to increase as the Debye–Waller increases, consistent with the reduction of the EXAFS signal in Fig. 7(c). We can conclude that MnP nanocrystals and film have a similar short range structure, within the experimental error, and are slightly different compared to bulk. A clear increase of the disorder in the GaP:MnP films, which is even larger in sample C (grown at a lower temperature), is detected. Note that the GaP:MnP epilayers grown at 650 °C show comparable disorder while the one grown at lower temperature and Mn flux (C) shows the largest Debye–Waller factor and spread of Mn–P distances. Since the coordination numbers (N_i) and Debye–Waller factors (σ_i) can be correlated EXAFS parameters, the variations of σ_i reflect two contributions: one is the disorder of the structure (in this case mainly related to the static disorder which is the dominant one in all cases since the spectra were collected at 30 K) and the other is related to a possible different coordination of Mn at the surface. Depending on the coordination of Mn at the surface and the weight of these Mn, i.e., the nanocrystal size, a reduction of the effective number of neighbors may occur. The obtained nanocrystal size of A and B samples is within 15–20 nm,³ in this case, about 10% of the Mn ions are located at the surface of the nanocrystals, which would not produce a significant reduction¹⁵ of effective N_i but can increase the overall disorder increasing σ_i . Sample C was prepared at lower temperature and Mn flux; therefore, the nanocrystals are expected to grow with a smaller size so that the fraction of Mn atoms at the surface is expected to be higher.

EXAFS fits discard the presence of Mn–Ga pairs in any of the samples that we have measured. In Fig. 9, several possible stackings of (010) MnP crystals on (001) GaP structures are presented. Figure 9 reveals that both compounds consist of a sequence of Ga and P layers for GaP along (001), and of Mn and P layers for MnP along (010), with quite different interplane distances and intraplane structures. The possibility of Mn–Ga interfaces exists among several others, so the weight of the Mn–Ga pairs in EXAFS signal is negligible since it would correspond only to a fraction of the estimated 10% of Mn at the interfaces. In any case, the coordination of Mn at the interfaces will be severely distorted due to the quite different intralayer and interlayer order compared to bulk MnP. Thus, the impact of the fraction of Mn ions at the surface of the nanocrystals with different bonding than in the bulk, while not very relevant in the structural measurements, may have an important role in determining the differences observed in the magnetic properties.

C. Magnetic transition temperatures T_N and T_C

In order to evaluate different possible origins of the observed magnetic properties, we analyzed the reported var-

FIG. 9. (Color online) Projections perpendicular to the sample surface of MnP on GaP with MnP (001) axis parallel to GaP (110) showing different possible stacking of GaP and MnP. Both compounds present alternating layers of Ga and P for GaP and of Mn and P for MnP.

iations of the magnetic behavior of MnP and related compounds caused by external pressure. Uniaxial pressure studies on MnP (Ref. 16) and hydrostatic pressure on MnAs (Ref. 17) give interesting information on the effects of lattice parameters' variation. The uniaxial pressure applied along the hard a axis produces the largest effects, increasing T_N and decreasing T_C . Along the easy c axis the changes are reversed (T_N decreases and T_C increases) and are smaller. Along b the same trend is observed with even smaller changes. Along any axis the variation of T_N and T_C is opposite and the major effects are on T_C . The MnAs structure is hexagonal at ambient pressure, with T_C around 320 K, and under relatively low hydrostatic pressures (2–4 kbar) transforms to the MnP orthorhombic structure accompanied by the change from high ($S = 2$) to low ($S = 1$) spin states of Mn in the transition. The volume per Mn ion is reduced and the substitution of As by P is found to be equivalent to positive hydrostatic pressure. In the orthorhombic phase, above 8 kbar, MnAs presents ferromagnetic and antiferromagnetic phases, whose transition temperatures vary in opposite directions: T_C increases drastically with pressure while the low temperature transition T_N decreases much less. The observations of the high temperature transition are discussed in terms of the relative filling of the Mn $3d$ orbitals and changes from their localized to delocalized character as a function of the structure and of the larger Mn–Mn distance.

Considering these results, our data, exhibiting almost identical T_C in MnP film and bulk, are consistent, since the cell volume in the film remains almost unchanged. The small increase of T_C for the MnP nanocrystals seems to indicate a small reduction of its unit cell compared to the bulk. However, clearly, none of the reported pressure effects measured on bulk crystals can explain the combination of our observations: the almost unchanged T_C and the important increase of T_N . Furthermore, the difference in thermal expansion coefficients between the MnP nanoclusters and the GaP matrix,

whose magnitude is difficult to evaluate precisely, can also be seen to predict a decrease of T_N . The signs and magnitudes of the linear thermal expansion along each of the three MnP axes, which can be obtained from Ref. 18, compared to the linear thermal expansion of GaP, indicate equivalent hydrostatic pressures whose signs point to a decrease of the T_N transition temperature.

Therefore, the combined variation of T_N and T_C cannot be explained by uniaxial or hydrostatic pressure, which might be applied to the MnP nanocrystals by the strain induced by GaP epilayers or substrate. Moreover, the structural information does not evidence significant differences compared to bulk samples. We conclude that the origin of the variation of T_N is not related to lattice parameter changes or to possible defects inside the MnP lattice. The nanometric size of the MnP nanocrystals, with a mean size around 20 nm in the MnP:GaP epilayers or 40 nm in the MnP film, may modify the different low temperature magnetic structures (Fig. 1), as well as the phase diagram, because of their confinement to a spatial region with a size comparable to the spread of one helix turn in the SCR phase (around 5 nm according to Ref. 19).

D. Coercive fields

As we previously explained, the anisotropy evidenced in Figs. 4 and 5 is not related to differences in the demagnetization for the different measurement configurations that may arise from sample shape or grain shape. Therefore, the anisotropy of the coercive field is a magnetocrystalline anisotropy related to the preferential orientations of the MnP nanocrystals in the GaP matrix as well as to the similar preferential orientations of the MnP nanograins in the MnP films. In principle, because of the small size of the nanocrystals, it is reasonable to expect that they are single domains and that the magnetization reverses coherently.

Since shape anisotropy is not important, the loops could correspond to “Stoner–Wohlfarth” processes, where the coercive fields are directly related to the anisotropy constants. Nevertheless, the field needed to fully reverse the magnetization can be estimated by $2K/\mu_0 M_s$ (K is an anisotropy constant and M_s the spontaneous magnetization) or, equivalently by $2k/\mu$, where k is the smallest anisotropy constant per magnetic moment and μ the magnetic moment. Using the values for k and μ in Ref. 20 (7.68×10^{-5} eV per dipole and 7.5×10^{-5} eV $T^{-1} \sim 1.3 \mu_B$), the needed field to reverse the magnetization by coherent reversal along the easy axis is $H_c = 20$ kOe, which is one order of magnitude larger than the larger observed coercive field values for GaP:MnP (Fig. 5). A reduction of the coercive field is usually observed for nanometric particles when the thermal energy is comparable to the anisotropy energy but here, particles of quite different diameters (from 15 to 40 nm) present almost the same coercive fields. The crystalline anisotropy energy $E_A = (1/2)Kv$ [where v = volume of the grain = $(15 \text{ nm})^3$] is ~ 5 eV, which is well above thermal or shape anisotropy energies. On the other hand, in a coherent reversal, perpendicular to the easy direction, the $M(H)$ curves do not show any coercive field but a linear increase of M up to the saturation at H_c . In the measure-

ments, the field may not be applied along the crystallographic axes, but since there are two perpendicular measurements, one of them has to be at most at 45° of the easy axis so the coercive field would be reduced at maximum by a factor of 2. This analysis suggests that coherent rotation is not the mechanism for magnetization reversal, and probably the different magnetic structures induced by the nanometric size as well as the different Mn environment at the surface of the nanocrystals provide a more energetically favorable mechanism.

IV. CONCLUSIONS

We presented a study of the magnetic properties of polycrystalline MnP films and MnP nanocrystals embedded in GaP epilayers grown on GaP substrates, particularly at low temperatures, and compared them to those of bulk MnP. The coercive fields H_c (T) for both embedded nanocrystals and polycrystalline film as a function of temperature strongly suggest that coherent rotation is not the mechanism for domain reversal. A large increase of the low transition temperature from the ferromagnetic to the screw phase is observed, while the Curie temperature T_C varies only slightly. As for the local structure, the symmetry and oxidation state of Mn in MnP nanocrystals, both in GaP:MnP epilayers and MnP thin films on GaP substrates, is very similar and the MnP lattice parameters are identical, within 0.5%, to those of bulk MnP. The observation of an increase of the disorder (Debye–Waller factor) as the grain size is reduced can be explained by the very different environment of Mn at the MnP–GaP interface due to their very different lattices while the average structure inside the MnP grains remains almost unchanged compared to the bulk. Moreover, the observed variation of the magnetic transitions temperatures, T_C and T_N , could not be explained by uniform hydrostatic or uniaxial strain in the grains, and is most likely related to changes at the surface of the nanostructures since the structure inside the grains seems unchanged compared to bulk while the surface is subject to strain and disorder. Therefore, our data strongly suggest that the changes in the low temperature magnetic structures and transition temperatures of MnP nanocrystals (both in Mn:GaP epilayers and in MnP films on GaP) are due to the nanometric size of the crystals and to the role of the different Mn environment at their surface.

ACKNOWLEDGMENTS

This work has been supported by the Spanish “Ministerio de Educación y Ciencia” (MAT2009-08786, MAT-2008-06517, and CSD2009-00013) and by “Comunidad Autónoma de Madrid” (S2009/MAT-1756). We thank ESRF for beamtime and GILDA personnel for technical support. We thank F. Mompeán for the asymmetric diffraction measurement at the ICMC diffraction service. We also acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC), the infrastructure support of the RQMP (Québec), and the technical assistance of Joël Bouchard.

¹G. A. Prinz, *Science* **282**, 1660 (1998).

²A. G. Monette, C. Lacroix, S. Lambert-Milot, V. Boucher, D. Ménard, and S. Francoeur, *J. Appl. Phys.* **107**, 09A949 (2010).

- ³S. Lambert-Milot, C. Lacroix, D. Ménard, R. A. Masut, P. Desjardins, M. García-Hernández, and A. de Andrés, *J. Appl. Phys.* **104**, 083501 (2009).
- ⁴C. Lacroix, S. Lambert-Milot, P. Desjardins, R. A. Masut, and D. Ménard, *J. Appl. Phys.* **103**, 07D908 (2008).
- ⁵C. Lacroix, S. Lambert-Milot, P. Desjardins, R. A. Masut, and D. Ménard, *J. Appl. Phys.* **105**, 07C119 (2009).
- ⁶S. Rundqvist and S. Nawapong, *Acta Chem Scand.* **19**, 1006 (1965).
- ⁷M. S. Reis, R. M. Rubinger, N. A. Sobolev, M. A. Valente, K. Yamada, K. Sato, Y. Todate, A. Bouravleuv, P. J. von Ranke, and S. Gama, *Phys. Rev. B* **77**, 104439 (2008).
- ⁸E. E. Huber and D. H. Ridgley, *Phys. Rev.* **135**, A1030 (1964).
- ⁹T. Komatsubara, H. Shinohara, T. Suzuki, and E. Hirahara, *J. Appl. Phys.* **49**, 1037 (1969).
- ¹⁰A. Zieba, C. C. Becerra, H. Fjellvag, N. F. Oliveira, and A. Kjekshus, *Phys. Rev. B* **46**, 3380 (1992).
- ¹¹H. Yoshikawa, S. M. Shapiro, and T. J. Komatsubara, *J. Phys. Soc. Jpn.* **54**, 3084 (1985).
- ¹²K. V. Klementev, VIPER for Windows, freeware: www.desy.de/klmn/viper.html; *J. Phys. D* **34**, 209 (2001).
- ¹³S. I. Zabinsky and J. J. Rehr, *Phys. Rev. B* **52**, 2995 (1995).
- ¹⁴The four Mn–P crystallographic distances have been averaged in the following way: $1 \text{ Mn–P}(2.2882) + 2 \text{ Mn–P}(2.3407) = 3 \text{ Mn–P}(2.323)$ and $2 \text{ Mn–P}(2.3873) + 1 \text{ Mn–P}(2.402) = 3 \text{ Mn–P}(2.392)$. The three Mn–Mn distances were grouped into two distances: $2 \text{ Mn–Mn}(2.704) + 2 \text{ Mn–Mn}(2.8155) = 4 \text{ Mn–Mn}(2.760)$ and $2 \text{ Mn–Mn}(3.172)$ (all distances are in angstrom).
- ¹⁵F. Jiménez-Villacorta, A. Muñoz, and C. Prieto, *J. Appl. Phys.*, **96**, 6224 (2004).
- ¹⁶E. Hirahara, T. Suzuki, and Y. Matsumura, *J. Appl. Phys.* **39**, 713 (1968).
- ¹⁷N. Menyuk, J. A. Kafalas, K. Dwight, and J. B. Goodenough, *Phys. Rev.* **177**, 942 (1969).
- ¹⁸N. Iwata, *J. Sci. Hiroshima Univ., Ser. A-2* **33**, 1 (1969).
- ¹⁹C. Becerra, H. J. Brumatto, and N. F. Oliveira, *Phys. Rev. B* **54**, 15997 (1996).
- ²⁰A. Zieba, M. Slota, and M. Kucharczyk, *Phys. Rev. B* **61**, 3435 (2000).