Abrupt changes in the temperature coefficient of resistivity induced by the phase transitions in MnAs films on GaAs

Y. Takagaki, L. Däweritz, and K. H. Ploog
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany
(Received 10 August 2006; revised manuscript received 22 December 2006; published 18 January 2007)

The scattering processes of conduction carriers in MnAs channels prepared on GaAs(001) and GaAs(111)B substrates are investigated through the temperature dependence of the resistivity in the regime where MnAs undergoes two phase transitions. The temperature coefficient changes discontinuously at the phase transitions and is negative for the β phase, indicating that a certain magnetic order exists in β-MnAs. The temperature dependence can be comprehensively understood if β-MnAs possesses an antiferromagetic order.

DOI: 10.1103/PhysRevB.75.035213 PACS number(s): 73.61.−r, 75.30.Kz, 75.50.Cc

Manganese arsenide is one of the prospective materials for spintronic applications as it is ferromagnetic at room temperature and can be integrated into GaAs-based electrical and optical devices by means of epitaxial growth.[1] At the Curie temperature $T_C \approx 40$ °C, a simultaneous magnetic and structural first-order phase transition takes place. In addition, the material undergoes a second-order structural phase transition at $T_s \approx 125$ °C. While the crystal structure is identical (hexagonal) for the low-temperature phase (α phase) and the high-temperature phase (γ phase), it transforms to orthorhombic for the medium-temperature phase (β phase).

The magnetic properties that accompany the phase transitions are unusual.[2,3] The ferromagnetic order is lost abruptly at T_C. The temperature dependence of the magnetization below T_C is described by the Brillouin function with T_s being the extrapolated Curie temperature. Moreover, the Curie-Weiss law is obeyed in the magnetic susceptibility only above T_s. For temperatures between T_C and T_s, the susceptibility anomalously increases with temperature, giving rise to a peak at T_s. These peculiar magnetic properties have fueled a debate that β-MnAs may be antiferromagnetic rather than paramagnetic.[2,4–6] It is known that MnAs develops antiferromagnetism under hydrostatic pressures[7] or when As is partly replaced by P with a concentration as low as several %.[8] Antiferromagnetic orders are thus not far-fetched for MnAs. However, neutron-scattering measurements have detected no sign of long-range magnetic order in β-MnAs.[9] With respect to the anomalies originating from the phase transitions, we note that the specific heat exhibits a peak at T_s in addition to that at T_C.[10] In conjecturing the magnetic order in β-MnAs, electrical transport properties have received little attention so far due to a lack of conclusive data.

In this paper, the transport properties in MnAs films on GaAs substrates are examined in the temperature region of the phase transitions in order to reveal variations in the carrier scattering processes associated with the phase transitions. Fischer and Pearson[11] reported the temperature dependence of the resistivity including the range of the γ phase half a century ago. Their MnAs specimen was prepared by heating a mixture of Mn and As up to the melting point. Inhomogeneities in the specimen were evident as microcracks were formed by the thermal cycles to measure the temperature dependence due to the strongly anisotropic thermal expansion of the material.[12] It was obviously impossible to determine the resistivity along specific crystal orientations. In the present study, we employ crystalline MnAs layers grown by molecular-beam epitaxy (MBE). The MBE-grown layers provide matchless material purity and crystal perfection. We demonstrate that the phase transitions give rise to discontinuous changes in the temperature coefficient of the resistivity. As this implies a qualitative change in the magnetic scattering at the phase transition between the β and γ phases, a certain magnetic correlation is concluded to exist in the β phase.

Two films were grown on GaAs(001) substrates by MBE at a growth temperature of 230 °C. On a GaAs(111)B substrate, another film was grown with the growth temperature 250 °C. The growth conditions were optimized to have the films on the GaAs(001) substrates to be $(1\bar{1}00)$-oriented with the [0001] and $[11\bar{2}0]$ directions of MnAs being parallel to, respectively, the $[1\bar{1}0]$ and [110] directions of GaAs, as illustrated in Fig. 1(a).[1,13] For the GaAs(111)B substrate, the *c* axis of MnAs was oriented to be normal to the surface, see Fig. 1(b). The $[1\bar{1}00]$ and $[11\bar{2}0]$ directions of MnAs were parallel to the $[11\bar{2}]$ and $[1\bar{1}0]$ directions of GaAs, respectively.[13] Hall-bar structures were patterned from the films by means of electron-beam lithography and etching techniques.[14] The width of the MnAs channels ranged between 10 and 30 μm. The distance between the voltage leads was 350–600 μm. The resistivity of the MnAs channels was measured using the four-probe lock-in technique in a temperature range between −16 and 142 °C. The excitation current was 100 nA. The samples were kept in a He gas atmo-

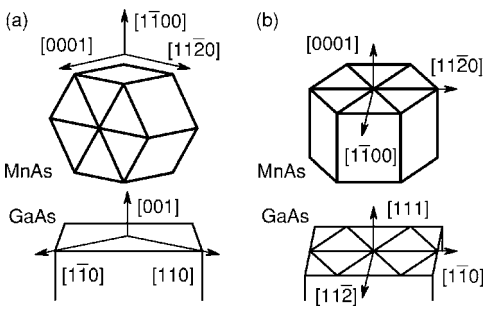

FIG. 1. Epitaxial relationship of MnAs layers on GaAs(001) (a) and GaAs(111)B (b) substrates.

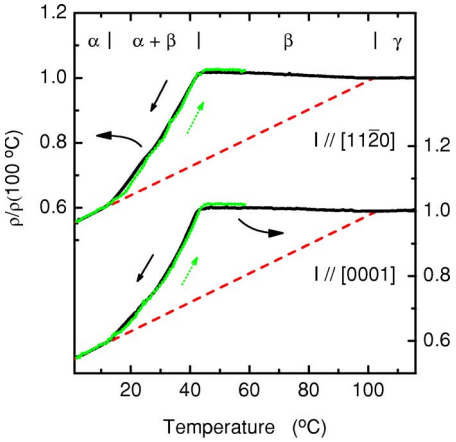

FIG. 2. (Color online) Temperature dependence of the resistivity ρ, normalized to the value at 100 °C, in MnAs channels on GaAs(001) when the current I is along the [11$\bar{2}$0] and [0001] directions of MnAs. The sample was cooled from 115 to 2 °C (solid curves) and then warmed to 58 °C (dotted curves). The phases in the MnAs channels are indicated at the top of the panel. The dashed lines show the extrapolation of the temperature dependence for α-MnAs to the phase transition temperature between β- and γ-MnAs.

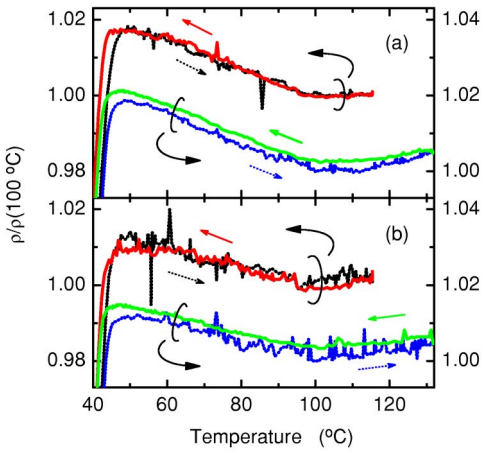

FIG. 3. (Color online) Temperature dependence of the resistivity ρ in MnAs channels on GaAs(001) when the sample is heated (dotted curves) and subsequently cooled (solid curves). The maximum temperature for the first and second measurement runs is 115 and 132 °C, respectively. The resistivity is normalized to the value at 100 °C. The current is along the [11$\bar{2}$0] (a) and [0001] (b) directions of MnAs.

sphere during the measurements to reduce the thermal oxidation of MnAs and to prevent the formation of a water layer on the surface, which may react with MnAs.[14]

Preliminary results of the measurements, obtained from MnAs channels on a GaAs(001) substrate with the width of a few μm, were reported in Ref. 14. For this crystal orientation, we present here only the results obtained from a representative device fabricated from a MnAs film different from that previously employed. The film thickness is 100 nm, instead of 50 nm for the film in Ref. 14. The two films were grown under different conditions. No qualitative difference was found between the two kinds of devices wherever we can make a comparison. The temperature dependence we present below is hence generic for MnAs layers. The thickness of the film grown on the GaAs(111)B substrate is 50 nm.

In Fig. 2, we show the temperature dependence of the resistivity ρ for a MnAs(1$\bar{1}$00)/GaAs(001) device in the regime of the phase transitions. The two thermal hysteresis curves were obtained from the channels stretched along the [0001] and [11$\bar{2}$0] directions of MnAs. The behavior is similar for both of the current directions. The phases of MnAs are identified as indicated at the top of the panel. The rapid increase of the resistivity with temperature for the α phase is due to spin-disorder and phonon scattering.[15] Above 43 °C for temperature sweep down and 45 °C for temperature sweep up, a linear negative temperature dependence abruptly emerges for the β phase, as we previously reported in Ref. 14.

The transition between the β and γ phases occurs at about 100 °C. This temperature is considerably lower than the transition temperature reported for bulk MnAs. The stress between the MnAs layer and the substrate is presumed to be responsible for the destabilization of the β phase. While hydrostatic pressure increases T_s,[7] the MnAs layers on GaAs substrates are tensile-stressed around T_s as the thermal expansion coefficient of MnAs is one order of magnitude larger than that of GaAs.[16] In our previous report,[14] the polarity of the temperature coefficient for the γ phase was inconclusive as the thermally activated parallel conduction in the semi-insulating GaAs substrates was not negligible and a resistance increase resulting from the oxidation of MnAs could not be isolated from the channel resistance. In the present study, therefore, the MnAs channels have been widened to allow us to ignore the substrate contribution.

In Fig. 3, the temperature dependence is shown when the sample was heated to a maximum temperature T_{max} and subsequently cooled. The measurements were carried out with T_{max}=115 °C for the first run and with T_{max}=132 °C for the second run. We find that the temperature coefficient turns positive discontinuously for the γ phase.[11,15] The resistivity was identical between up and down sweeps when T_{max} =115 °C, i.e., the oxidation of MnAs was insignificant. In contrast, the oxidation led to a slight increase of the resistivity for sweep down in comparison to that for sweep up when T_{max}=132 °C. Nevertheless, the abrupt change in the polarity of the temperature coefficient between the β and γ phases is undisputable as the coefficient is still positive for the γ phase even for the latter sweep down. We also note that the thermally activated parallel conduction cannot play a role with respect to the abrupt change to the positive polarity as it shifts the temperature coefficient only to the negative direction.

The resistivity in a MnAs(0001)/GaAs(111)B device, which is plotted in Fig. 4, reveals the same trend. Here, the MnAs channels were aligned along the [1$\bar{1}$00] and [11$\bar{2}$0] directions for the two traces. The transport properties are found to be almost isotropic and exhibit only a negligibly small thermal hysteresis. As T_{max}=142 °C, the resistivity in temperature sweep down is larger than that in temperature

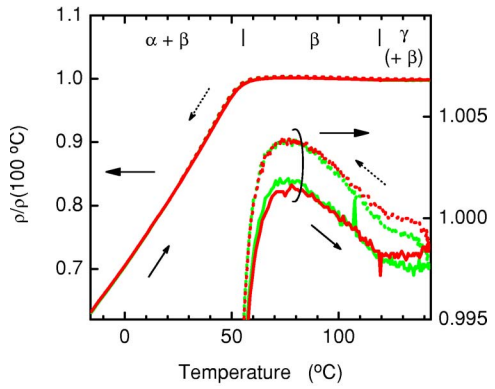

FIG. 4. (Color online) Temperature dependence of the resistivity ρ in MnAs channels on GaAs(111)B when the sample is heated (solid curves) and subsequently cooled (dotted curves). The resistivity is normalized to the value at 100 °C. The phases in the MnAs channel are indicated at the top of the panel. The current is along the $[1\bar{1}00]$ and $[11\bar{2}0]$ directions of MnAs for the red and green curves, respectively. The high-temperature portion is shown with an expanded scale on the right-hand side.

sweep up. The temperature coefficient is again negative for β-MnAs, indicating that the stress imposed by the substrates is unlikely to be responsible for the negative temperature dependence. In contrast to the films on GaAs(001) substrates, the coexistence of the α and β phases[17] persists down to the lowest temperature (−16 °C) of the measurement. For the GaAs(111)B substrate, the c axis of MnAs is normal to the surface. Therefore, the crystal distortion of the orthorhombic β-MnAs structure from the hexagonal symmetry (about 0.2%) has to be taken into account.[9] It turns out that the orthorhombic distortion along the b axis increases the phase-transition stress resulting from the discontinuous expansion of about 1% of the hexagonal plane at the transition from the β phase to the α phase. The temperature range of the phase coexistence is thus widened. As a reversed structural transformation takes place at the phase transition between the β and γ phases, β- and γ-MnAs may coexist around T_s for the GaAs(111)B substrate. The magnitudes of the temperature coefficient of the resistivity for the β and γ phases are almost identical in Fig. 3. If the β and γ phases coexist, the temperature coefficient will be canceled to be almost zero, as one finds in Fig. 4.

In order to understand the origin of the sudden polarity change in the temperature coefficient at the transition between the β and γ phases, one has to identify the mechanism for the negative temperature dependence of β-MnAs. Although it has not been clarified in detail so far, we point out two possible scenarios.

The resistivity decreases with increasing temperature above T_C also, among others, in (Ga,Mn)As films. Matsukura *et al.*[18] concluded that the critical fluctuations arising in the order parameter[19] were the dominant scattering mechanism. The probability of giant magnetic moments is increased by the correlations between neighboring magnetic moments. These giant magnetic moments scatter long-wavelength conduction carriers more efficiently than a collection of the individual moments fluctuating completely randomly from each other.[20,21] Thus, the resistivity decreases in the course of a complete loss of the magnetic correlation above T_C. A microscopic calculation has revealed that this scattering process can both increase and decrease the resistivity at temperatures around T_C exhibiting a damped oscillatory dependence on $k_F d$, where k_F is the Fermi wave number and d is the distance between the magnetic moments.[20] The effect is, nevertheless, strongest when $k_F d \sim 1$, for which the scattering yields an excess resistivity. Instead of the critical scattering, however, Hirakawa *et al.*[22] have suggested that thermal activation is responsible for the negative temperature dependence as infrared absorption spectroscopy indicates that holes, which are the conduction carriers in (Ga,Mn)As, are nearly localized. The carriers in MnAs are, however, unlikely to be localized, and so the critical scattering may account for the negative temperature dependence for β-MnAs.

The other explanation assumes that β-MnAs is antiferromagnetic.[4,6] The antiferromagnetic spin order with a period incommensurate with the ionic lattices acts as a magnetic superlattice. The Fermi surface is consequently distorted as magnetic superzone gaps are generated. The opening up of the energy gap leaves less of the Fermi surface available for the conduction, and thus reduces the effective number of conduction carriers.[19] The energy gap diminishes while the temperature rises to the Néel temperature T_N. The restoration of the carrier density decreases the resistivity. Cr[23] and its alloys[24] are typical materials in which spin-density-wave antiferromagnetism gives rise to a negative temperature coefficient. In this interpretation, the transition temperature T_s between the β and γ phases corresponds to T_N.

In the first case, the scattering rate is responsible for the negative temperature dependence, whereas its origin lies in the carrier density in the second case. In either case, the dramatic change in the temperature dependence observed in our devices is interpreted to mean that β-MnAs possesses a certain magnetic order, a residual ferromagnetic-like order or an antiferromagnetic order. The total disappearance of the order at T_s unmasks the ordinary positive temperature dependence for γ-MnAs due to phonon scattering.

The fact that the resistivity is discontinuous at T_C but continuous at T_s may have a significant implication. (Note that the resistivity in Fig. 2 changes continuously due to the coexistence of the α and β phases around T_C.[14] By extrapolating the low- and high-temperature curves, the ratio of the resistivities of the α and β phases is estimated to be 1.40 at 40 °C.) Notice that the temperature-dependence curve of the α phase can be extrapolated without difficulty to the resistivity value at T_s, as shown by the dashed lines in Fig. 2. If it were not for the β phase, the resistivity curve would have developed merely a kink at the phase transition (at T_s). With regard to the resistivity continuity at T_s, an antiferromagnetic order will smoothly vanish at T_N $(=T_s)$, whereas there is no reason for such a coincidence if the magnetic order in β-MnAs is a residue of the ferromagnetic order in α-MnAs. The antiferromagnetism scenario hence appears to be more comprehensive than the critical-scattering scenario.

Antiferromagnetic order in β-MnAs has never been observed in neutron-scattering measurements.[9] Based on their

density-functional calculations, Niranjan, Sahu, and Kleinman[4] ascribed the failure to weak interlayer correlations. That is, although an antiferromagnetic order can be well established within the "hexagonal" plane,[4,5] the spin orientations of Mn in adjacent planes are practically independent from each other. The randomness can eliminate signs of antiferromagnetism in the neutron-scattering measurements. The superzone gaps prevail even in this circumstance as long as the superlattice that generates the gap is intact in the plane. Taking advantage of the c axis of MnAs being parallel to the surface for the MnAs layers on GaAs(001), one can, in principle, explore anisotropic behavior in the resistivity when the magnetic modulation is unidirectional in the surface plane, as mentioned above. However, the consequent anisotropy in MnAs will be too small to be verified, as the resistivity change in the temperature dependence of β-MnAs only amounts to about 1% in Fig. 3.

The magnetic hysteresis of a ferromagnet exhibits the exchange-biasing effect[25] when it is embedded in an antiferromagnetic matrix. In fact, the effect was observed for MnAs layers when α- and β-MnAs coexisted.[26] As β-MnAs is generally considered to be paramagnetic, the apparent antiferromagnetism in β-MnAs was attributed to having been induced by the stress[5,7] imposed by the substrate. However, as the phase coexistence greatly reduces the stress in the $[11\bar{2}0]$ direction,[14] the presence of the exchange-biasing effect might be an indication of the antiferromagnetism without stress in β-MnAs.

In conclusion, the temperature dependence of the resistivity in MnAs channels fabricated on GaAs(001) and GaAs(111)B substrates has been investigated in the phase-transition regime. While the resistivity increases with temperature for the α and γ phases, the temperature coefficient is negative for the β phase. The changes in the temperature coefficient take place discontinuously at the phase transitions. The polarity change at the transition between the β and γ phases manifests the presence of a magnetic order in β-MnAs that smoothly vanishes at T_s. These characteristics are anticipated if the magnetic order in β-MnAs is of an antiferromagnetic type.

This work was supported in part by the Federal Ministry of Education and Research under the "nanoQUIT" program.

[1] M. Tanaka, Semicond. Sci. Technol. **17**, 327 (2002).
[2] C. Guillaud, J. Phys. Radium **12**, 223 (1951).
[3] H. Ido, J. Appl. Phys. **57**, 3247 (1985).
[4] M. K. Niranjan, B. R. Sahu, and L. Kleinman, Phys. Rev. B **70**, 180406(R) (2004).
[5] I. Rungger and S. Sanvito, Phys. Rev. B **74**, 024429 (2006).
[6] H. Yamaguchi, A. K. Das, A. Ney, T. Hesjedal, C. Pampuch, D. M. Schaadt, and R. Koch, Europhys. Lett. **72**, 479 (2005).
[7] N. Menyuk, J. A. Kafalas, K. Dwight, and J. B. Goodenough, Phys. Rev. **177**, 942 (1969).
[8] U. Neitzel and K. Bärner, J. Phys. C **11**, 4975 (1978).
[9] R. H. Wilson and J. S. Kasper, Acta Crystallogr. **17**, 95 (1964).
[10] H.-J. Krokoszinski, C. Santandrea, E. Gmelin, and K. Bärner, Phys. Status Solidi B **113**, 185 (1982).
[11] G. Fischer and W. B. Pearson, Can. J. Phys. **36**, 1010 (1958).
[12] S. Haneda, N. Kazama, Y. Yamaguchi, and H. Watanabe, J. Phys. Soc. Jpn. **42**, 1201 (1977).
[13] The lattice mismatch along the a axis of MnAs is 7.5%. The mismatch along the c axis of MnAs when the substrate is GaAs(001) is 30%.
[14] Y. Takagaki, E. Wiebicke, L. Däweritz, and K. H. Ploog, J. Solid State Chem. **179**, 2271 (2006).
[15] K. Bärner, Phys. Status Solidi B **84**, 385 (1977).
[16] T. Suzuki and H. Ido, J. Phys. Soc. Jpn. **51**, 3149 (1982).
[17] Y. Takagaki, E. Wiebicke, L. Däweritz, and K. H. Ploog, Appl. Phys. Lett. **85**, 1505 (2004).
[18] F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, Phys. Rev. B **57**, R2037 (1998).
[19] M. Ausloos, in *Magnetic Phase Transitions*, edited by M. Ausloos and R. J. Elliott (Springer, Berlin, 1983), p. 99.
[20] P. G. de Gennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958).
[21] S. von Molnár and T. Kasuya, Phys. Rev. Lett. **21**, 1757 (1968).
[22] K. Hirakawa, S. Katsumoto, T. Hayashi, Y. Hashimoto, and Y. Iye, Phys. Rev. B **65**, 193312 (2002).
[23] E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).
[24] E. Fawcett, H. L. Alberts, V. Y. Galkin, D. R. Noakes, and J. V. Yakhmi, Rev. Mod. Phys. **66**, 25 (1994).
[25] J. Nogués and I. K. Schuller, J. Magn. Magn. Mater. **192**, 203 (1999).
[26] S. H. Chun, S. J. Potashnik, K. C. Ku, J. J. Berry, P. Schiffer, and N. Samarth, Appl. Phys. Lett. **78**, 2530 (2001).