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Thermodynamic limits to the maximum Curie temperature in $Ga_{1-x}Mn_xAs$

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Abstract. Using the ion channeling techniques we find that a substantial fraction (up to 15%) of the Mn atoms reside in interstitial sites in $Ga_{1-x}Mn_xAs$ alloys (with x ranging from 0.02 to 0.09). Moreover, the T_C of $Ga_{1-x}Mn_xAs$ is found to be very sensitive to annealing at temperatures close to the growth temperature of 265°C. Ion channeling results demonstrate that the increase of T_C after annealing at 282°C can be attributed to a relocation of Mn atoms from interstitial sites to form random clusters. A series of $Ga_{1-x-y}Mn_xBe_yAs$ layers, in which the magnetic moments and free holes are independently controlled by the Mn and Be contents, respectively, are also investigated. A dramatic increase of the concentration of Mn interstitials and a reduction of T_C are observed as the Be concentration increases, while the free hole concentration stays relatively constant at $\sim 5x10^{20}cm^{-3}$. These results demonstrate that the concentrations of free holes as well as uncompensated Mn spins are governed by the position of the Fermi level, which controls the formation energy of compensating interstitial Mn acceptors. This Fermi-level-induced hole saturation is responsible for the commonly observed upper limit of 110 K for the Curie temperature of this material system.

1. Introduction

The recent discovery of III-V ferromagnetic semiconductors, specifically $Ga_{1-x}Mn_xAs$ (x<0.1) with the Curie temperature T_C as high as 110 K [1,2] has stimulated much interest in experimental and theoretical investigations on this materials system. It was established experimentally that T_C in $Ga_{1-x}Mn_xAs$ increases with increasing Mn concentration x and with the hole concentration up to x~0.05 [2]. Recent theoretical work by Dietl *et al.* [3] based on the Zener model in the mean-field approximation predicted that T_C in $Ga_{1-x}Mn_xAs$ can be further improved by increasing the Mn content and the free hole concentration in the alloy.

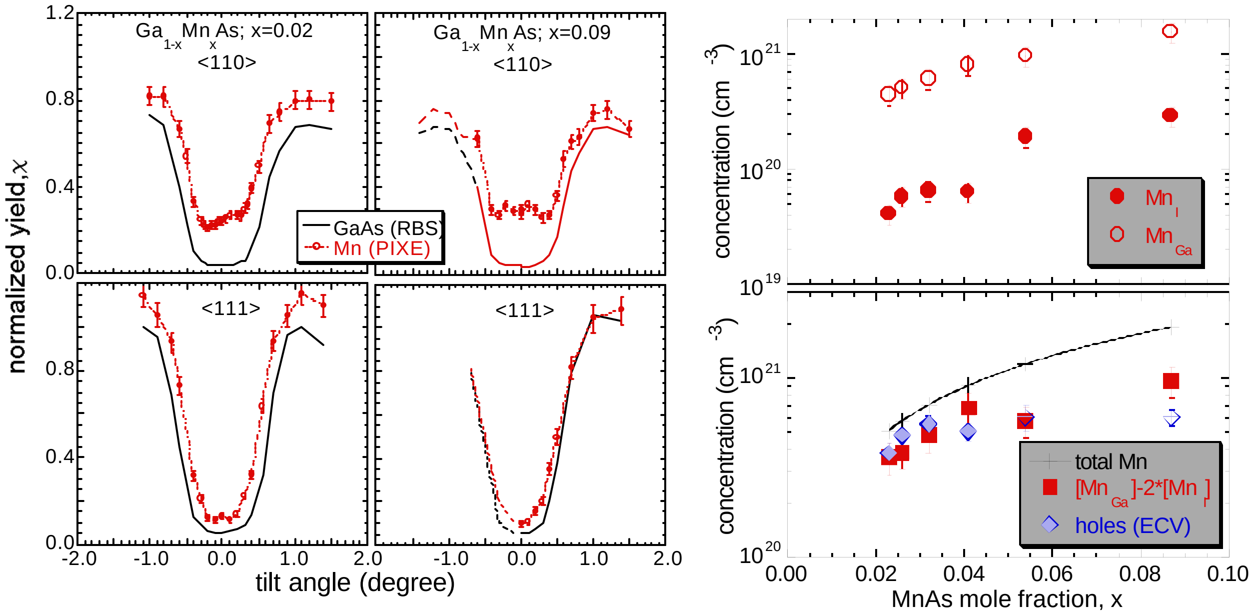
Despite intense efforts, similar maximum values of T_C of ~110K were found in $Ga_{1-x}Mn_xAs$ thin films synthesized in different laboratories with rather different values of *x*, ranging from ~0.05 to 0.10 and optimally annealed at low temperatures in the range of 250-280°C [2, 4-7]. A recent report by Potashnik *et al.* showed that in $Ga_{1-x}Mn_xAs$ alloys, the T_C, conductivity and ferromagnetic exchange energy saturate for x> 0.05 [8]. These authors suggested that an increasing fraction of Mn spins do not participate in the ferromagnetism and attributed this to local electronic structure associated with certain defects. These intriguing findings suggest the possibility that there could be a *fundamental limit* on the value of T_C in the $Ga_{1-x}Mn_xAs$ alloy system.

In this paper, we first investigate the dependence of Mn interstitials on the Mn content in $Ga_{1-x}Mn_xAs$. We then address the fundamental limit on T_C by studying the lattice location of Mn in Be-doped $Ga_{1-x}Mn_xAs$ alloys ($Ga_{1-x-y}Mn_xBe_yAs$), in which the concentration of Mn moments is determined by the Mn content and the free hole concentration depends on the concentrations of Mn and Be acceptors. For a fixed Mn concentration we find a dramatic increase in the concentration of Mn_I as well as electrically inactive Mn in random clusters with increasing Be concentration. This is accompanied by a strong decrease of T_C. Nevertheless, the free hole concentration in the $Ga_{1-x-y}Mn_xBe_yAs$ layers is nearly constant, independent of the Be doping level (up to y=0.11). Based on these results we suggest a Fermi level controlled mechanism which puts an upper limit on T_C in $Ga_{1-x}Mn_xAs$.

2. Experimental details

Two sets of thin film samples, namely $Ga_{1-x}Mn_xAs$ (with x ranging from 0.02 to 0.09) and $Ga_{1-x-y}Mn_xBe_yAs$ (with x=0.05 and y varying from 0.01 to 0.11) were grown on semi-insulating (001) GaAs substrates in a Riber 32 R&D MBE system. Details of the growth have been discussed elsewhere [6,9]. Magnetoresistance, Hall effect, and superconducting quantum interference device (SQUID) magnetometry were used for electrical and magnetic characterization and for determining T_C. Hall effect measurements were performed in either the Van der Pauw or the six-probe geometry. To circumvent the problems associated with the *anomalous Hall effect* (AHE) in ferromagnets [2,8], we have used the electrochemical capacitance voltage (ECV) profiling method to measure the depth distribution of acceptors in our alloy thin films [9]. The composition of the thin films was determined by x-ray diffraction as well as by particle-induced x-ray emission (PIXE).

The locations of Mn sites in the $Ga_{1-x}Mn_xAs$ lattice were studied by directly comparing the Mn K_α x-ray signals obtained by channeling particle-induced x-ray emission (c-PIXE) with the channeling Rutherford backscattering (c-RBS) signals of GaAs from the $Ga_{1-x}Mn_xAs$ film simultaneously obtained using a 1.95MeV $^4He^+$ beam. The normalized yield for the RBS (χ_{GaAs}) or the PIXE Mn x-ray signals (χ_{Mn}) is defined as the ratio of the channeled yield to the corresponding unaligned yield [10].



(a) (b)

Figure 1. (a) Mn and GaAs angular scans about the <110> and <111> channels for $Ga_{1-x}Mn_xAs$ alloys with x=0.02 and 0.09. (b) The concentrations of interstitial and substitutional Mn (top panel) and the net uncompensated Mn acceptor concentration ($[Mn_{Ga}]$-2x$[Mn_I]$) (lower panel) as measured by channeling experiments together with the hole concentration obtained by electrochemical capacitance-voltage (ECV) profiling for x ranging from 0.02 to 0.09.

3. Results and discussion

Mn atoms incorporated into ferromagnetic $Ga_{1-x}Mn_xAs$ can occupy three distinct types of lattice site: substitutional positions in the Ga sublattice Mn_{Ga}, where Mn^{++} ions act as acceptors and also contribute to uncompensated spins; interstitial positions Mn_I, where they act as donors and tend to passivate Mn_{Ga} acceptors; and random locations Mn_{ran} that form clusters of Mn or MnAs clusters. Fig. 1 (a) shows the c-PIXE and c-RBS angular scans about the <110> and <111> axes for two $Ga_{1-x}Mn_xAs$ samples with x=0.02 and 0.09. The angular scans about the <100> directions (not shown) are similar to those about the <111> direction for the two samples. The higher χ_{Mn} observed in the <110> direction in both samples as compared to those in the <100> and <111> directions suggests that a fraction of the non-random Mn atoms is located at *interstitial* sites. Atoms in either the tetrahedral or hexagonal interstitial positions in a diamond lattice are shadowed by the host atoms when viewed along both the <100> and <111> axes but are exposed in the <110> axial channel [10,11]. This gives rise to higher normalized yields in the <110> angular scan due to the flux peaking effect of the ion beam in axial channels.

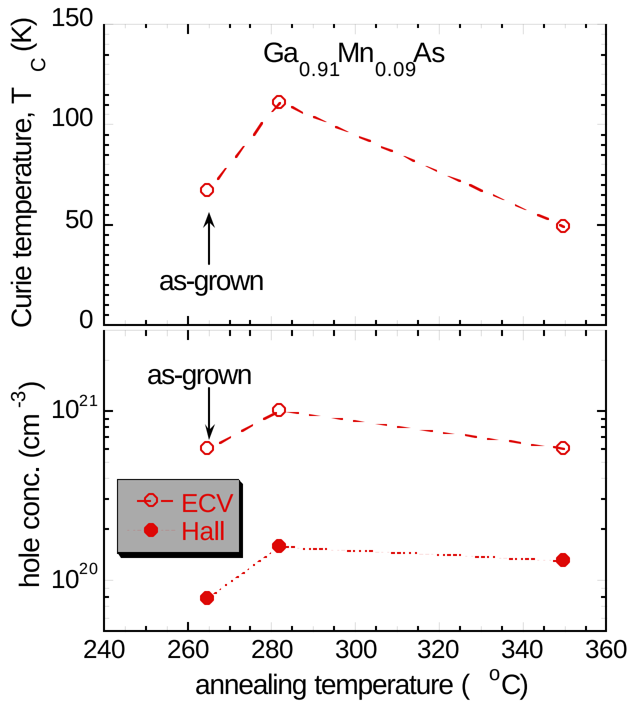


Figure 2. Variation of the Curie temperature T_C with the annealing temperature for the $Ga_{0.91}Mn_{0.09}As$ thin films (top panel). The free hole concentrations measured by ECV are directly compared to the *apparent* free hole concentrations obtained by Hall measurement performed at room temperature at 0.5T in the lower panel of the figure

Angular scan studies show an increase in Mn interstitials (from 5 to 15%) and a decrease in substitutional Mn acceptors as the Mn content increases. These Mn_I are expected to be highly mobile positively charged double donors [12,13]. They can, however, be immobilized by occupying the interstitial sites *adjacent* to the negatively charged Mn_{Ga} acceptors, thus forming antiferromagnetically ordered Mn_I-Mn_{Ga} pairs, which renders Mn_{Ga} inactive as acceptors and at the same time cancels its magnetic moment [6,12]. The upper panel of Fig. 1 (b) shows the Mn_{Ga} and Mn_I as measured by channeling experiments for increasing MnAs mole fraction x. A comparison of the net uncompensated Mn acceptors ($[Mn_{Ga}]-2x[Mn_I]$) and free hole concentration obtained by electrochemical capacitance-voltage (ECV) profiling together with the total Mn concentration in the samples is shown in the lower panel of Fig. 1 (b). We have previously demonstrated the accuracy of determinating free hole concentration in $Ga_{1-x}Mn_xAs$ alloys by the ECV technique [9]. The concentration of free holes agrees well with the net Mn acceptors for $Ga_{1-x}Mn_xAs$ samples except for the sample with with x=0.09. For the sample with high Mn content (x=0.09), compensation by Mn_I alone cannot fully account for the low hole concentration. In this case, As antisite (As_{Ga}) donors can also compensate some of the substitutional Mn acceptors [14].

In a previous post-growth low temperature annealing study of $Ga_{0.91}Mn_{0.09}As$ thin films, we found that the T_C of $Ga_{1-x}Mn_xAs$ is very sensitive to annealing at temperatures close to the growth temperature of 265°C. As shown in Fig. 2 annealing at 282°C for one hour increases T_C from 65 K to 111 K and the hole concentration from $6x10^{20}$ cm^{-3} to $1x10^{21}$ cm^{-3}. Annealing of as grown sample at a higher temperature of 350°C reduces T_C to 49 K. Channeling results demonstrated that the increase of T_C after annealing at 282°C could be attributed to the lattice site rearrangement of the highly unstable Mn interstitials Mn_I [6]. The concentrations of free holes determined by ECV and of uncompensated Mn^{++} spins determined from SQUID magnetization measurements were found to depend on the concentration of Mn_I. Low temperature annealing breaks up the relatively weak antiferromagnetically ordered Mn_I-Mn_{Ga} pairs leading, as noted above, to a higher concentration of uncompensated Mn spins, thus resulting in increase in saturation magnetization as well as hole concentration and T_C [4-7]. Moreover, the presence of the Mn_I in $Ga_{1-x}Mn_xAs$ can also explain the recently reported *saturation* of T_C, conductivity and ferromagnetic exchange energy for optimally annealed $Ga_{1-x}Mn_xAs$ with x>0.05 [7].

The relationships between the concentration of Mn interstitial defects and the ferromagnetism in $Ga_{1-x}Mn_xAs$ are further investigated in Be and Mn co-doped alloys ($Ga_{1-x-y}Mn_xBe_yAs$) with x=0.05 and y ranging from 0 to 0.11. Fig. 3 shows the c-PIXE and c-RBS angular scans about the <110> (upper panels) and <111> (lower panels) axes for the $Ga_{1-x-y}Mn_xBe_yAs$ films with increasing y. For all the samples studied, in the <111> axis the Mn scans (c-PIXE) behave qualitatively as the host GaAs (RBS) scans, indicating that a dominant fraction of the Mn atoms are shadowed by the host atoms that are commensurate with the lattice [10,11]. At the same time the Mn <111> scans of $Ga_{1-x-y}Mn_xBe_yAs$ show a gradual increase in yield as the Be content increases, that deviates from the corresponding host scans and indicates that an increased fraction of Mn atoms is present in the form of random clusters.

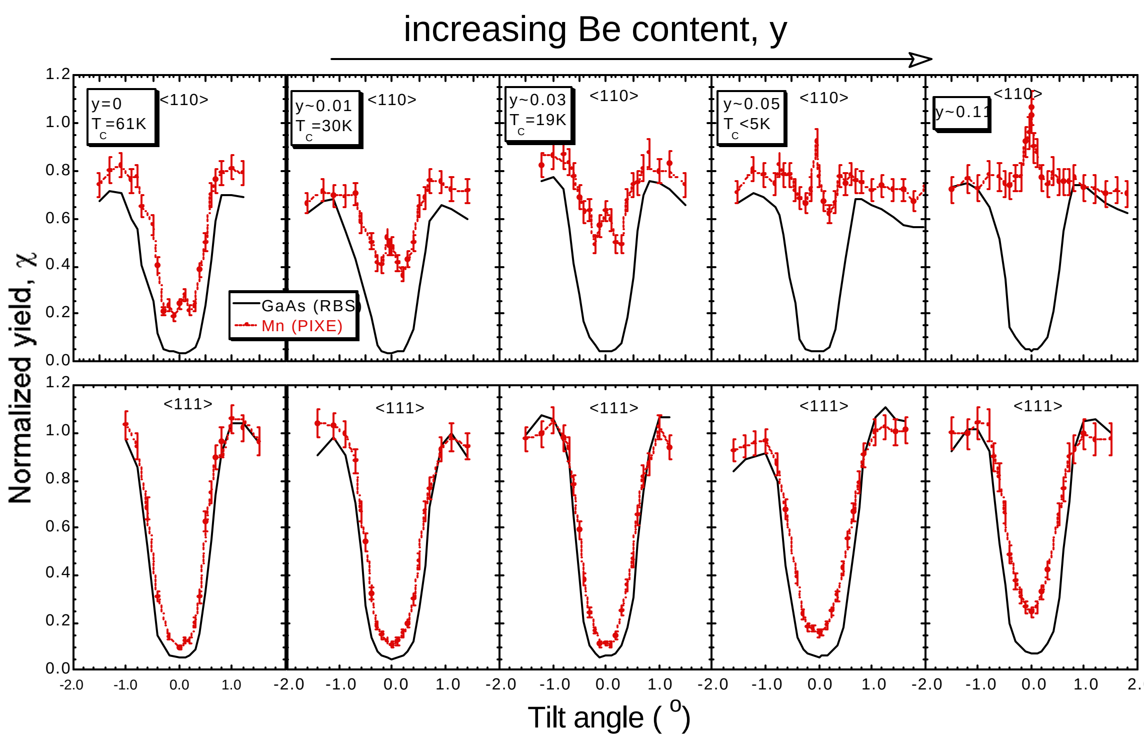


Figure 3. Mn K_α x-ray and GaAs RBS angular scans about the <110> and <111> axes for $Ga_{1-x-y}Mn_xBe_yAs$ samples with Be content y=0, 0.01, 0.03, 0.05, and 0.11

In contrast to the <111> angular scans, the Mn <110> scans are strikingly different from their corresponding host scans in Fig. 3. As the Be content increases, the <110> Mn angular scan shows a definite peak at the center of the channel with increasing intensity. These results unambiguously reveal that the fraction of Mn_I as well as random Mn-related clusters in the $Ga_{1-x-y}Mn_xBe_yAs$ increases monotonically with Be content.

The concentrations of Mn atoms in the various different lattice sites -- substitutional (Mn_{Ga}), interstitial (Mn_I) and in random-cluster form -- as measured from the angular scans are shown in Fig. 4 (a). The net uncompensated Mn ions ($[Mn_{Ga}]$-$[Mn_I]$) together with the free hole concentration obtained from ECV and Hall measurements is displayed in Fig. 4 (b). The influence of the anomalous Hall effect (AHE) in the ferromagnetic samples is not taken into account and thus the free hole concentrations obtained by Hall measurement here do not reflect the true values and are included only for comparison. Notice that as the Be content y approaches the Mn content (x=0.05), the concentration of Mn_I becomes larger than that of Mn_{Ga}.

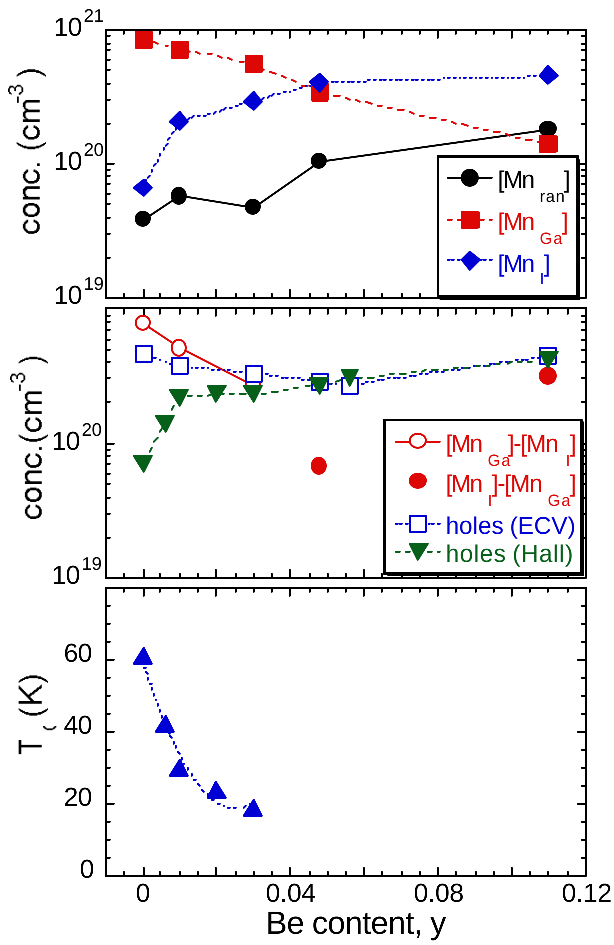


Figure 4. The concentration of Mn atoms in the various different lattice sites, as measured from the angular scans (a), the net uncompensated concentration of Mn ($[Mn_{Ga}]$-$[Mn_I]$) together with the hole concentration measured by ECV and Hall (b), and the Curie temperature T_C (c) for the $Ga_{1-x-y}Mn_xBe_yAs$ films with increasing BeAs mole fraction y.

It is particularly worth noting that the T_C (shown in Fig. 4(c)) of the $Ga_{1-x-y}Mn_xBe_yAs$ films drops rapidly as y increases while the free hole concentration measured by ECV remains rather constant throughout the whole Be composition range. In fact T_C of the samples becomes lower than 5K for y>0.04. For the ferromagnetic $Ga_{1-x}Mn_xAs$ thin film where the T_C is high (T_C= 60K) a large discrepancy in the hole concentration (as much as an order of magnitude) measured by Hall effect is observed due to the strong AHE even at room temperature. As the Be concentration in the film increases (y>0.04), the $Ga_{1-x-y}Mn_xBe_yAs$ films lose its ferromagnetic property and the hole concentrations measured by Hall effect agree with those measured by the ECV method.

It has been established that in compound semiconductors the carrier concentrations are limited by the formation of compensating native defects. The formation energies of these defects are governed by the position of the Fermi level [15,16]. The relatively constant hole concentration shown in Fig. 4 indicates that the holes in these $Ga_{1-x-y}Mn_xBe_yAs$ samples are at the free hole saturation limit. At this hole saturation limit, the formation energies of Mn_{Ga} acceptors and compensating Mn_I become comparable. Therefore introduction of additional Be acceptors into the $Ga_{1-x-y}Mn_xBe_yAs$ samples leads to a downward shift of the Fermi energy, that in turn increases the formation energy of negatively charged Mn_{Ga} acceptors and reduces the formation energy of Mn_I donors. As a result, an increasing fraction of the Mn is incorporated in the form of Mn_I donors and/or electrically inactive precipitates. As mentioned earlier, the Mn_I donors may form antiferromagnetically ordered Mn_I-Mn_{Ga} pairs, rendering Mn_{Ga} inactive as acceptors as well as reducing the total number of uncompensated Mn spins participating in the ferromagnetism. Moreover, even unpaired Mn_I do not participate in the RKKY-ferromagnetism because Mn_I *d*-orbitals do not hybridize with the *p*-states of the holes at the top of the valence band [12]. Consequently T_C drops drastically as y increases.

Our electrical, magnetization and ion channeling results on LT-grown $Ga_{1-x-y}Mn_xBe_yAs$ alloys and the previously reported low temperature annealing of $Ga_{1-x}Mn_xAs$ reveal that the ferromagnetism in $Ga_{1-x}Mn_xAs$ is related to the total number of uncompensated Mn ions, which are in turn controlled by the formation energies of compensating native defects. We have demonstrated that there is a maximum doping limit in $Ga_{1-x}Mn_xAs$ (~$5x10^{20}$-$1x10^{21}cm^{-3}$). As the Mn doping increases beyond this doping limit, it is energetically favorable to form compensating Mn_I, keeping the concentration of free holes (related to $[Mn_{Ga}]$-2x$[Mn_I]$) and the net uncompensated Mn spins participating in the ferromagnetism (related to $[Mn_{Ga}]$-$[Mn_I]$) relatively constant at the maximum level. Since the ferromagnetism in this system is related to the uncompensated Mn spins and mediated by holes, such Fermi-level-induced hole saturation effect necessarily imposes a fundamental limit on the Curie temperature of the system.

4. Conclusion

In conclusion, we have investigated the role of interstitial Mn atoms in $Ga_{1-x}Mn_xAs$. A monotonic increase in the Mn_I fraction as well Mn in random clusters is observed in $Ga_{1-x-y}Mn_xBe_yAs$ thin films with increasing Be concentration. Such transformation in Mn lattice sites in $Ga_{1-x-y}Mn_xBe_yAs$ is correlated with the free hole concentration and the Curie temperature in the material. These results show that the introduction of additional Be acceptors increases the formation energies of negatively charged defects, thus making the incorporation of substitutional Mn acceptors energetically unfavorable. On the other hand the formation of Mn_I donors and/or electrically inactive precipitates now becomes the favorable. The upper limit of free hole concentration in LT $Ga_{1-x-y}Mn_xBe_yAs$ is found to be ~$5x10^{20}$-$1x10^{21}/cm^3$. We suggest that this saturation doping limit imposes an upper limit on the Curie temperature in this materials system.

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