Electron paramagnetic resonance of Mn in $In_{1-x}Mn_xAs$ epilayers

J. Szczytko and A. Twardowski
Institute of Experimental Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland

M. Palczewska and R. Jabłoński
Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland

J. Furdyna
University of Notre Dame, Notre Dame, Indiana 46556

H. Munekata
Imaging Science and Engineering Laboratory, Tokyo Institute of Technology Yokohama 226, Japan
(Received 23 December 1999; revised manuscript received 21 August 2000; published 6 February 2001)

Electron paramagnetic resonance was measured in $In_{1-x}Mn_xAs$ epilayers with $0.0014 \leqslant x \leqslant 0.014$, with the intention of identifying the state of the Mn ion when it enters the InAs lattice. The data were taken at low temperatures. The observed spectra were attributed to ionized Mn acceptor A^- (d^5). No neutral Mn acceptor centers (d^5+h) were detected.

DOI: 10.1103/PhysRevB.63.085315 PACS number(s): 71.55.Eq, 75.50.Pp, 75.70.−i, 76.30.Fc

I. INTRODUCTION

Recent progress in the preparation of III-V compounds containing substitutional Mn ions[1,2] stirred enormous interest in the scientific community, inasmuch as it holds significant promise of introducing spin-based effects into III-V-based electronics. On the theoretical front, it also refreshed the interest of the scientific community in s,p-d and d-d exchange interactions, which were previously studied extensively in so-called diluted magnetic semiconductors (DMS's) based on II-VI compounds.[3]

It is clear that the nature of the Mn impurity in the III-V lattice holds the key to the physical behavior of III-V-based alloys containing Mn (Refs. 1 and 4–9) (such as, e.g., the ferromagnetic ordering of Mn magnetic moments observed for relatively low Mn concentrations). In particular, this problem is decisive for understanding the exchange interaction of the band electrons with the localized magnetic ions (i.e., the so-called s,p-d exchange),[10] as well as the magnetic coupling between the magnetic ions themselves (the d-d exchange).[10,11] The purpose of this paper to use electron paramagnetic resonance (EPR) measurements for identifying the state of the Mn ion in $In_{1-x}Mn_xAs$ alloys (the first such alloys to be grown by molecular-beam epitaxy), which hold significant promise for spintronic applications along their better-known $Ga_{1-y}Mn_yAs$ alloy systems.

II. BACKGROUND: POSSIBLE MN IMPURITY STATES IN THE III-V LATTICE

The manganese impurity in the III-V lattice has been studied for a long time.[12–28] The results of those investigations can be summarized as follows: There are essentially three types of Mn centers which can exist in the III-V lattice. The first one (we denote it as center $C1$) is formed by substitutional manganese Mn^{3+}, which is in the so-called d^4 configuration, with to the ground state spin of $S=2$. This configuration is equivalent to the case of Cr^{2+} in II-VI DMS's, and has all the features characteristic of that case, including the Jahn-Teller effect and magnetic anisotropy. The second type of Mn center (denoted here as $C2$) forms when the $C1$ center traps an electron and binds it tightly to the d shell. Such a center can be regarded effectively as a d^5 configuration, with a ground-state spin S of 5/2. Finally, since the $C2$ Mn center is negatively charged, it can attract and (weakly) bind a hole, forming a (d^5+h) complex (referred to as a $C3$ center).[15] Due to the exchange interaction between the d shell $(S=5/2)$ and the bound hole $(j=3/2)$, the ground state of $C3$ may have a total angular momentum of $J=4$ (when the S-j interaction is ferromagnetic) or $J=1$ (for antiferromagnetic interaction). Centers $C1$ and $C3$ can be viewed as neutral acceptor centers $A^0(d^4)$ and $A^0(d^5+h)$, respectively, while center $C2$ is an ionized acceptor A^-.

Experiments on GaP:Mn revealed the existence of both $A^0(d^4)$ and A^- centers.[28] In contrast, the presence of $A^0(d^4)$ centers was not observed in EPR measurements on GaAs:Mn.[15] Moreover, the available magnetization data on GaAs:Mn do not match the behavior expected for Mn in the form of $A^0(d^4)$ centers.[20,24,25,29] For most GaAs:Mn crystals, on the other hand, ionized acceptor centers A^- were consistently visible, as shown by EPR spectra with the characteristic six-line hyperfine manifold centered at $g^*=2.00$.[13,14] We mention here parenthetically that the spectrum of Mn in zinc-blende lattices consists of 30 lines (six hyperfine lines, each split into five fine-structure lines associated with the crystal field of the zinc-blende structure). However, in highly conducting materials the fine-structure lines are frequently not seen, presumably due to the screening of the crystal field by the free carriers.[30] We believe that in the cases showing the six hyperfine lines in GaAs:Mn the fine-structure lines have been similarly screened out by the conducting properties of the material.

TABLE I.

Sample	Mn molar contents x	Growth temp. (°C)	Presence of the second phase	Carrier concentration (cm^{-3})	EPR line
*R*1114	0.00 (InAs)	300	no		no
*R*1251	0.0014	200	no	$n=1.1\times10^{18}$ (4.2 K)	yes
*R*1126	0.014	200	no	$n=1.1\times10^{16}$ (4.2 K)	yes

In some cases additional lines were also observed for $g^*=2.77$ and $g^*=5.72$,[15] and were interpreted as triplet transitions for $\Delta m=1$ and 2, where Δm represents the change of J_z.[15] These transitions were ascribed to an A^0 (d^5+h) center with a $J=1$ ground state. This model was corroborated by IR spectroscopy data, which revealed the presence of an acceptor level at about 0.113 eV above the top of the valence band.[12] Recently the spectrum of this acceptor was thoroughly studied in the presence of uniaxial stress and magnetic field.[24,25,31] The results give strong support for the A^0 (d^5+h) impurity center concept. Also the magnetic data of GaAs:Mn could be successfully described, taking into account A^0 (d^5+h) and A^- centers.[20,29] The lack of A^0 (d^4) centers was recently explained by configuration cluster-model calculations, which showed that for GaAs the ground state of a neutral acceptor is dominated by the (d^5+h) configuration.[32] It therefore seems rather well established that for bulk GaAs the manganese impurity occurs either as a neutral (d^5+h) or as an ionized (d^5) acceptor center. Ionization of A^0 (d^5+h) then gives rise to *p*-type conductivity of this material.

However, the situation for $Ga_{1-x}Mn_xAs$ grown by molecular beam epitaxy appears to be different. For epilayers with low Mn content, $x<0.01$ (which one could expect to be rather similar to the bulk Mn-doped samples) only one single line is visible for $g^*\simeq2.0$.[33] This line may be viewed as a broadened A^- multiplet, since it occurs at the same magnetic field as the signal already identified as A^- in bulk GaAs:Mn. The collapse of the EPR multiplet of the d^5 center with increasing Mn concentration into a single line is well known for II-VI Mn-based DMS's.[34]

The important result of this work is the absence of EPR absorption for $g^*=2.7$, indicating the absence of A^0 centers in the epilayers.[33] A possible reason for this is the high concentration of free holes in the epilayer,[35,36] which screen the Coulomb potential of the A^- center and reduce the hole binding energy. The holes can then easily ionize, leaving only the A^- centers.

In contrast to $Ga_{1-y}Mn_yAs$, for $In_{1-x}Mn_xAs$, there exist no comprehensive data that would enable us to establish the nature of the Mn impurity in that system.[37–40] The purpose of the present paper is to present EPR data which strongly suggest that Mn ions in InAs occur predominantly as A^- centers.

III. EXPERIMENT

The $In_{1-x}Mn_xAs$ epilayers studied in this paper were grown by MBE on (100) GaAs substrates on an InAs buffer, as described elsewhere.[4] The growth temperature ranged from 200 to 340 °C. We used two different epilayers (with Mn concentrations $x=0.0014$ and 0.014), along with a reference InAs/GaAs sample, as listed in Table I.

The samples were characterized by measuring magnetization as a function of temperature $(2<T<300$ K) and magnetic field (up to 6 T). The magnetic moment of each sample, measured by a superconducting quantum interference device magnetometer, was corrected for the diamagnetic contribution of the substrate. This contribution was evaluated from the high temperature extrapolation of the substrate InAs/GaAs magnetization measured in the temperature range 10–300 K. At low temperatures (below 10–15 K, depending on the Mn concentration), $In_{1-x}Mn_xAs$ is in general expected to be ferromagnetic,[4] while at higher temperatures $(T>10-15)$ $In_{1-x}Mn_xAs$ should reveal paramagnetic behavior. In particular, the magnetization of the paramagnetic phase should decay with temperature roughly as $1/T$.

Electron paramagnetic resonance was measured with the use of a standard EPR spectrometer operating at 9.5 GHz and in the temperature range from 5 to 300 K. The samples were attached to a quartz sample holder by teflon tape. In some cases there was an additional absorption from the holder, but this contribution could be easily distinguished from the EPR absorption of the sample by measuring the holder without $In_{1-x}Mn_xAs$. The magnetic field was calibrated in each measurement using an Al_2O_3:Cr marker.

For each sample, EPR was measured at a series of temperatures (from 6 to 300 K). The two $In_{1-x}Mn_xAs$ epilayers revealed clear and pronounced EPR absorption lines, and no EPR lines were visible for background InAs sample (*R*1114).

IV. RESULTS AND DISCUSSION

For the epilayer with the lowest Mn concentration (*R*1251), a single EPR line was observed with the *g* factor around 2.015 ($H=3.3$ kG), as illustrated by Fig. 1. The weak line seen in the figure at about 2.8 kG was identified as resulting from the quartz sample holder. We ascribe the observed line at 3.3 kG to the A^- center (*C*2), described in Sec. I. The identification is based on the following arguments: (i) Since in earlier studies A^- was easily visible both for bulk GaAs:Mn and for $Ga_{1-y}Mn_yAs$ epilayers,[10,15] we expect that this should be also the case for InMnAs epilayers. (ii) Mn is the dominant impurity in $In_{1-x}Mn_xAs$ and thus should dominate the EPR absorption, while the possible other impurities should contribute much less to EPR absorption, as is evident from the absence of EPR in our reference

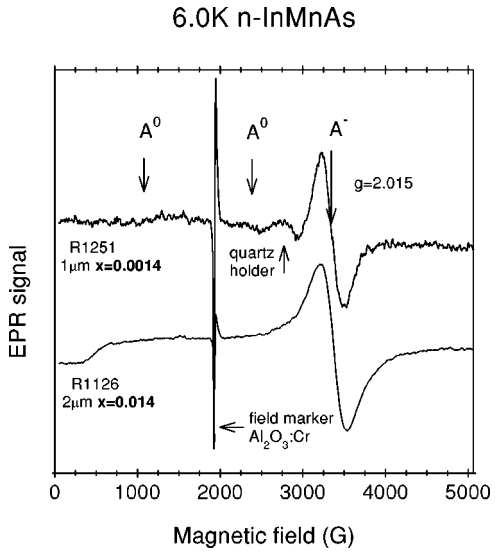

FIG. 1. EPR spectrum of $In_{1-x}Mn_xAs$ epilayers with $x=0.0014$ ($R1251$) and $x=0.014$ ($R1126$) taken at 6 K. The theoretical positions of A^- and A^0 lines are marked by arrows. The line at about 2.8 kG results from the quartz sample holder. The sharp lines at 1.9 and 5.4 kG are magnetic-field markers of Al_2O_3:Cr. It is clear that the EPR signal from the epilayer originates only from the A^- center.

InAs/GaAs sample. (iii) The effective g factor of the observed line agrees well with the center of the A^- multiplet structure observed for GaAs:Mn. We believe that the collapse of the EPR multiplet into a single line results from exchange narrowing of the multi line structure due to Mn-Mn interaction, which is apparently already signifiant even at this Mn concentration. As mentioned above, collapse is well known for II-VI Mn-based DMS's,[34] and was also observed for $Ga_{1-y}Mn_yAs$.[10] The A^- line for $R1251$ shows practically no anisotropy as the magnetic field is rotated from the in-plane direction (we denote it as 0° configuration) to a direction perpendicular to the epilayer (90° configuration). The sample reveals paramagnetic behavior throughout the experimental temperature range i.e., its magnetization decreases with increasing temperature (becoming vanishingly small at room temperature, Fig. 2).

For the epilayer with the higher Mn content the single line of the A^- center becomes more pronounced (as seen from the improved signal-to-noise ratio in Fig. 1). It is an interesting consequence of the increased Mn concentration that the resonance also becomes slightly anisotropic with rotation of magnetic field [in Fig. 3, where we note a shift of about 12 G between the parallel (0°) and perpendicular (90°) configurations]. We interpret this anisotropy as resulting from the demagnetizing fields which is unavoidably present for finite geometries (such as thin layers) in systems with a pronounced magnetization. Such anisotropy can be formulated using the formalism developed for ferromagnetic resonance (with crystalline anisotropy neglected),[41] where the effects of such demagnetizing fields are invariably present and must be explicitly taken into account,

$$\omega_0=\gamma(H_{90^\circ}-4\pi M), \quad \gamma=g\mu_B/\hbar, \tag{1}$$

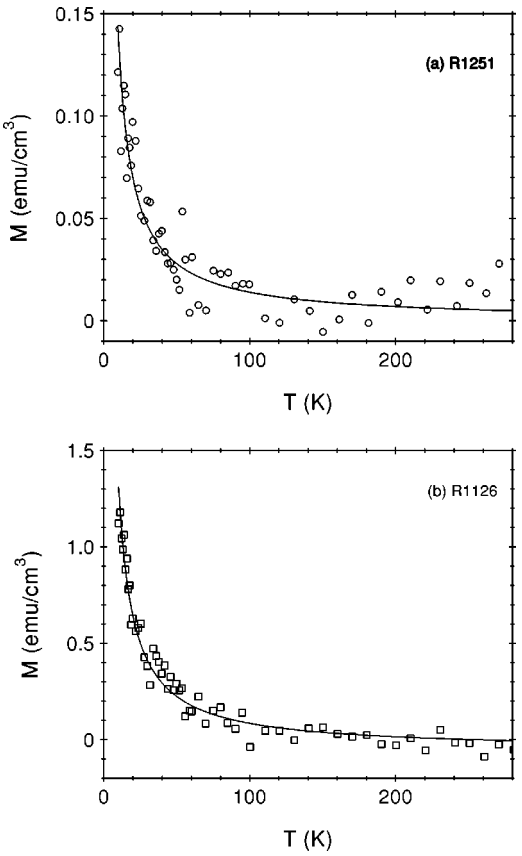

FIG. 2. Magnetization of $In_{1-x}Mn_xAs$ ($R1251$) as a function of temperature measured at $H=1$ kG for a sample with $x=0.0014$ ($R1251$) (a) and at $H=10$ kG for a sample with $x=0.014$ ($R1126$) (b). The contribution from the substrate is subtracted. The solid line corresponds to the Brillouin function fit with $S=5/2$, yielding $x=0.0011\pm0.0003$ (a) and $x=0.011\pm0.003$ (b). No contribution of the second phase MnAs is visible.

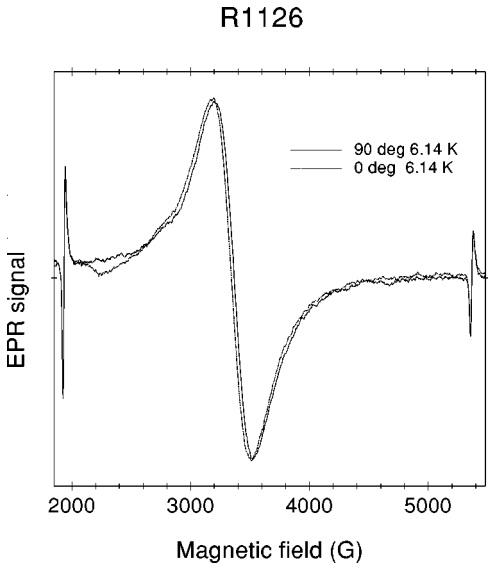

FIG. 3. EPR spectrum of $In_{1-x}Mn_xAs$ with $x=0.014$ ($R1126$) at 6.1 K for a magnetic field parallel (0°) and perpendicular (90°) to the epilayer plane. The sharp lines at 1.9 and 5.4 kG are magnetic-field markers of Al_2O_3:Cr.

$$\omega_0 = \gamma[H_{0^\circ}(H_{0^\circ} + 4\pi M)]^{1/2}, \quad (2)$$

for 90° and 0° configurations, respectively. With these equations one can estimate both the g factor and the average (local) magnetization M of the $In_{1-x}Mn_xAs$ epilayer. In the case of sample $R1126$ one then obtains $g = 2.008 \pm 0.004$ and M $(H = 3.3\,\text{kG}, T = 6\,\text{K}) = 0.90 \pm 0.3\,\text{emu/cm}^3$ $(4\pi M = 11.3$ G). The magnetization of this epilayer measured at the same temperature and magnetic field (3.3 kG) is $0.9\,\text{emu/cm}^3$, which is in rather good agreement with the value estimated from EPR. We note, however, that such agreement is probably somewhat fortuitous, since the value of the measured magnetization (per unit volume) relies critically on the epilayer thickness. The difference between the nominal thickness, which we used to evaluate M, and the real thickness is currently the source of large uncertainties in the measured magnetization. These uncertainties notwithstanding, we consider both the g factor and the magnetization to be in reasonable agreement with expectations for the A^- center of Mn^{2+}.

It is important to note that for both $In_{1-x}Mn_xAs$ samples only one distinct EPR line (attributed to A^- Mn center) was observed (neglecting the absorption of the sample holder mentioned above). In particular, no lines are observed around the field corresponding to $g = 2.7$ ($H \simeq 2.5$ kG) and $g = 5$ to 6 ($H \simeq 1.3$ to 1.1 kG), which could be ascribed to A^0. Since in bulk GaAs:Mn crystals the A^0 center had been observed by authors,[15] the present result can be viewed as an evidence that the A^0 centers are practically absent in the $In_{1-x}Mn_xAs$ epilayers. We note that the observed behavior of $In_{1-x}Mn_xAs$ is very similar to that of $Ga_{1-y}Mn_yAs$ epilayers, where only A^- centers were visible, while A^0 were not detected.[33]

V. CONCLUSIONS

The data obtained for $In_{1-x}Mn_xAs$ epilayers suggest that the dominant Mn impurity in $In_{1-x}Mn_xAs$ is Mn^{2+} (d^5), described as ionized acceptor A^-. This conclusion was derived from EPR experiments, which revealed a strong absorption line with an effective g factor very close to 2.00, the value typical for ionized Mn acceptor A^-. As the Mn conentration increases this line begins to show the presence of anisotropy arising from the magnetization of the epilayer. On the other hand, no structures typical for neutral Mn acceptor A^0 were visible, which suggests that A^0 centers are absent in the epilayers under investigation. The observed behavior is similar to that of $Ga_{1-y}Mn_yAs$ epilayers.

ACKNOWLEDGMENTS

This work was supported by NEDO under the project ''Magnetic International.'' Partial support was provided by The State Committee of Scientific Research (Poland), in particular under Grant No. 2 P03B 110 16. One of us (J.S.) acknowledges support from The Foundation for Polish Science (FNP).

[1] H. Ohno, Science **281**, 951 (1998), and references therein.
[2] H. Ohno, J. Magn. Magn. Mater. **200**, 110 (1999).
[3] *Diluted Magnetic Semiconductors*, edited by J. K. Furdyna and J. Kossut, Semiconductors and Semimetals, Vol. 25 (Academic Press, New York, 1988); *Diluted Magnetic Semiconductors*, edited by M. Balkanski and M. Averous (Plenum Press, New York, 1991); J. Kossut and W. Dobrowolski, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (North Holland, Amsterdam, 1993), Vol. 7, p. 231; J. Kossut and W. Dobrowolski, in *Narrow Gap II-VI Compounds for Optoelectronic and Electromagnetic Applications*, edited by P. Capper (Chapman & Hall, London, 1997).
[4] H. Munekata, H. Ohno, S. von Molnar, A. Segmuller, L.L. Chang, and L. Esaki, Phys. Rev. Lett. **63**, 1849 (1989); H. Munekata, H. Ohno, S. von Molnar, A. Harwit, A. Segmuller, and L.L. Chang, J. Vac. Sci. Technol. B **8**, 176 (1990); S. Koshihara, A. Oiwa, M. Hirasawa, S. Katsumoto, Y. Iye, C. Urano, H. Takagi, and H. Munekata, Phys. Rev. Lett. **78**, 4617 (1997).
[5] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and H. Iye, Appl. Phys. Lett. **69**, 363 (1996); H. Ohno, in *Proceeding of the International Workshop on Diluted Magnetic Semiconductors* (Linz, Austria, 1994), edited by H. Heinrich and J. P. Mullin, Material Science Forum Vols. 182-184 (Trans Tech, Aedermannsdorf, 1995), p. 443.
[6] T. Hayashi, M. Tanaka, K. Seto, T. Nishinaga, and K. Ando, Appl. Phys. Lett. **71**, 1825 (1997).
[7] F. Matsukura, H. Ohno, A. Shen, and Y. Sugarawa, Phys. Rev. B **57**, R2037 (1998).
[8] A. van Esch, L. van Bockstal, J. De Boeck, G. Verbanck, A.S. van Steenbergen, P.J. Wellmann, B. Grietens, R. Bogaerts, F. Herlach, and G. Borghs, Phys. Rev. B **56**, 13 103 (1997).
[9] K. Ando, T. Hayashi, M. Tanaka, and A. Twardowski, J. Appl. Phys. **83**, 6548 (1998).
[10] J. Szczytko, W. Mac, A. Twardowski, F. Matsukura, and H. Ohno, Phys. Rev. B **59**, 12 935 (1999).
[11] H. Akai, Phys. Rev. Lett. **81**, 3002 (1998).
[12] R.A. Chapman and W.G. Hutchinson, Phys. Rev. Lett. **18**, 443 (1967).
[13] R. Blekenrode, J. Dielman, and H.J. Vegter, Phys. Lett. **2**, 355 (1962).
[14] N. Almeleh and B. Goldstein, Phys. Rev. **128**, 1568 (1962).
[15] J. Schneider, U. Kaufmann, W. Wilkening, M. Baeumler, and F. Kohl, Phys. Rev. Lett. **59**, 240 (1987).
[16] A. Petrou, M.C. Smith, C.H. Perry, J.M. Worlock, J. Warnock, and R.L. Aggarwal, Solid State Commun. **55**, 865 (1985); X. C. Liu, D. Heiman, J. Hao, and K. C. Hsieh (unpublished).
[17] V.F. Masterov, K.F. Shtelmakh, and M.N. Barbashov, Fiz. Tekh. Poluprovodn. **22**, 654 (1988) [Sov. Phys. Semicond. **22**, 408 (1988)].
[18] N.S. Avierkiev, A.A. Gutkin, O.G. Krasikova, E.B. Osipov, and M.A. Reshchikov, Fiz. Tekh. Poluprovodn. **23**, 73 (1989) [Sov. Phys. Semicond. **23**, 44 (1989)].
[19] M. Baeumler, B.K. Meyer, U. Kaufmann, and J. Schneider, Mater. Sci. Forum **38-41**, 797 (1989).
[20] T. Frey, M. Maier, J. Schneider and M. Gehrke, J. Phys. C **21**, 5539 (1988).

[21] D.G. Andrianow, Y.B. Bolsheva, G.V. Lazareva, A.S. Savelev, and S.M. Yakubenya, Fiz. Tekh. Poluprovodn. **17**, 810 (1983) [Sov. Phys. Semicond. **17**, 506 (1983)].

[22] D.G. Andrianow, Y.A. Grigoriev, S.O. Klimonskii, A.S. Savelev, and S.M. Yakubenya, Fiz. Tekh. Poluprovodn. **18**, 262 (1984) [Sov. Phys. Semicond. **18**, 162 (1984)].

[23] Y. Dawei, B.C. Cavenett, and M.S. Scolnick, J. Phys. C **16**, L647 (1983).

[24] M. Klevermann, E. Janzen, M. Linnarsson, and B. Monemar, in *Impurities, Defects and Diffusion in Semiconductors: Bulk and Layerd Structures*, edited by D.J. Wolford, J. Bernholc, and E. E. Muller, MRS Symposia Proceedings No. 163 (Materials Research Society Pittsburgh, 1990), p. 207.

[25] M. Klevermann, E. Janzen, A. Thilderkvist, M. Linnarsson, and B. Monemar, in *Proceedings of the 21th ICPS*, edited by P. Jiang and H. Zheng (World Scientific, Singapore, 1992), p. 1687.

[26] B. Lambert, B. Clerjaud, C. Naud, B. Devaud, G. Picoli, and Y. Toudic, J. Electron. Mater. **14a**, 1141 (1985).

[27] B. Plot-Chan, B. Devaud, A. Rupert, and B. Lambert, J. Phys. C **19**, 5651 (1985).

[28] J. Kreissl, W. Ulrici, H. El-Metoni, A.M. Vasson, A. Vasson, and A. Gavaix, Phys. Rev. B **54**, 10 508 (1996).

[29] W. Mac, A. Twardowski, and A. M. Hennel, in *Proceedings of the 22nd International Conference on The Physics of Semiconductors (Vancouver, 1994)*, edited by D.J. Lockwood (World Scientific, Singapore, 1995), p. 2569.

[30] R.E. Kremer and J. Furdyna, Phys. Rev. B **37**, 4875 (1988).

[31] M. Linnarsson, E. Janzen, B. Monemar, M. Kleverman, and A. Thilderkvist, Phys. Rev. B **55**, 6938 (1997).

[32] J. Okabayashi, A. Kimura, O. Rader, T. Mizokawa, A. Fujimori, T. Hayashi, and M. Tanaka, Phys. Rev. B **58**, R4211 (1998).

[33] J. Szczytko, A. Twardowski, K. Świątek, M. Palczewska, M. Tanaka, T. Hayashi, and K. Ando, Phys. Rev. B **60**, 8304 (1999).

[34] S. Oseroff, and P. H. Keesom, in *Diluted Magnetic Semiconductors* (Ref. 3); Y. Ishikawa, J. Phys. Soc. Jpn. **21**, 1473 (1966).

[35] T. Hayashi, M. Tanaka, K. Seto, T. Nishinaga, and K. Ando, Appl. Phys. Lett. **71**, 1825 (1997).

[36] F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, Phys. Rev. B **57**, R2037 (1998).

[37] D.G. Andrianow, Y.B. Muravlev, W.I. Fistul, and A.F. Szczevakin, Fiz. Tekh. Poluprovodn. **12**, 1512 (1978).

[38] D.G. Andrianow, W.W. Karataev, G.W. Lazarieva, Y.B. Myravlev, and A.S. Savelev, Fiz. Tekh. Poluprovodn. **11**, 1252 (1977) [Sov. Phys. Semicond. **11**, 738 (1977)].

[39] D.G. Andrianow and A.S. Savelev, Fiz. Tekh. Poluprovodn. **14**, 539 (1980) [Sov. Phys. Semicond. **14**, 317 (1980)].

[40] D.G. Andrianow, A.S. Savelev, S.M. Yakubenya, and O.W. Kabanova, Fiz. Tekh. Poluprovodn. **16**, 1365 (1982) [Sov. Phys. Semicond. **16**, 876 (1982)].

[41] C. Kittel, Phys. Rev. **71**, 270 (1947); **73**, 155 (1948); C.P. Slichter, *Principles of Magnetic Resonance* (Springer, New York, 1978).