

**$\alpha$ - $\beta$  phase transition in MnAs/GaAs(001) thin films: An optical spectroscopic investigation**

F. Vidal, O. Pluchery, N. Witkowski, V. Garcia, M. Marangolo, V. H. Etgens, and Y. Borensztein  
*Institut des Nanosciences de Paris, UMR 7588 CNRS-Universités Pierre et Marie Curie et Denis Diderot, Campus Bouicaut,  
 140, rue de Lourmel, 75015 Paris, France*

(Received 10 May 2006; revised manuscript received 13 July 2006; published 26 September 2006)

The  $\alpha$ - $\beta$  phase transition in MnAs thin (100 nm) films epitaxied on GaAs(001) is studied using optical spectroscopies. It is found that reflectance anisotropy spectra differ markedly for the two phases. Although no prominent feature appears in the spectrum related to the  $\beta$  phase, the spectrum of the  $\alpha$  phase exhibits two features centered at 2.9 and 5.0 eV. The origin of these spectral features has been further investigated using temperature-dependent differential reflectance. It is shown that the band centered at 2.9 eV can be assigned to interband transitions for light polarized along the  $c$  axis of  $\alpha$ -MnAs. We show that reflectance anisotropy spectroscopy can be used to monitor the  $\alpha$ - $\beta$  phase transition within the thin film. The observed spectral features and their evolution across the coexistence region are discussed in light of band-structure models in the literature. The data suggest that each phase retains its electronic structure in the coexistence region and that the transition between the  $\alpha$  exchange-split band structure and the  $\beta$  band structure is sharp.

DOI: [10.1103/PhysRevB.74.115330](https://doi.org/10.1103/PhysRevB.74.115330)

PACS number(s): 68.35.Rh, 64.70.Kb, 78.20.-e, 78.40.-q

## I. INTRODUCTION

Manganese arsenide (MnAs) is a material that has attracted considerable interest, both from an experimental and a theoretical point of view, since the beginning of the last century.<sup>1</sup> At room temperature under atmospheric pressure, MnAs is a ferromagnetic metal. It exhibits interesting properties such as “colossal-like” magnetoresistance,<sup>2</sup> or colossal magnetocaloric effect.<sup>3</sup> Furthermore, this material, like other manganese pnictides, has a magneto-optical response.<sup>4</sup> MnAs also presents the advantage that it can be deposited as thin films with sharp and well-defined interfaces on technologically relevant semiconducting substrates.<sup>5-9</sup> This makes it an appealing material for spintronics devices using semiconductors. However, a major issue to be tackled is the injection of spins into the semiconductor. In this respect, the fact that it is possible, using modern molecular beam epitaxy (MBE) techniques, to grow high-quality MnAs/GaAs junctions, with limited interdiffusion and chemical reactivity at the interface, is particularly interesting.<sup>10</sup> Recent studies on MnAs/(GaAs,AlAs)/MnAs junctions have demonstrated the existence of a spin polarization of 60% for MnAs at the interface with GaAs, a value even higher than for bulk MnAs.<sup>11</sup>

At equilibrium and room temperature, bulk MnAs has a hexagonal NiAs-type lattice structure ( $B8_1$ , space group  $P6_3/mmc$ ) with lattice constants  $a=0.372$  nm and  $c=0.571$  nm.<sup>12</sup> This  $\alpha$ -MnAs phase is metallic and ferromagnetic.<sup>13</sup> Bulk MnAs displays a first-order phase transition at 40 °C from the  $\alpha$  phase to the  $\beta$  phase.<sup>14</sup>  $\beta$ -MnAs is a nonferromagnetic phase of orthorhombic MnP-type symmetry ( $B31$ , space group  $Pnma$ ) with  $a=0.572$  nm,  $b=0.3676$  nm, and  $c=0.6379$  nm.<sup>15</sup> The type of magnetic ordering in  $\beta$ -MnAs has been controversial for a long time. In bulk sample, there is evidence that  $\beta$ -MnAs is paramagnetic (Ref. 16, and references therein). At 126 °C, there is a second-order phase transition from the orthorhombic  $\beta$  phase to the hexagonal  $\gamma$  phase.<sup>15</sup>

These properties and the phase diagram are different when MnAs is grown as thin films using molecular beam

epitaxy. The structural properties of MnAs thin films grown on GaAs(001) have been thoroughly investigated recently. It has been shown that MnAs can be MBE deposited in high-quality layers on GaAs(001) with its  $c$  axis,  $[00.1]$ , parallel to the  $[1\bar{1}0]$  direction of the substrate and MnAs( $1\bar{1}.0$ ) $\parallel$ GaAs(001), as illustrated in Fig. 1. In this particular epitaxial system, it was found that  $\alpha$ -MnAs (hexagonal) and  $\beta$ -MnAs (orthorhombic) coexist between 10 and 45 °C. This is different from what is observed in bulk MnAs, where the hexagonal-orthorhombic transition is a first-order phase transition and is complete within a narrow temperature range around 40 °C under ambient pressure.<sup>17,18</sup> Recent experimental work suggests that the  $\beta$  phase would be antiferromagnetic in MnAs/GaAs(001) thin films.<sup>19</sup>

The transition and the coexistence of the  $\alpha$  and  $\beta$  phases in MnAs epitaxial films were studied using x-ray diffraction and scanning probe microscopies.<sup>21-24</sup> It was shown that, in

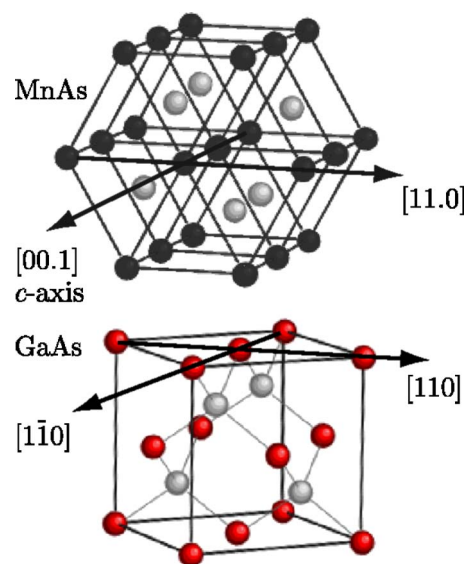


FIG. 1. (Color online) Schematic illustration of the  $\alpha$ -MnAs/GaAs(001) epitaxy.

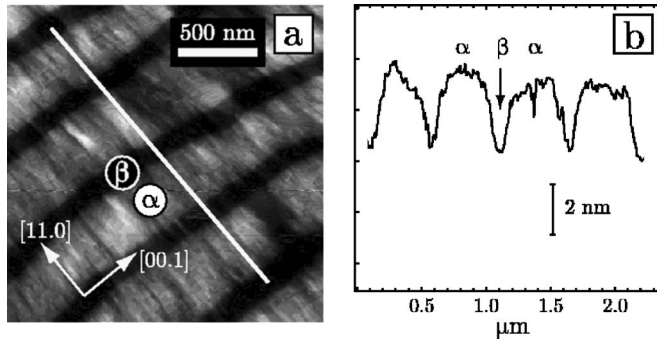


FIG. 2. (a) STM image of the  $\alpha$ - $\beta$  stripes pattern for a 220 nm thick MnAs film at room temperature. The image was recorded at  $-1.73$  V sample bias and 0.11 nA tunneling current. (b) Height profile perpendicular to the stripes, along the white line drawn in (a).

the coexistence region, the  $\alpha$  and  $\beta$  phases do not mix, but self-organize into a pattern composed of stripes-shaped domains running along the  $[00.1]$  direction, as a result of the epitaxial constraints imposed by the substrate. This pattern can be seen in Fig. 2(a) where a typical scanning tunneling microscopy (STM) image, obtained for a 220 nm thick film, is displayed. Also shown in Fig. 2(b) is a height profile of the  $\alpha$ - $\beta$  stripes pattern in a direction perpendicular to the stripes.

Without the structural phase transition from  $\alpha$  to  $\beta$ , the Curie temperature of  $\alpha$ -MnAs would be  $126$  °C (see Ref. 16, and references therein). As the epitaxial constraints have a dramatic effect on the  $\alpha$ - $\beta$  transition, one can think of using strain as a parameter to extend the temperature domain of the  $\alpha$  phase and, therefore, of the ferromagnetic ordering. This has indeed been observed for MnAs epitaxied on GaAs(111) substrates.<sup>25</sup>

In this paper, we report the study of the  $\alpha$ - $\beta$  phase transition in MnAs thin (100 nm) films epitaxied on GaAs(001) using optical spectroscopies [reflectance anisotropy spectroscopy, RAS, and temperature-dependent differential reflectance (TDDR)]. As (i) both  $\alpha$ - (NiAs-type) and  $\beta$ - (MnP-type) phases display crystalline anisotropy, and (ii) the electronic structure of both phases are different,<sup>20</sup> one expects distinct optical anisotropy for both phases. Consequently, an optical technique sensitive to anisotropy may be an effective probe to follow the  $\alpha$ - $\beta$  phase transition. For  $\alpha$ -MnAs, calculation by Ravindran *et al.* predicted that reflectance should be different for light polarized along the  $c$ -axis and perpendicular to it.<sup>26</sup> In this paper, we demonstrate experimentally that reflectance anisotropy spectra differ significantly for  $\alpha$  and  $\beta$  phases and that RAS can be used to follow the phase transition. In the investigated spectral range, the spectrum related to the  $\beta$  phase displays no prominent feature. The  $\alpha$  phase spectrum exhibits two features centered at 2.9 and 5.0 eV, the origin of which has been further investigated using temperature-dependent differential reflectance. Exploiting the difference in  $\alpha$  and  $\beta$  spectra, we show that reflectance anisotropy spectroscopy can be used to monitor the  $\alpha$ - $\beta$  phase transition within the thin film. This transition is found to take place between 10 and 45 °C, in excellent agreement with data in the literature, obtained using x-ray diffraction. Although the  $\alpha$ - $\beta$  phase transition has been thoroughly studied from a structural point of view, our

work is a spectroscopic study of thin films across the transition. We discuss the optical spectroscopic data in connection with band structure calculations available in the literature.

This paper is organized as follows: in Sec. II, we describe briefly the experimental setups used in this study and in Sec. III, we present the results of the spectroscopy experiments that are discussed in Sec. IV.

## II. EXPERIMENTAL

The growth was carried out in a multichamber molecular beam epitaxy system equipped with reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy facilities. MnAs thin films were grown on GaAs(001) buffer layers deposited on GaAs(001) substrates. The epitaxial orientation with respect to the substrate is MnAs( $1\bar{1}.0$ ) $\parallel$ GaAs(001) and MnAs $[00.1]\parallel$ GaAs $[1\bar{1}0]$  as checked by *in situ* RHEED measurements. The thickness of the MnAs films studied in this work was fixed at 100 nm. The reflectance anisotropy (RA) spectroscopy (RAS) experiments were carried out using a spectrometer built following Aspnes' setup.<sup>27</sup> Throughout this work, the RAS signal is  $\text{Re}(\Delta r/r) = \text{Re}\{r_{[11.0]} - r_{[00.1]}/r\}$ , where  $r$  is the mean value of the normal incidence complex reflectance coefficients of light along both crystalline orientations:  $r_{[11.0]}$  and  $r_{[00.1]}$ . A thermocouple and a Peltier unit were used to control and monitor the temperature. Throughout this work, we estimate that the measured temperatures are accurate within  $\pm 1$  °C. The temperature-dependent differential reflectance (TDDR) experiments were performed using a dedicated optical set-up and the same Peltier unit. TDDR was measured for light polarized along the  $[11.0]$  and  $[00.1]$  directions. The TDDR signals,  $\Delta R/R_{[11.0]}$  and  $\Delta R/R_{[00.1]}$ , are defined by  $[R(35\text{ °C}) - R(29\text{ °C})]/R(29\text{ °C})$ , where  $R$  is the normal incidence reflectance in intensity along either the  $[11.0]$  or  $[00.1]$  directions.

## III. RESULTS

### A. Reflectance anisotropy spectra

Figure 3(a) displays a typical reflectance anisotropy spectrum obtained at 10 °C, where only the  $\alpha$  phase is present. The spectrum exhibits a prominent feature at 2.9 eV, and another one, less intense, can be distinguished around 5 eV. In contrast, the RA spectrum obtained at 50 °C and drawn in Fig. 3(b), which corresponds to the  $\beta$  phase, does not display any particular feature, but only a continuously increasing (in magnitude) signal with decreasing photon energy. Before discussing the possible origin of the features observed for the  $\alpha$  phase, we briefly compare our results to previous ones reported in the literature. Despite the great interest of MnAs/GaAs(001)—having in mind potential spintronics application or from a fundamental point of view—only a few optical studies have been performed on this system. Even on bulk MnAs, optical data are rather limited in the literature and are available for only the  $\alpha$  phase,<sup>28</sup> collected on a polycrystalline sample. Polarization-sensitive light transmission measurements were used by Iikawa *et al.* on MnAs/GaAs

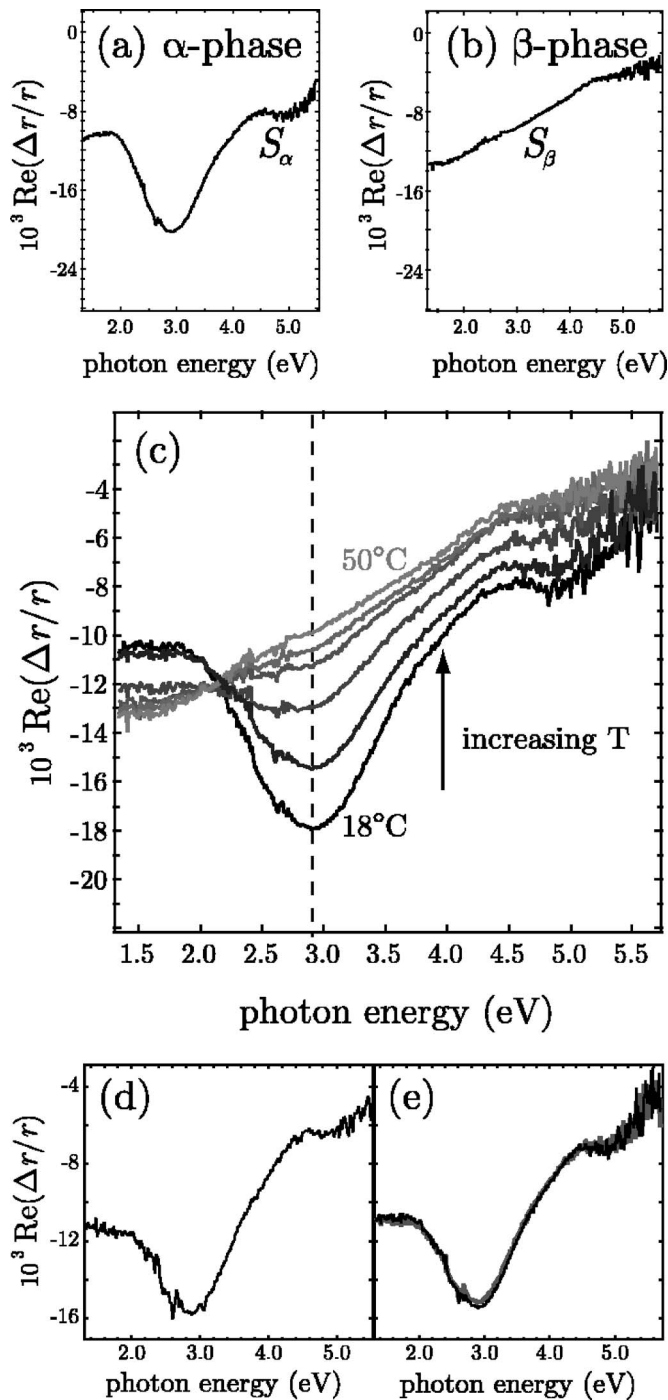


FIG. 3. (a) RA spectrum of the MnAs layer in the  $\alpha$  phase ( $T = 10^\circ\text{C}$ ). (b) RA spectrum of the MnAs layer in the  $\beta$  phase ( $T = 50^\circ\text{C}$ ). (c) RA spectra taken at different temperatures across the  $\alpha$ - $\beta$  transition. (d,e) Evolution of RA spectra recorded at  $T = 25^\circ\text{C}$  for a sample after exposure to air (d), 24 h later before (black thin line) and after (gray thick line) thermal cycling (e). The scale is the same in (d) and (e).

heterostructures, but this work focused on the optical anisotropy induced on GaAs and its link with the strain in the substrate.<sup>29</sup> Optical conductivity measurements below 1.5 eV for MnAs thin films grown on GaAs were reported in a recent work by Burch *et al.*,<sup>30</sup> but the focus of this study was

the carrier dynamics in GaMnAs digital ferromagnetic heterostructures.

To our knowledge, there is only one example of study using reflectance anisotropy to probe MnAs thin films in the literature.<sup>31,32</sup> However, in the study of Kästner *et al.*, RAS was measured for temperatures larger than  $250^\circ\text{C}$ , where MnAs displays a hexagonal  $\gamma$ -phase, different from the  $\alpha$  and  $\beta$  phases, which are investigated in the present paper. A direct comparison with Kästner *et al.* results is therefore not possible.

In most cases, RAS is used to investigate cubic crystals, for which no optical anisotropy occurs from bulk, but only from the possible anisotropic surface.<sup>33</sup> The surface RAS signal is usually of the order of a few  $10^{-3}$  [for instance it is lower than  $10 \cdot 10^{-3}$  in the case of the different surface structures of GaAs(001)<sup>34</sup>]. In our measurements the RA spectra were recorded with samples maintained in air. The resulting oxidation and contamination of the surface removed any surface optical anisotropy that could originate from an anisotropic surface crystalline reconstruction. The signal was actually unaffected by further surface contamination as shown by the reproducibility of the results over time. Figures 3(d) and 3(e) show spectra obtained for the  $\alpha$  phase at 24 h interval. The spectra are quite similar. The spectra obtained before and after thermal cycling are shown on Fig. 3(e) and are found to be nearly identical, the slight difference between them could be due in part to the incertitude on the temperature ( $\pm 1^\circ\text{C}$ ). The strong temperature dependence of the signal, as it will be seen later, argues against a contribution coming from a thin layer of surface oxide. We measure only the optical anisotropy coming from bulk MnAs, i.e., taking its origin mainly from the bulk structural anisotropies of the hexagonal  $\alpha$  phase and of the orthorhombic  $\beta$  phase.

The origin of the structure observed at 2.9 eV could be related to different processes. One possibility would be the excitation of surface plasmons. It is known that surface plasmons can be excited by light when the surface exhibits some roughness, which makes possible the coupling between surface plasmons and photons with different wave vectors.<sup>35</sup> In principle, the “gratinglike” morphology due to the stripe pattern in the  $\alpha$ - $\beta$  coexistence region is favorable for the excitation of surface plasmons. As the  $\alpha/\beta$  proportion depends on the temperature in the coexisting region, the width of  $\alpha$  and  $\beta$  stripes depends also on the temperature. The period remains constant in the coexistence region.<sup>36</sup> When a single phase ( $\alpha$  or  $\beta$ ) is present, the corrugation has a minimal amplitude and the coupling with light is expected to be weak. Accordingly, if the feature at 2.9 eV were due to surface plasmons excitation, one would expect it to be maximal at intermediate  $\beta$  compositions, and to disappear for pure  $\alpha$  or  $\beta$  phase. This is not observed, as it can be seen in Fig. 3(c), where RA spectra measured for various temperatures between 18 and  $50^\circ\text{C}$  have been drawn. On the contrary, the fact that the features at 2.9 and 5 eV have a maximal intensity in the RA spectrum when only the  $\alpha$  phase is present indicates clearly that these spectral features have another origin. Consequently, they must likely originate from intraband (free electrons response) or interband transitions of the  $\alpha$  phase.



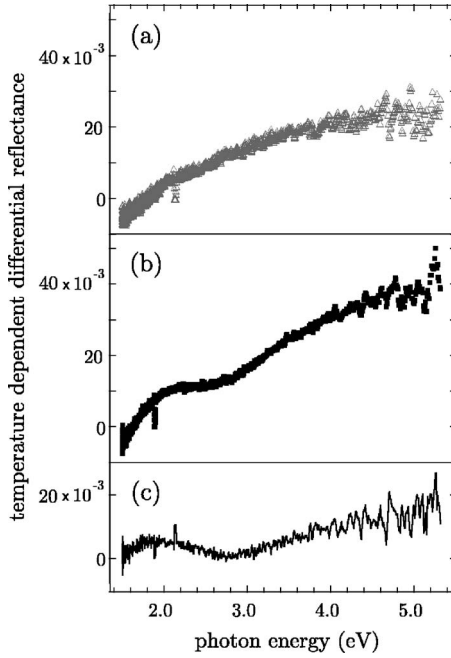


FIG. 4. Temperature dependent differential reflectance spectra  $\Delta R/R$  measured on MnAs film when increasing temperature from 29 to 35 °C. (a) Gray open triangles: TDDR along [11.0] direction. (b) Black squares: TDDR along [00.1] direction. (c) Black thin line: difference of the TDDR spectra.

**B. Temperature-dependent differential reflectance**

In order to analyze deeper, the features observed in the RAS spectrum for the  $\alpha$  phase, we have to determine which crystalline direction it is related to, as RAS only gives the optical anisotropy between the [11.0] and [00.1] directions. For this purpose, temperature-dependent differential reflectance has been measured for light polarized along both orientations, for various increases of temperature. Figure 4(a) and 4(b) give the TDDR spectra, when increasing the sample temperature from 29 to 35 °C. In the present case, as the MnAs film undergoes phase transition from  $\alpha$  to  $\beta$  phases, the TDDR is dominated by the change in the optical reflectance due to the different optical responses of both phases. It is clear that no peculiar feature is visible along the [11.0] direction of MnAs, while some feature can be seen along the [00.1]  $c$  axis: the feature at 2.9 eV observed in the RAS spectra for the  $\alpha$  phase, originates from optical absorptions for light parallel to the  $c$  axis. Figure 4(c) shows the difference of the two previous temperature-dependent differential reflectance spectra, which gives the anisotropy of the TDDR; therefore, the effect of change in temperature on the RAS. The spectrum is, as expected, similar to the RAS spectra presented in Fig. 3.

**IV. DISCUSSION**

The reflectance anisotropy spectrum obtained at  $T = 50$  °C, labeled  $S_\beta$  [Fig. 3(b)], where only the  $\beta$  phase is present, differs notably from the one obtained for the  $\alpha$  phase [Fig. 3(a), spectrum labeled  $S_\alpha$ ]. The spectral features at 2.9

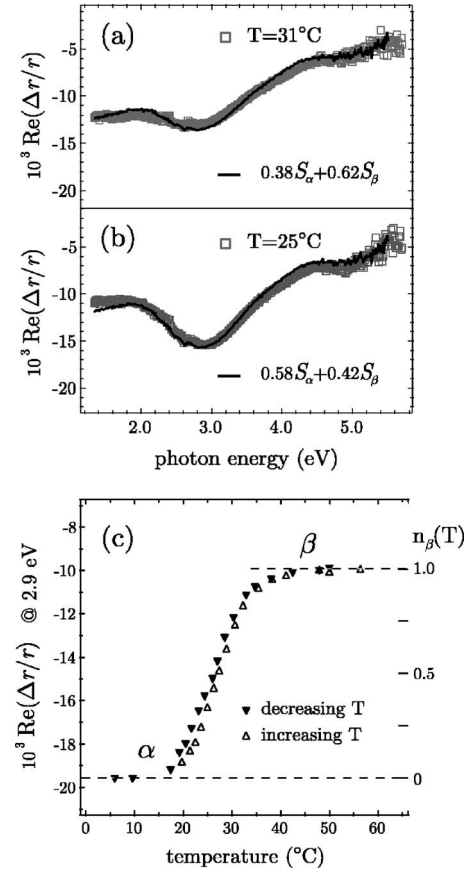


FIG. 5. (a) Experimental RA spectrum obtained at  $T=31$  °C ( $\square$ ) and fit based on a linear combination of  $S_\alpha$  and  $S_\beta$  (thick line). (b) Same as (a) for  $T=25$  °C. (c) RA signal at 2.9 eV as a function of the sample’s temperature. The scale on the right axis displays the amount of  $\beta$  phase deduced from the RA signal.

and 5 eV are absent in spectrum  $S_\beta$ , a monotonic response is observed instead. The distinct spectral responses from  $\alpha$ -MnAs and  $\beta$ -MnAs can be exploited to study the  $\alpha$ - $\beta$  transition, offering the opportunity to follow in real time the proportion of these phases in the MnAs thin layer.

The coexistence of  $\alpha$  and  $\beta$  phases within the film implies that the RA spectra  $S(T)$  measured at intermediate temperatures should be a linear combination of  $S_\alpha$  and  $S_\beta$ :  $S(T) = n_\alpha(T)S_\alpha + n_\beta(T)S_\beta$ , with  $n_\beta(T) = 1 - n_\alpha(T)$ .  $n_\alpha(T)$  and  $n_\beta(T)$  represent the proportion of the  $\alpha$  phase and  $\beta$  phase in the layer at the temperature  $T$ , respectively. We have actually checked, using effective medium theory for lamellar structures,<sup>37</sup> that a mixture of two phases, which display different reflectance anisotropies, results in a RA signal that is a linear combination of both RA with coefficients equal to the relative proportions of each phase. The spectra obtained at intermediate temperatures can indeed be reproduced very well using a linear combination of  $S_\alpha$  and  $S_\beta$ , as shown in Figs. 5(a) and 5(b) for two temperatures ( $T=25$  °C and  $T=31$  °C). This also reinforces the conclusion reached previously that the RAS of MnAs films does not originate from the surface but from the bulk anisotropy of the  $\alpha$  and  $\beta$  phases. It is therefore possible to deduce from the RA spectra the respective proportions of  $\alpha$  and  $\beta$  phases at any interme-

diate temperature. Consequently, it is possible to follow the transition, by real-time monitoring the RA signal. We have chosen to monitor the signal at 2.9 eV, while the temperature was stepped in the transition region. The results are displayed in Fig. 5(c). The deduced proportion (from the above analysis) of  $\beta$ -MnAs phase shows that the transition starts around 10 °C and is complete at 45 °C, in excellent agreement with data in the literature.<sup>22</sup> The observed general behavior is qualitatively similar to the one obtained from x-ray-diffraction experiments in Ref. 22, except that we observe a weaker hysteresis in our case, almost zero. As noted in Ref. 22, the amplitude of the hysteresis should depend strongly on the defect density of the films. Our results demonstrate that reflectance anisotropy spectroscopy can be used as an efficient technique to follow in real-time the  $\alpha$ - $\beta$  phase transition in MnAs heteroepitaxial films.

As stated before, the observed anisotropic reflectance originates from intraband and interband transitions in MnAs. We first discuss the possibility that the observed spectral features might be linked to the intraband (free electrons) response. The free electrons contribution can usually be described as a Drude-like term involving two parameters: the plasma frequency  $\omega_p$  and the scattering rate. For  $\alpha$ -MnAs, the observed anisotropy originates from difference in currents generated along and normal to the easy axis. Concerning the intraband part of  $\alpha$ -MnAs response, it is possible that scattering rates might differ for the two directions because of domain walls or spin-disorder scattering, leading to an anisotropic response. Such effects could be quite pronounced at the plasma edge, when the photons energy approaches  $\hbar\omega_p$ . When the optical response is dominated by the free carriers response, the reflectivity can drop dramatically at energies slightly above  $\hbar\omega_p$ .<sup>38</sup> Measurements performed on polycrystalline samples established that  $\hbar\omega_p \sim 3.0$  eV for MnAs.<sup>28</sup> Recent results obtained on thin films are consistent with this value.<sup>30</sup> Therefore, one has to examine the hypothesis that the feature centered at 2.9 eV might be related to an anisotropic response of the free carriers possibly enhanced in the vicinity of the plasma edge. In metal or doped semiconductors, the reflectivity change is quite abrupt around  $\hbar\omega_p$  when the imaginary part of the dielectric constant is close to 0. In such a case, an anisotropic Drude-like response would result in a spectral feature in the vicinity of  $\hbar\omega_p$  in the RAS spectrum. In the case of MnAs, the reflectance exhibits a smooth variation in the spectral region centered on  $\hbar\omega_p$ .<sup>28</sup> Furthermore, TDDR experiments establish that the feature located at 2.9 eV is present when light is polarized along the  $c$  axis and absent in the opposite direction. Therefore, this spectral feature is not related to an anisotropic response of free carriers in the vicinity of the plasma edge: it is intrinsically related to excitations around 2.9 eV for light polarized along the  $c$  axis. Although intraband excitations are likely to contribute to the overall RAS signal, the observed spectral features could be the signature of interband transitions. Indeed, the imaginary part of the dielectric constant of MnAs is dominated by an important contribution from the bound electrons for energies above  $\sim 1-2$  eV.<sup>28</sup>

Before discussing the origin of the observed spectral features in term of interband transitions, we recall briefly some results about  $\alpha$ -MnAs band structure models and calcula-

tions. In older studies, Goodenough and co-workers established a one-electron band model for the  $d$ -state manifold of  $\alpha$ -MnAs,<sup>17,18</sup> assuming that these exchange-split bands lie in the gap between a filled valence band formed by  $s$ - $p$  bonding orbitals and an empty conduction band formed by  $s$ - $p$  antibonding orbitals. Recent works reporting band structure first principle calculations<sup>26,39-42</sup> based on density functional theory (DFT) give the following picture of the band structure in  $\alpha$ -MnAs. The  $4s$  states of As are hardly affected by the Mn exchange energy and lie at high binding energies, at  $\sim -10$  eV (in what follows, negative energies correspond to levels below the Fermi level,  $E_F$ ). Closer to  $E_F$ , one can find the spin-split Mn  $3d$  bands hybridized with As  $4p$  bands. Sanvito and Hill identified three distinct regions for these bands:<sup>40</sup> a low-energy  $p$ - $d$  bonding region ( $-6$ – $-2.5$  eV for majority spin and  $-6$ – $0$  eV for minority spin), an almost dispersionless intermediate region with a strong  $d$  character ( $\sim -2$  eV for majority spin and  $1$  eV for minority) and a high-energy  $p$ - $d$  antibonding region ( $-1.5$ – $3$  eV for majority spin and  $1.5$ – $4$  eV for minority). The shift between the spin-split degenerate  $d$  bands is not rigid due to strong  $p$ - $d$  hybridization. However, it is possible to estimate that the exchange splitting is  $\sim 3$  eV for Mn  $3d$  bands.<sup>42</sup> The existence of filled bands at  $\sim -2$  and  $\sim -4$  eV was confirmed by photoemission studies.<sup>43,44</sup>

The feature observed at 2.9 eV in the RA spectra can be assigned to transitions between occupied bands and empty ones above the Fermi level. In order to identify the observed interband transitions, we have to find optical transitions in the Brillouin zone satisfying the following rules: (i)  $\Delta\vec{k}=0$ , i.e., the initial and final states have the same wave vector (vertical transition), (ii) the joint density of states (JDOS) should have a local maximum corresponding to the situation where the difference in the gradient in  $\vec{k}$  between the two bands involved go to zero, (iii) the transition matrix elements should not be zero, i.e.,  $\langle\phi_f|\vec{A}\cdot\vec{p}|\phi_i\rangle\neq 0$ , where  $|\phi_f\rangle$  and  $|\phi_i\rangle$  are the final and initial states, respectively, for the component corresponding to a transition along the  $c$ -axis. As a consequence of (ii), transition can occur when two bands are parallel or when the gradient in  $\vec{k}$  goes to zero at a critical point of the Brillouin zone for both bands involved in the optical transition. In the later case, the DOS exhibit local maxima for the two bands. In what follows, we present some hypothesis about the origin of interband transition in MnAs based on published band-structure calculations. The discussion will focus on the DOS of MnAs and the energetic position of DOS local maxima, in order to track possible transitions. This approach remains speculative, as one would need information on the JDOS to determine the involved transitions unambiguously.

It is possible to find, from the features of the calculated band structures in the literature, several couples of occupied and unoccupied bands flat near the  $\Gamma$  and  $A$  symmetry points of the Brillouin zone (resulting in a high value of the DOS) separated by roughly 3 eV.<sup>39,40</sup> Therefore, a detailed analysis of the spectra based on the afore-mentioned rules turns out to be difficult. The observed spectral feature at 2.9 eV is quite broad. This tends to confirm that it is possibly related to interband transitions at several critical points in the band

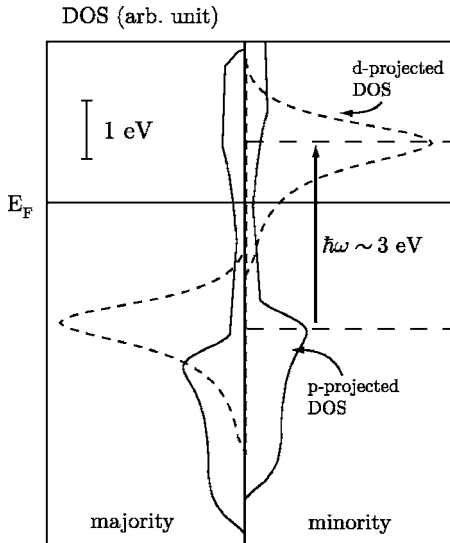


FIG. 6. Schematic representation of the  $p$ - (continuous line) and  $d$ -projected (dashed line) densities of states of minority and majority spin electrons in  $\alpha$ -MnAs adapted from Refs. 26, 41, 42, and 45. The shift in energy between the position of maxima in the minority and the majority DOS is  $\sim 3$  eV for  $d$ -states and  $\sim 1$  eV for  $p$ -states. The vertical arrow indicates possible transitions at energies close to the observed peak at 2.9 eV.

structure and cannot be assigned to a single transition.

Although the nature of the observed transitions cannot be determined simply, their observation is consistent with the calculated DOS in the framework of a band model with  $p$ - $d$  hybridization. In the minority DOS, the maximum of the  $p$ -projected DOS is located around  $\sim -2.5/-2$  eV and the maximum of the  $d$ -projected DOS is at  $\sim 1$  eV.<sup>26,42,45</sup> This would lead to a maximum around 3–3.5 eV for the joint density of states connecting  $p$  and  $d$  states. The associated transitions verify the condition  $\Delta l = \pm 1$  (dipolar selection rule) and should therefore have a stronger cross-section than  $d$ - $d$  transitions for example.

Figure 6 depicts the schematic DOS of  $\alpha$ -MnAs for majority and minority spins adapted from Refs. 26, 41, 42, and 45. Although pronounced maxima distant from  $\sim 3$  eV are absent in the majority DOS, one can see maxima in the  $p$ -projected DOS (occupied, below  $E_F$ ) and in the  $d$ -projected DOS (unoccupied, above  $E_F$ ), distant from  $\sim 3$  eV for the minority spins. This suggests that the band at 2.9 eV could be linked to transitions in the minority channel, connecting occupied  $p$ -states and unoccupied  $d$ -states.

The exchange splitting is not the same for  $p$ - and  $d$ -states. The shift in energy between the position of maxima in the minority and the majority DOS is roughly 3 eV for  $d$ -states and 1 eV for  $p$ -states.<sup>26,41,42,45</sup> If we assume that the exchange splitting vanishes in the paramagnetic state, the difference in energy between the maxima of  $p$ -DOS and  $d$ -DOS should vary when passing from a ferromagnetic state to a paramagnetic state. This would imply a shift in energy (toward lower energies) of the band related to  $p$ - $d$  excitations and its possible disappearance in the spectral range under investigation. This is consistent with our experimental observations. In order to analyze deeper the spectra and their evo-

lution across the transition, one would need the band structure and projected DOS of  $\beta$ -MnAs. Unfortunately, there are only a limited number of published band structures and DOS of  $\beta$ -MnAs.<sup>20,46</sup> We are currently performing band-structure calculations for the  $\alpha$  and  $\beta$  phase and group theory analysis in order to identify unequivocally the interband transitions and to explain the polarization dependence of the spectra, i.e., the fact that the spectral features related to  $\alpha$ -MnAs are observed for light polarized along the  $c$  axis.

Recent studies suggest that the ferromagnetic  $\alpha$  phase is possibly orthorhombically distorted when MnAs is epitaxially on GaAs(001) and that a slight further distortion is sufficient to transit to the  $\beta$  phase.<sup>47</sup> From the above-mentioned remarks, we can relate the evolution of the spectra and the progressive disappearance of the features with increasing temperature to the change of the electronic band structure across the transition. The change in the optical response is related to the transition from the exchange-split band structure of  $\alpha$ -MnAs to the band structure of  $\beta$ -MnAs. The absence of shift of the  $\alpha$ -related peaks with the temperature and the fact that their intensities are proportional to the proportion of  $\alpha$ -MnAs might indicate that each phase retains its electronic structure in the coexistence region and that the transition between the two band structures is abrupt. This is coherent with the fact that the  $\alpha$ - $\beta$  transition is a first-order transition and with the idea that a minute change in the Mn-As-Mn configuration responsible for the ferromagnetism in  $\alpha$ -MnAs is sufficient to transit to the  $\beta$  phase.<sup>47</sup>

## V. CONCLUSION

We have studied the  $\alpha$ - $\beta$  phase transition in MnAs thin (100 nm) layers epitaxially on GaAs(001) using optical spectroscopies. The reflectance anisotropy spectra differ significantly for the two phases. Although no prominent feature appears in the spectrum related to the  $\beta$  phase, the spectrum of the  $\alpha$  phase exhibits two features centered at 2.9 and 5.0 eV. The origin of these spectral features has been further investigated using temperature-dependent differential reflectance. It is shown that the band centered at 2.9 eV can be assigned to interband transitions for light polarized along the  $c$  axis of bulk  $\alpha$ -MnAs. We demonstrate that reflectance anisotropy spectroscopy can be used to monitor the  $\alpha$ - $\beta$  phase transition within the thin layer. The transition takes place between 10 and 45 °C in excellent agreement with data in the literature. Our results suggest that reflectance anisotropy spectroscopy could be used as a convenient and efficient tool to monitor the phase transition in MnAs thin layers as a function of parameters, such as applied pressure or strain imposed by the substrate. The evolution of the spectra also suggests that the  $\alpha$  and  $\beta$  phases, retain their band structures in the coexistence region and that the transition from the exchange-split band structure of the ferromagnetic phase to the  $\beta$  band structure proceeds sharply.

## ACKNOWLEDGMENTS

F.V. thanks B. Gallas and M. Lazzeri for helpful discussion and M. Eddrief for valuable comments. Part of this work was supported by ANR program PNANO, MOMES Project, 2005.



- <sup>1</sup>F. Heusler, Z. Elektrochem. Angew. Phys. Chem. **17**, 260 (1904).
- <sup>2</sup>J. Mira, F. Rivadulla, J. Rivas, A. Fondado, T. Guidi, R. Caciuffo, F. Carsughi, P. G. Radaelli, and J. B. Goodenough, Phys. Rev. Lett. **90**, 097203 (2003).
- <sup>3</sup>S. Gama, A. A. Coelho, A. de Campos, A. M. G. Carvalho, F. C. G. Gandra, P. J. von Ranke, and N. A. de Oliveira, Phys. Rev. Lett. **93**, 237202 (2004).
- <sup>4</sup>A. M. Nazmul, M. Shimizu, and M. Tanaka, J. Appl. Phys. **87**, 6791 (2000).
- <sup>5</sup>M. Tanaka, J. P. Harbison, M. C. Park, Y. S. Park, T. Shin, and G. M. Rothberg, J. Appl. Phys. **76**, 6278 (1994).
- <sup>6</sup>K. Akeura, M. Tanaka, M. Ueki, and T. Nishinaga, Appl. Phys. Lett. **67**, 3349 (1995).
- <sup>7</sup>M. Tanaka, Physica E (Amsterdam) (Amsterdam) **2**, 372 (1998).
- <sup>8</sup>F. Schippan, A. Trampert, L. Däweritz, K. H. Ploog, B. Dennis, K. U. Neumann, and K. R. A. Ziebeck, J. Cryst. Growth **201-202**, 674 (1999).
- <sup>9</sup>V. H. Etgens, M. Eddrief, D. Demaille, Y. L. Zheng, and A. Ouerghi, J. Cryst. Growth **240**, 64 (2002).
- <sup>10</sup>V. Garcia, M. Marangolo, M. Eddrief, H. Jaffrès, J.-M. George, and V. H. Etgens, Phys. Rev. B **73**, 035308 (2006).
- <sup>11</sup>V. Garcia, H. Jaffrès, M. Eddrief, M. Marangolo, V. H. Etgens, and J.-M. George, Phys. Rev. B **72**, 081303(R) (2005).
- <sup>12</sup>B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. London, Sect. B **67**, 290 (1954).
- <sup>13</sup>S. Hilpert and T. Dieckmann, Ber. Dtsch. Chem. Ges. B **44**, 2378 (1911).
- <sup>14</sup>C. P. Bean and D. S. Rodbell, Phys. Rev. **126**, 104 (1962).
- <sup>15</sup>R. H. Wilson and J. S. Kasper, Acta Crystallogr. **17**, 95 (1964).
- <sup>16</sup>I. Rungger and S. Sanvito, Phys. Rev. B **74**, 024429 (2006).
- <sup>17</sup>J. B. Goodenough and J. A. Kafalas, Phys. Rev. **157**, 389 (1967).
- <sup>18</sup>N. Menyuk, J. A. Kafalas, K. Dwight, and J. B. Goodenough, Phys. Rev. **177**, 942 (1969).
- <sup>19</sup>H. Yamaguchi, A. K. Das, A. Ney, T. Hesjedal, C. Pampuch, D. M. Schaadt, and R. Koch, Europhys. Lett. **72**, 4790 (2005).
- <sup>20</sup>M. K. Niranjan, B. R. Sahu, and L. Kleinman, Phys. Rev. B **70**, 180406(R) (2004).
- <sup>21</sup>V. M. Kaganer, B. Jenichen, F. Schippan, W. Braun, L. Däweritz, and K. H. Ploog, Phys. Rev. Lett. **85**, 341 (2000).
- <sup>22</sup>V. M. Kaganer, B. Jenichen, F. Schippan, W. Braun, L. Däweritz, and K. H. Ploog, Phys. Rev. B **66**, 045305 (2002).
- <sup>23</sup>T. Plake, M. Ramsteiner, V. M. Kaganer, B. Jenichen, M. Kästner, L. Däweritz, and K. H. Ploog, Appl. Phys. Lett. **80**, 2523 (2002).
- <sup>24</sup>M. Kästner, C. Herrmann, L. Däweritz, and K. H. Ploog, J. Appl. Phys. **92**, 5711 (2002).
- <sup>25</sup>N. Mattoso, M. Eddrief, J. Valda, A. Ouerghi, D. Demaille, V. H. Etgens, and Y. Garreau, Phys. Rev. B **70**, 115324 (2004).
- <sup>26</sup>P. Ravindran, A. Delin, P. James, B. Johansson, J. M. Wills, R. Ahuja, and O. Eriksson, Phys. Rev. B **59**, 15680 (1999).
- <sup>27</sup>D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, Appl. Phys. Lett. **52**, 957 (1988).
- <sup>28</sup>K. Bärner, R. Braunstein, and E. Chock, Phys. Status Solidi B **80**, 451 (1977).
- <sup>29</sup>F. Iikawa, P. V. Santos, M. Kästner, F. Schippan, and L. Däweritz, Phys. Rev. B **65**, 205328 (2002).
- <sup>30</sup>K. S. Burch, E. J. Singley, J. Stephens, R. K. Kawakami, D. D. Awschalom, and D. N. Basov, Phys. Rev. B **71**, 125340 (2005).
- <sup>31</sup>M. Kästner, F. Schippan, P. Schützendübe, L. Däweritz, and K. H. Ploog, Phys. Status Solidi B **460**, 144 (2000).
- <sup>32</sup>M. Kästner, F. Schippan, P. Schützendübe, L. Däweritz, and K. H. Ploog, J. Vac. Sci. Technol. B **18**, 2052 (2000).
- <sup>33</sup>D. E. Aspnes and A. A. Studna, Phys. Rev. Lett. **54**, 1956 (1985); P. Chiaradia and G. Chiarotti, in *Photonic Probes of Surfaces*, edited by P. Halevi (Elsevier, Amsterdam, 1995); D. E. Aspnes, E. Colas, A. A. Studna, R. Bhat, M. A. Koza, and V. G. Kerasmidas, Phys. Rev. Lett. **61**, 2782 (1988); Y. Borenstein, W. L. Mochan, J. Tarriba, R. G. Barrera, and A. Tadjeddine, *ibid.* **71**, 2334 (1993).
- <sup>34</sup>I. Kamiya, D. E. Aspnes, L. T. Florez, and J. P. Harbison, Phys. Rev. B **46**, 15894 (1992); V. L. Berkovits, P. Chiaradia, D. Paget, A. B. Gordeeva, and C. Goletti, Surf. Sci. **441**, 26 (1999); F. Arciprete, C. Goletti, E. Placidi, P. Chiaradia, M. Fanfoni, F. Patella, C. Hogan, and A. Balzarotti, Phys. Rev. B **68**, 125328 (2003); A. I. Shkrebtii, N. Esser, W. Richter, W. G. Schmidt, F. Bechstedt, B. O. Fimland, A. Kley, and R. Del Sole, Phys. Rev. Lett. **81**, 721 (2004).
- <sup>35</sup>H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings* (Springer, New York, 1988).
- <sup>36</sup>R. Magalhães-Paniago, L. N. Coelho, B. R. A. Neves, H. Westfahl, F. Iikawa, L. Däweritz, C. Spezzani, and M. Sacchi, Appl. Phys. Lett. **86**, 053112 (2005).
- <sup>37</sup>P. Lalanne and M. Hutley, in *Encyclopedia of Optical Engineering* (Marcel Dekker, New York, 2003), pp. 62–71.
- <sup>38</sup>P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer, New York, 2001).
- <sup>39</sup>A. Continenza, S. Picozzi, W. T. Geng, and A. J. Freeman, Phys. Rev. B **64**, 085204 (2001).
- <sup>40</sup>S. Sanvito and N. A. Hill, Phys. Rev. B **62**, 15553 (2000).
- <sup>41</sup>Y.-J. Zhao, W. T. Geng, A. J. Freeman, and B. Delley, Phys. Rev. B **65**, 113202 (2002).
- <sup>42</sup>M. Shirai and Y. Tokioka, J. Electron Spectrosc. Relat. Phenom. **88-91**, 357 (1998).
- <sup>43</sup>K. Shimada, O. Rader, A. Fujimori, A. Kimura, K. Ono, N. Kamakura, A. Kakizaki, M. Tanaka, and M. Shirai, J. Electron Spectrosc. Relat. Phenom. **88-91**, 207 (1998).
- <sup>44</sup>J. Okabayashi, M. Mizuguchi, K. Ono, M. Oshima, A. Fujimori, H. Kuramochi, and H. Akinaga, Phys. Rev. B **70**, 233305 (2004).
- <sup>45</sup>H.-M. Hong, Y.-J. Kang, J. Kang, E.-C. Lee, Y.-H. Kim, and K.-J. Chang, Phys. Rev. B **72**, 144408 (2005).
- <sup>46</sup>K. Motizuki, K. Katoh, and A. Yanase, J. Phys. C **19**, 495 (1986).
- <sup>47</sup>A. K. Das, C. Pampuch, A. Ney, T. Hesjedal, L. Däweritz, R. Koch, and K. H. Ploog, Phys. Rev. Lett. **91**, 087203 (2003).