

# Unconventional Carrier-Mediated Ferromagnetism above Room Temperature in Ion-Implanted (Ga, Mn)P:C

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Ion implantation of Mn ions into hole-doped GaP has been used to induce ferromagnetic behavior above room temperature for optimized Mn concentrations near 3 at. %. The magnetism is suppressed when the Mn dose is increased or decreased away from the 3 at. % value, or when *n*-type GaP substrates are used. At low temperatures the saturated moment is on the order of 1 Bohr magneton, and the spin wave stiffness inferred from the Bloch-law  $T^{3/2}$  dependence of the magnetization provides an estimate  $T_c = 385$  K of the Curie temperature that exceeds the experimental value,  $T_c = 270$  K. The presence of ferromagnetic clusters and hysteresis to temperatures of at least 330 K is attributed to disorder and proximity to a metal-insulating transition.

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The rather short interval between discovery of ferromagnetism in the Mn doped III-V semiconductor GaAs [1] and the demonstration of unique phenomena such as field-effect control of ferromagnetism [2], efficient spin injection to produce circularly polarized light [3,4], and spin-dependent resonant tunneling [5] opens a rich and varied landscape for technological innovation in magnetoelectronics [6]. Although the Curie temperature,  $T_c = 110$  K, of (Ga,Mn)As is spectacularly high, it is not high enough, and any real breakthrough with respect to applications will require diluted magnetic semiconductors (DMS) which exhibit ferromagnetism above room temperature [6]. Already there are reports of room-temperature ferromagnetism in the DMS chalcopyrite  $\text{Cd}_{1-x}\text{Mn}_x\text{GeP}_2$  [7], (Ga,Mn)N formed by diffusion [8], and Co-doped ZnO [9] and  $\text{TiO}_2$  anatase [10,11].

In this Letter we report on carrier-mediated ferromagnetism in (Ga,Mn)P, doped *p* type with carbon, that persists to above room temperature. We find a high  $T_c$  in samples that are prepared at an optimal Mn concentration near 3 at. % on heavily *p*-doped GaP substrates. When electron-doped substrates are simultaneously implanted with the same Mn concentration, the observed  $T_c$  is smaller. Hysteresis in the 3 at. % material extends to temperatures well above the temperature where the dc susceptibility,  $\chi(T)$ , diverges and the “saturated” moment is observed to have strong temperature dependence. These observations suggest a percolation type of picture [12,13] in which isolated ferromagnetic magnetic clusters, immersed in a

background of paramagnetic moments, grow in size as the temperature is lowered until, at  $T = T_c$ , long-range order extends through the whole system. The characteristics, which we have observed and describe below, thus reveal phenomenology that can be used to assess the relevance of distinct yet complementary theoretical viewpoints [12–17].

The use of GaP as a host semiconductor for magnetic dopants is advantageous: it has a large bandgap (2.2 eV), it is an important component of the AlGaInP materials system, which is used for visible light-emitting diodes and high speed electronics, and it is also nearly lattice matched to Si, offering the possibility of combining DMS with conventional Si circuitry. Epitaxial films of (Ga,Mn)P have shown single-phase material up to Mn atomic concentrations of 9% and hysteretic magnetic behavior that persists up to 250 K [18]. By single phase we mean the absence of impurity phases such as MnGa or MnP. There is however a random Mn-Mn nearest neighbor separation because of the random substitution of Mn for Ga at the Ga sites.

Two types of GaP substrates were used in these experiments. The first were bulk (100) substrates with nominally undoped *n*-type ( $10^{16} \text{ cm}^{-3}$ ) background carrier densities and the second were 0.4  $\mu\text{m}$ -thick epilayers grown by gas source molecular beam epitaxy on top of GaP substrates. These layers were heavily C doped ( $p \approx 10^{20} \text{ cm}^{-3}$ ,  $10^{-2} \text{ Ohm cm}$ ) using carbon tetrabromide ( $\text{CBr}_4$ ) as the dopant source [19]. The samples were implanted with

250 keV  $\text{Mn}^+$  ions to doses of  $(3\text{--}5) \times 10^{16} \text{ cm}^{-2}$  at a temperature of  $350^\circ\text{C}$  to maximize crystallinity [20]. These conditions produce relatively flat Mn concentration profiles with peak volume concentrations of 3 or 5 at. % over a projected  $\approx 0.2 \mu\text{m}$  depth in each sample. Following a rapid thermal anneal, the samples were characterized by transmission electron microscopy, selected area diffraction pattern analysis, and double crystal x-ray diffraction [21]. No evidence of secondary phase formation of GaMn or MnP was found. All magnetic measurements were made with a quantum design SQUID magnetometer with the applied field parallel to the film surface. We attribute our observation of similar results in perpendicular fields to a polycrystalline structure, induced by implant damage and subsequent annealing, which tends to average over any magnetocrystalline anisotropy.

Shown in Fig. 1 is a plot of the temperature-dependent magnetization for the 3 at. %  $(\text{Ga}_{0.94}\text{Mn}_{0.06}\text{P})$  sample cooled in a field of 500 Oe. A temperature independent diamagnetic contribution, obtained at high field, was subtracted from the background. In contrast to  $(\text{Ga,Mn})\text{As}$  [22] the temperature-dependent magnetization has the classic convex outwards shape but with a substantial tail extending to higher temperatures. The Curie temperature,  $T_c = 270 \text{ K}$ , indicated by the vertical dashed line, is defined as the inflection point and does not shift in position

for similar data sets taken in different fields and sample orientations.

At low temperatures the saturated moment,  $M_0 = g\mu_B S$ , is calculated to be about 1 Bohr magneton ( $\mu_B$ ) per Mn ion, thus implying that for a  $g$  factor of 2, the spin  $S = 1/2$ . This value is a factor of 5 less than  $S = 5/2$  expected for the half-filled  $d$  band of divalent Mn, a discrepancy due in part to strong antiferromagnetic coupling among the more closely spaced randomly positioned Mn ions [14], but also due to disorder effects which give rise to a wide distribution of exchange couplings and hopping integrals, thereby excluding the participation of many of the Mn ions in the ferromagnetism [12]. The solid line is a three parameter fit to an expression of the form,  $M(T) = M_0(1 - \alpha T^\eta)$ , over the temperature range  $T \leq 160 \text{ K}$ . The observation of a Bloch-law dependence with exponent  $\eta = 3/2$  is expected for ferromagnets and reflects the presence of long-wavelength thermally excited spin waves. The dashed lines delineate the 95% confidence band for the best-fit parameters  $\eta = 1.51(6)$  and  $\alpha = 1.09(35) \times 10^{-4}$ . We obtain an equally good fit with almost identical parameters for data taken at 1000 Oe.

The inset of Fig. 1 shows the temperature-dependent difference  $\Delta M = M_{\text{FC}} - M_{\text{ZFC}}$  between field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves taken at 500 Oe. This subtraction advantageously eliminates para- and diamagnetic contributions and simultaneously indicates the presence of hysteresis if the difference is nonzero. It should be noted that the knee of this curve occurs at a lower temperature than the knee of the FC curve (main panel) and moves to an even lower temperature at higher measuring fields. This trend can be understood by realizing that at a given temperature,  $\Delta M = 0$  if the measuring field is higher than the maximum field at which hysteresis is observed in  $M(H)$  loops acquired at the same temperature. Examples of such loops are shown in Fig. 2. Hysteresis with a coercive field  $H_c = 100 \text{ Oe}$  is quite pronounced at  $250 \text{ K}$  (lower panel) to fields as high as 600 Oe. At lower fields, hysteresis similar to that shown at  $300 \text{ K}$  in the upper panel of Fig. 2 extends to  $330 \text{ K}$ .

The FC-ZFC subtraction is particularly effective when there are small amounts of ferromagnetic material in the presence of a large diamagnetic and/or paramagnetic background. This situation ensues when  $n$ -type rather than  $p$ -type GaP is implanted with 3 at. % Mn (Fig. 3, upper panel) or  $p$ -type GaP is implanted with 5 at. % Mn (Fig. 3, lower panel). The  $p$ - and  $n$ -type samples were implanted at the same time and subjected to identical anneals. These data show that the maximum FC-ZFC difference,  $\Delta M$ , is reduced by a factor of 15–20 and the  $T_c$  by a factor of  $\approx 6$ , over the temperature range  $300 \text{ K}$  to near  $50 \text{ K}$ . Accordingly, an optimized  $T_c$  is sensitive to both the carrier and the Mn concentrations. Furthermore, ferromagnetic impurity phases such as MnGa ( $T_c > 300 \text{ K}$ ) [22] and MnP ( $T_c = 291 \text{ K}$ ) [23] are not responsible, since an increase of Mn leads to less, not more, magnetism.

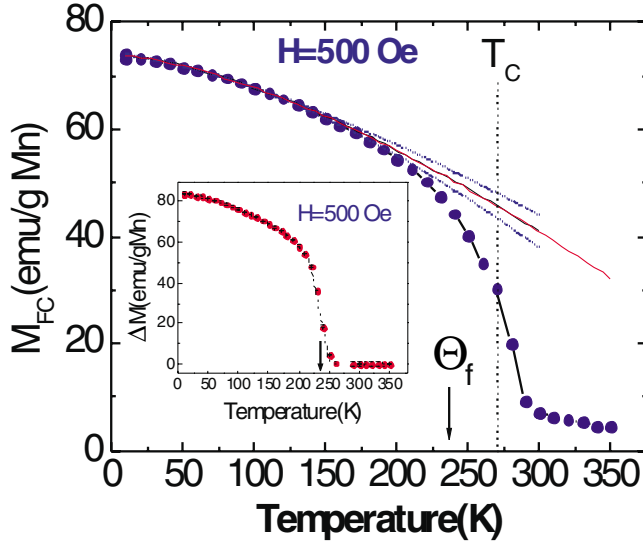


FIG. 1 (color online). Temperature dependence of field-cooled (FC) magnetization (per gram Mn) at an applied field  $H = 500 \text{ Oe}$ . At low temperatures a Bloch-law ( $T^{3/2}$ ) dependence (solid line) was found. The dashed lines are 95% confidence bands. The dashed line at  $T_c = 270 \text{ K}$  marks the field independent inflection point (Curie temperature) and the vertical arrows in the main panel and the inset mark the ferromagnetic Curie temperature,  $\Theta_f = 236 \text{ K}$ . Inset: Temperature dependence of the difference  $\Delta M$  between FC and zero-field cooled (ZFC) magnetizations taken in a field of 500 Oe.

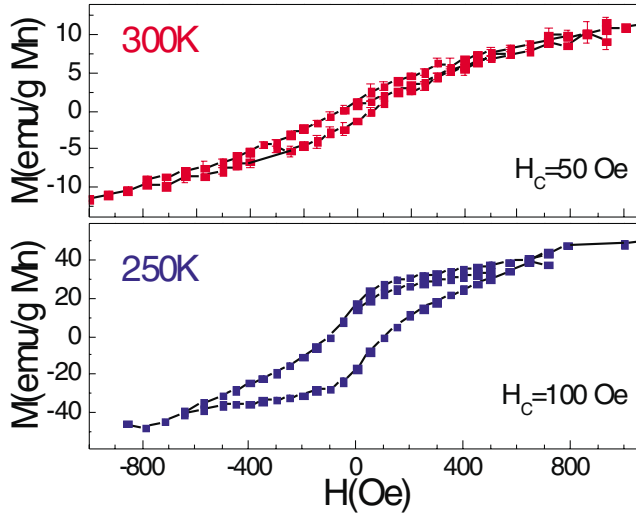


FIG. 2 (color online). Magnetization loops showing moderate hysteresis with coercive field,  $H_c = 50$  Oe (upper panel) at 300 K and a stronger hysteresis with  $H_c = 100$  Oe (lower panel) at 250 K.

Although our observations confirm conventional ferromagnetism at low temperatures, the magnetic behavior is considerably more complicated at higher temperatures as shown by the Fig. 4 plots of the temperature-dependent inverse dc susceptibility  $\chi^{-1}(T)$  (main panel) and saturation moment  $M_s(T)$  (inset). The data for these plots were obtained at selected temperatures by recording  $M_{ZFC}(H)$  to the maximum available field of 5 T. A diamagnetic contribution, obtained at high field, varied less than 1% over the temperature range studied and was subtracted from the

data. We used a Langevin functional dependence to determine  $\chi = dM_{ZFC}/dH$  and  $M_s(T)$  at each temperature. At low fields,  $M_{ZFC}$  is linear in  $H$ , thereby allowing a convincing determination of  $\chi$ . We identify the ferromagnetic Curie temperature  $\Theta_f = 236$  K (vertical arrow) by a linear extrapolation of  $\chi^{-1}(T)$  to zero. The hysteresis and accompanying saturated moment extend with diminishing magnitude to substantially higher temperatures: 330 K for the measured hysteresis and 390 K for a presumptuous linear extrapolation of  $M_s(T)$  to zero.

To interpret the enhanced Curie constant derived from the susceptibility data in Fig. 4, we assume for simplicity the presence of uniform size clusters each containing  $p_c$  Mn ions per cluster. Each Mn ion carries a magnetic moment  $\mu_{Mn}$ . Using the expression for the Curie constant,  $C = p_c N_0 \mu_{Mn}^2 / 3k_B$ , where  $N_0$  is the number of Mn atoms per gram Mn and  $k_B$  is the Boltzmann constant, we calculate from the slope of  $\chi^{-1}(T)$ , the result,  $p_c \mu_{Mn}^2 = 410 \mu_B^2$ . For divalent Mn ions with half-filled  $d$  shells,  $\mu_{Mn} = 5 \mu_B$ , and we thus find  $p_c \approx 8$ .

The data presented here not only show that room-temperature ferromagnetism is obtainable in (Ga,Mn)P:C but also provide a meaningful confrontation with present theories [12–17] describing ferromagnetism in DMS. The ferromagnetism is clearly carrier mediated [12–16] and is optimized for hole-doped substrates with Mn concentrations near 3 at. %. Higher concentrations of Mn are deleterious because of increased antiferromagnetic coupling [14] and a possible disorder-induced self-compensation [16].

Our experimental determination of the prefactor  $\alpha$  discussed above allows a direct calculation of the spin wave

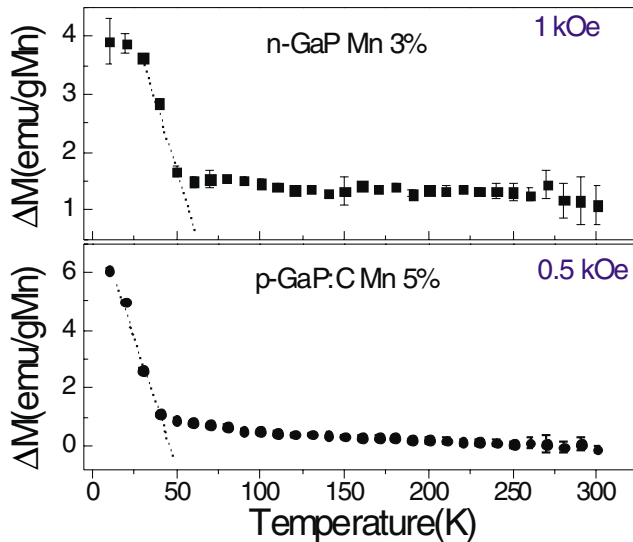


FIG. 3 (color online). Temperature dependence of the difference between FC and ZFC magnetizations (per gram Mn) for (upper panel)  $n$ -type GaP implanted with 3 at. % Mn and (lower panel)  $p$ -type GaP:C implanted with 5 at. % Mn. The measuring fields are indicated in the upper right-hand corners of each panel.

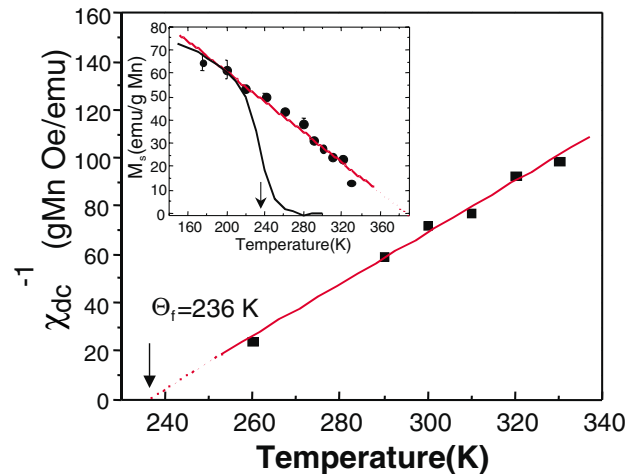


FIG. 4 (color online). Temperature dependent inverse susceptibility extrapolated (dashed line) to  $\Theta_f = 236$  K. The inset shows the temperature-dependent “saturated magnetization” derived from fits of the field-dependent magnetization at each temperature to a Langevin function dependence as described in the text. For comparison, the solid line reproduces  $\Delta M(T)$  at 1000 Oe shown in the inset of Fig. 1.

stiffness  $D$ , a parameter which describes the energy dispersion,  $E = Dk^2$ , of the spin wave excitations (magnons). We find from the thermodynamic result [24], corrected by a spin-dependent prefactor [15], the value  $D = 167 \text{ meV } \text{\AA}^2$ . For comparison,  $D = 281 \text{ meV } \text{\AA}^2$  for Fe. Substituting  $D = 167 \text{ meV } \text{\AA}^2$ ,  $S = 5/2$ , and  $N_{\text{Mn}} = 1.5 \times 10^{21} \text{ cm}^{-3}$  for the volume density of Mn ions into the expression [25],  $k_B T_c^{\text{coll}} = (2S + 1)D(6\pi^2 N_{\text{Mn}})^{2/3}$  gives an estimate  $T_c^{\text{coll}} = 385 \text{ K}$  for the upper bound on  $T_c$  due to long-wavelength collective fluctuations. This value is higher than the measured  $T_c = 270 \text{ K}$  and consistent with the fact that mean field theory usually overestimates the ordering temperature.

At temperatures near and above  $T_c$ , clusters in a disordered medium seem to be playing an important role [12,13,16,17]. The presence of spin clusters is often associated [26] with a  $\chi^{-1}(T)$  dependence, which approaches zero with positive curvature but which, at sufficiently high temperatures, has a linear dependence extrapolating to the paramagnetic Curie temperature,  $\Theta_p$ . It is therefore reasonable to argue that at higher temperatures  $\chi^{-1}(T)$  must eventually curve upwards and approach a slope larger than shown in Fig. 4. If so, then a linear extrapolation to  $\chi^{-1}(T = \Theta_p) = 0$  would give a  $\Theta_p$  considerably larger than  $\Theta_f$ . As  $T$  increases beyond  $T_c$  and the ferromagnetic clusters decrease in size and number, there is a decreasing saturated moment (Fig. 4, inset), since the remaining paramagnetic regions cannot be driven into saturation without the assistance of internal Weiss fields. Disorder and proximity to a metal-insulator transition, which may be responsible for the enhanced  $T_c$ 's of the clusters [12], may also give rise to a reduced spin stiffness and the anomalously high Curie constant. Based on this evidence of ferromagnetic behavior above room temperature, it is not unreasonable to expect that even higher  $T_c$  can be obtained by further optimization of the Mn and hole dopant concentrations.

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