Fundamental Curie Temperature Limit in Ferromagnetic $Ga_{1-x}Mn_xAs$

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ABSTRACT

We provide unambiguous experimental evidence that the upper limit of ~110 K commonly observed for the Curie temperature T_C of $Ga_{1-x}Mn_xAs$ is caused by the Fermi-level-induced hole saturation. This conclusion is based on parallel studies of the location of Mn in the lattice, the effectiveness of acceptor center, and ferromagnetism on a series of $Ga_{1-x-y}Mn_xBe_yAs$ layers, in which the concentration of magnetic moments and of free holes can be independently controlled by the Mn and Be contents. Ion channeling and magnetization measurements show a dramatic increase of the concentration of Mn interstitials accompanied by a reduction of T_C with increasing Be concentration. At the same time the free hole concentration remains relatively constant at ~$5x10^{20}cm^{-3}$. These results indicate that the concentrations of free holes as well as of ferromagnetically active Mn spins are governed by the position of the Fermi level, which controls the formation energy of compensating interstitial Mn donors. Based on these results, we propose to use heavy n-type counter-doping of $Ga_{1-x}Mn_xAs$ (by, e.g., Te) to suppress the formation of Mn interstitials at high x, and thus improve the T_C of the alloy system.

PACS numbers: 75.50.Pp, 73.61.Ey, 61.10.Ht, 81.40.Rs

The recent discovery of III-V ferromagnetic semiconductors, specifically $Ga_{1-x}Mn_xAs$ with Curie temperatures T_C as high as 110 K [1-2] is a major step toward the implementation of spintronic devices for processing, transferring, and storing of information [3]. The potential for this wide range of applications has stimulated much interest in both experimental and theoretical investigation of this materials system. Experimentally it has been well established that T_C in $Ga_{1-x}Mn_xAs$ increases with increasing Mn concentration x (as long as MnAs precipitates are not formed) and with hole concentration. Although in principle each Mn atom in the Ga sublattice is expected to contribute a hole to the system, it was also found that the hole concentration in this material is significantly lower than the Mn concentration (typically by a factor of three) [1,2]. Recent ion channeling experiments demonstrated that such low Mn acceptor activation could be attributed to the presence of *interstitial Mn donors* in $Ga_{1-x}Mn_xAs$ [4].

Calculations based on the Zener model [5] predicted that T_C in $Ga_{1-x}Mn_xAs$ could be improved by increasing the Mn content and/or the free hole concentration in the alloy. These predictions led to extensive experimental effort aimed at achieving higher Curie temperatures for $Ga_{1-x}Mn_xAs$ by improving the crystalline quality, varying the alloy composition, and by increasing the doping level through modification of the growth process as well as post-growth processing. Despite intense efforts, similar maximum values of T_C of ~110K were found in thin $Ga_{1-x}Mn_xAs$ films prepared 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 250-280ºC [2, 6-9]. A recent report by Potashnik *et al.* showed that in optimally annealed $Ga_{1-x}Mn_xAs$ alloys, the T_C and conductivity saturate for x> 0.05 [8], suggesting that as x increases, an increasing fraction of Mn spins do not participate in the ferromagnetism.

In an earlier post-growth annealing study of $Ga_{0.91}Mn_{0.09}As$ films [4,9] we found that annealing at 280ºC 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}. Ion channeling results demonstrated that

this increase of both T_C and the hole concentration can be attributed to the lattice site rearrangement of the highly unstable Mn interstitials Mn_I. These Mn_I are expected to be highly mobile positively charged double donors [10,11]. They can, however, be immobilized by occupying the interstitial sites *adjacent* to the negatively-charged substitutional Mn acceptors (Mn_{Ga}), thus forming antiferromagnetically ordered Mn_I-Mn_{Ga} pairs, which not only render Mn_{Ga} inactive as acceptors, but additionally cancels its magnetic moment [4,10]. Low temperature annealing breaks up the relatively weak antiferromagnetically ordered Mn_I-Mn_{Ga} pairs, leading to a higher concentration of uncompensated Mn spins, thus resulting in increase in saturation magnetization as well as a higher hole concentration and a higher T_C [4,6-9]. These conclusions were fully confirmed by measurements of the concentrations of free holes using electrochemical capacitance-voltage profiling [12] and of uncompensated Mn^{++} spins concentration using superconducting quantum interference device (SQUID) magnetization measurements carried out on the same $Ga_{1-x}Mn_xAs$ samples. The above results further suggested the possibility that there exists a *fundamental limit* on T_C, governed by a limit on the hole concentration allowed by the $Ga_{1-x}Mn_xAs$ alloy. In this paper we use co-doping of $Ga_{1-x}Mn_xAs$ by Be as a tool to provide unambiguous experimental evidence that such a limit does in fact exist.

Specifically, we address the issue of thermodynamic limitations on T_C by correlating the free hole concentration and the lattice location of Mn in $Ga_{1-x-y}Mn_xBe_yAs$, in which the free hole concentration depends on the concentrations of Mn and Be acceptors. We show that the free hole concentration p in $Ga_{1-x-y}Mn_xBe_yAs$ with x=0.05 is *nearly constant*, independent of the Be doping level (up to y = 0.11). In spite of this saturation of p, we observe for a fixed Mn concentration of 0.05 a dramatic increase in the concentrations of Mn_I and of electrically inactive random Mn clusters at the expense of Mn_{Ga} as the Be concentration is increased, accompanied by *a strong decrease of T_C.*

These results strongly indicate that a Fermi-level-controlled mechanism puts an upper limit on T_C in $Ga_{1-x}Mn_xAs$ [13].

Thin films of $Ga_{1-x-y}Mn_xBe_yAs$ were grown on semi-insulating (001) GaAs substrates in a Riber 32 R&D MBE system. Fluxes of Ga, Be and Mn were supplied from standard effusion cells, and As_2 flux was produced by a cracker cell. Prior to film deposition we grew a 450 nm GaAs buffer layer at 590ºC (i.e., under normal GaAs growth conditions). The substrate was then cooled down for the growth of a 3 nm thick low-temperature (LT) GaAs, followed by a 230 nm thick layer of $Ga_{1-x-y}Mn_xBe_yAs$ at a substrate temperature of 270ºC. The As_2:Ga beam equivalent pressure ratio of 20:1 was maintained during the growth.

Magnetoresistance, Hall effect, and SQUID magnetometry were used for electrical and magnetic characterization of the samples and for determining T_C. Hall effect measurements were performed in the Van der Pauw or the six-probe geometry. To circumvent the problems associated with the *anomalous Hall effect* (AHE) in ferromagnets [2, 14], we have used the electrochemical capacitance voltage (ECV) profiling method to measure the depth distribution of acceptors in our specimens. ECV profiling measurements were carried out using a BioRad PN4300 Semiconductor Profile Plotter with a 0.2M NaOH: EDTA solution as the electrolyte. By comparing the Hall and ECV results on non-ferromagnetic $Ga_{1-y}Be_yAs$ thin films grown under similar conditions as the LT-$Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Be_yMn_xAs$ films, we have established that ECV can be reliably used to obtain the free hole concentration profiles in ferromagnetic LT-$Ga_{1-x}Mn_xAs$ [12].

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 channeled particle-induced x-ray emission (c-PIXE) with channeled Rutherford back-scattering (c-RBS) simultaneously obtained from $Ga_{1-x}Mn_xAs$ films 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 "random" yield.

Figure 1 shows the PIXE and RBS angular scans (normalized yield as a function of the tilt angle around the channeling axis) about the <110> and <111> axes for the $Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Be_yMn_xAs$ films with increasing y. The angular scans about the <100> directions are similar to those about the <111> direction for all samples and are therefore not shown in the figure. The <110> angular scans are taken along the {110} planar direction. The total Mn content in all samples was determined by PIXE to be ~0.05. The Be contents was estimated from the lattice constant determined by x-ray diffraction. The lattice constant versus Be content calibration curve was obtained by determining the concentration of Be in a series of $Ga_{1-y}Be_yAs$ samples from RHEED intensity oscillation and by assuming that the same Be cell temperature produces the same Be concentration in $Ga_{1-y}Be_yAs$ and $Ga_{1-x-y}Be_yMn_xAs$ films.

For all the samples studied, the <111> axial Mn scans (c-PIXE) follow the host GaAs (RBS) scans, indicating that the dominant fraction of the Mn atoms are either on substitutional sites or are on specific sites shadowed by the host atoms [15,16]. This reveals that the majority of the Mn atoms is on specific (non-random) sites commensurate with the lattice, but does not necessarily imply that all of the Mn atoms are in *substitutional* positions. At the same time the normalized yields χ_{Mn} (ratio of channeled and random Mn yields) in the <111> scans also shows a gradual increase, deviating from the corresponding host scans as the Be content increases, indicating an increase in Mn atoms in the form of random clusters not commensurate with the GaAs lattice.

In contrast to the <111> angular scans, the Mn <110> angular scans are strikingly different from their corresponding host scans in Fig. 1. In the sample without Be (y = 0), we observe that the <110> χ_{Mn} is significantly higher than that in the <111> scan, particularly in the middle of the channel, suggesting that a significant fraction of the non-random Mn shadowed in the <111> scans do not all occupy substitutional sites, and can

thus be assumed to be located at the *interstitial* sites lying along the <111> axis of the zinc-blende crystal lattice. Atoms in these interstitial positions, tetrahedral or hexagonal in a diamond cubic lattice are shadowed by the host atoms when viewed along both the <100> and <111> axial as well as the (100) and (110) planar directions. They are, however, exposed in the <110> axial channel [15,16], giving rise to a double-peak (tetrahedral site) or a single peak (hexagonal site) feature in the <110> angular scan due to the flux-peaking effect of the ion beam in that channel [15]. Although the χ_{Mn} is clearly higher, the peak at the center of the <110> scan for the Be-free sample is itself within experimental error. We find from the difference between the <110> and <111> scans for this sample that the fraction of Mn in interstitial sites amounts to ~7%.

As the Be content increases, the <110> Mn angular scans show a definite peak at the center of the channel that increases in intensity -- a clear signature for the presence of an increasing concentration of Mn interstitials in the alloy [17]. These results unambiguously reveal that the fraction of Mn_I as well as random Mn-related clusters increases monotonically in $Ga_{1-x-y}Be_yMn_xAs$ films with increasing Be content. The fractions of Mn atoms at the various sites -- substitutional (Mn_{Ga}), interstitial (Mn_I) and in random-cluster form (Mn_{ran}) -- as measured from the angular scans are shown in Fig. 2. Mn atoms in various configurations for a sample with y~0.08 and annealed at 280ºC for 1 hr. are also shown. When the sample is annealed a dramatic increase of Mn as random clusters at the expense of Mn_I is observed while the Mn_{Ga} fraction stays the same. We also note that in the as-grown sample where Be and Mn contents are similar ($x \approx y$), the distribution of non-random Mn ([Mn_{Ga}] and [Mn_I]) is approximately equal between interstitial and substitutional sites.

Figure 3 (a) shows the concentrations of Mn atoms at the various sites in the $Ga_{1-x}Mn_xAs$ lattice. The free hole concentration obtained from ECV and Hall measurements is displayed in Fig. 3(b), while the Curie temperature T_C is shown in 3(c). The influence of the anomalous Hall effect (AHE) in the ferromagnetic samples is not taken into

account here, and thus the free hole concentrations obtained by Hall measurements do not reflect the true values and are included only for comparison. It is particularly worth noting that T_C of the $Ga_{1-x-y}Mn_xBe_yAs$ films drops rapidly as y increases – in fact the samples become non-ferromagnetic for $y > 0.05$ -- while the free hole concentration measured by ECV remains rather constant throughout the entire Be composition range. Note that for the ferromagnetic $Ga_{1-x}Mn_xAs$ film where the T_C is high ($T_C = 60K$) a large discrepancy (as much as an order of magnitude) between the real hole concentration and that determined from Hall effect measurements 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 their ferromagnetic property and the hole concentrations measured by Hall effect is seen to approach that measured by the ECV method.

The ECV data show that the different $Ga_{1-x-y}Be_yMn_xAs$ films have similar values of free hole concentration of ~4 to $6x10^{20}/cm^3$. This evident saturation of the hole concentration can be understood as follows. It has been established that in compound semiconductors the carrier concentration is limited by the formation of compensating native defects. The formation energies of these defects are governed by the position of the Fermi level [18,19]. The relatively constant hole concentration of about $5x10^{20}/cm^3$ shown in Fig. 2(b) indicates that the hole concentration in these $Ga_{1-x-y}Mn_xBe_yAs$ samples is at the free hole saturation limit. As this limit is reached, the formation energies of Mn_{Ga} acceptors and compensating Mn_I become comparable. Introduction of additional Be acceptors into the $Ga_{1-x-y}Mn_xBe_yAs$ samples then leads to a downward shift of the Fermi energy, that in turn increases the formation energy of negatively charged Mn_{Ga} acceptors. As a result, an increasing fraction of Mn is incorporated in the form of Mn_I donors and/or electrically inactive MnAs or Mn clusters [20]. The creation of Mn_I not only puts a limit on the maximum hole concentration, but also has a profound effect on the number of ferromagnetically active spins and -- for a constant hole concentration -- on the RKKY coupling of these spins.

Specifically, there are three mechanisms to note in this context. First, it has been shown theoretically that Mn_I on tetrahedral sites do not participate in the RKKY-mediated ferromagnetism because Mn_I *d*-orbitals do not hybridize with the *p*-states of the holes at the top of the valence band [10]. Second, as mentioned earlier, the Mn_I donors may form antiferromagnetically ordered Mn_I-Mn_{Ga} pairs [10], which not only renders Mn_{Ga} inactive as acceptors, but also reduces the total number of *uncompensated Mn spins participating in the ferromagnetism.* Such drop in the number of active spins reduces T_C. Finally, we wish to call attention to a third effect that pushes the $Ga_{1-x-y}Be_yMn_xAs$ system out of ferromagnetic state: when the number of active spins becomes approximately equal to the hole concentration (as is seen in Fig. 2), then the average distance between the active Mn spins becomes larger than the first node in the oscillatory RKKY exchange coupling (at $\approx 1.17\ r_{hole}$, where r_{hole} is the average distance between holes [21]). In this situation some substitutional Mn ions may couple antiferromagnetically between themselves. This would at first lead to the drop in T_C, and eventually should drive the system into a spin-glass state [21-23]. We believe that some or all of the above factors contribute to the strong drop in T_C and to the disappearance of ferromagnetism in $Ga_{1-x-y}Mn_xBe_yAs$ with increasing Be content.

In conclusion, our present work on LT- $Ga_{1-x-y}Mn_xBe_yAs$ alloys, together with previously reported studies of the 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. As the Mn concentration x increases beyond the doping limit p_{max}, it is energetically favorable to form compensating Mn_I, thus keeping the product of the free hole concentration and of the concentration of the net uncompensated Mn spins participating in the ferromagnetism relatively constant at the maximum level. Since the ferromagnetism in this system is related to the uncompensated Mn spins and is mediated by holes, such Fermi-level-induced hole saturation effect necessarily imposes a

fundamental limit on the Curie temperature of the system. Co-doping of $Ga_{1-x}Mn_xAs$ with Be acceptors, which --according to intuition -– should increase T_C, actually makes the situation worse, since the total number of acceptors (in $Ga_{1-x-y}Mn_xBe_yAs$ the quantity x+y) has to be maintained below p_{max}. In other words, adding Be creates a huge increase of Mn_I, thus killing ferromagnetism. This experimental observation leads us to propose using *heavy n-type counter-doping* of $Ga_{1-x}Mn_xAs$ (with, e.g., Te) as a remedy for the otherwise unavoidable creation of Mn interstitials at higher values of x. In such $Ga_{1-x}Mn_xTe_zAs_{1-z}$ it should be possible to achieve values of $x \approx p_{max}+z$. Although the hole concentration will still be "pinned" at p_{max} by the limit imposed on the Fermi level, the number of active Mn would increase in proportion to x, thus increasing T_C.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098; by NSF Grant DMR00-72897; and by the DARPA SpinS Program.

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T_C of as high as 140K has been suggested by Edmonds et al. (http://arXiv.org/abs/cond-mat/0209554) for thin $Ga_{1-x}Mn_xAs$ layers (~45nm) annealed at very low temperature (175ºC) for as long as 120 hours. Surface and/or interface effects are expected to play an important role in this case. Some improvements on T_C have been also achieved by Ohno et. al in Be co-doped double layer structures. However, considerations of the thermodynamic equilibrium in such nonuniform systems are beyond the scope of this article.

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FIGURE CAPTION

Fig. 1 Angular scans about the <110> and <111> axes for undoped and for Be-doped $Ga_{1-x}Mn_xAs$ samples. The <110> angular scans are taken along the {110} planar channel.

Fig. 2 The fractions of Mn atoms at the various sites -- substitutional (Mn_{Ga}), interstitial (Mn_I) and in random-cluster form (Mn_{ran})-- as measured from the angular scans shown in Fig. 1. The Mn fractions for the sample with y~0.08 annealed at 280ºC for 1 hr. are also shown as closed symbols.

Fig. 3 The concentration of Mn atoms at various lattice sites, as measured from the angular scans (a); hole concentrations determined by ECV and Hall measurements (b); and the Curie temperatures T_C (c) for $Ga_{1-x-y}Mn_xBe_yAs$ films with increasing Be concentration y.

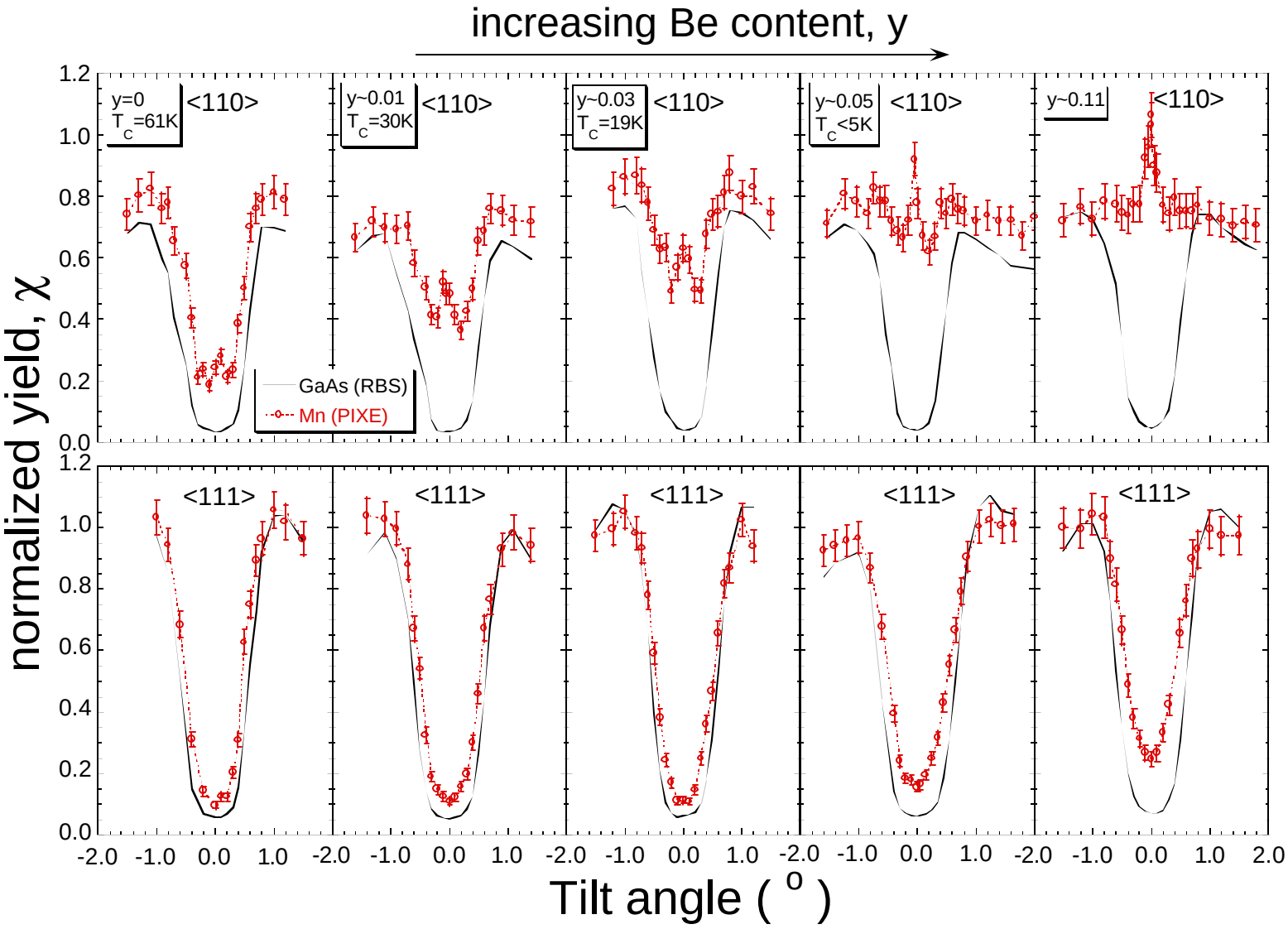
increasing Be content, y
y=0
T_C=61K
<110>
y~0.01
T_C=30K
<110>
y~0.03
T_C=19K
<110>
y~0.05
T_C<5K
<110>
y~0.11
<110>
GaAs (RBS)
Mn (PIXE)
<111>
<111>
<111>
<111>
<111>
normalized yield, χ
Tilt angle (o)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
-2.0
-1.0
0.0
1.0
2.0

Fig. 1

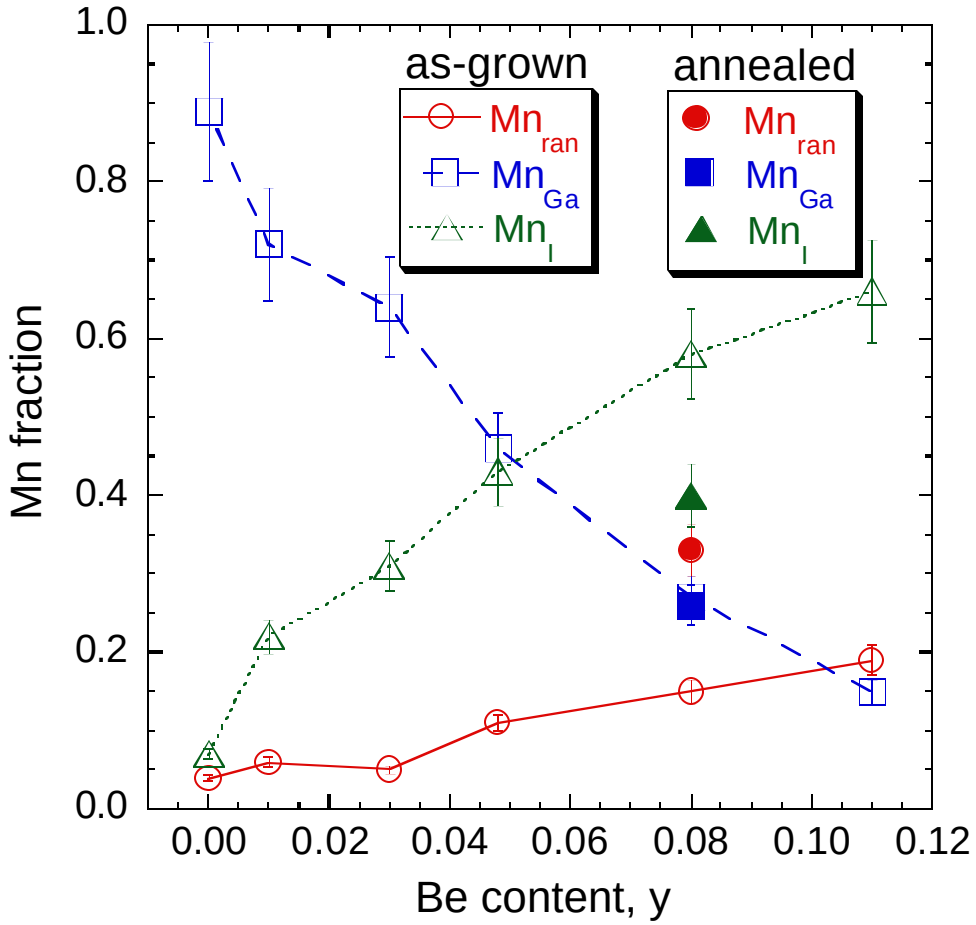
as-grown
annealed
Mn ran
Mn Ga
Mn I
Mn fraction
Be content, y
0.0
0.2
0.4
0.6
0.8
1.0
0.00
0.02
0.04
0.06
0.08
0.10
0.12

Fig. 2

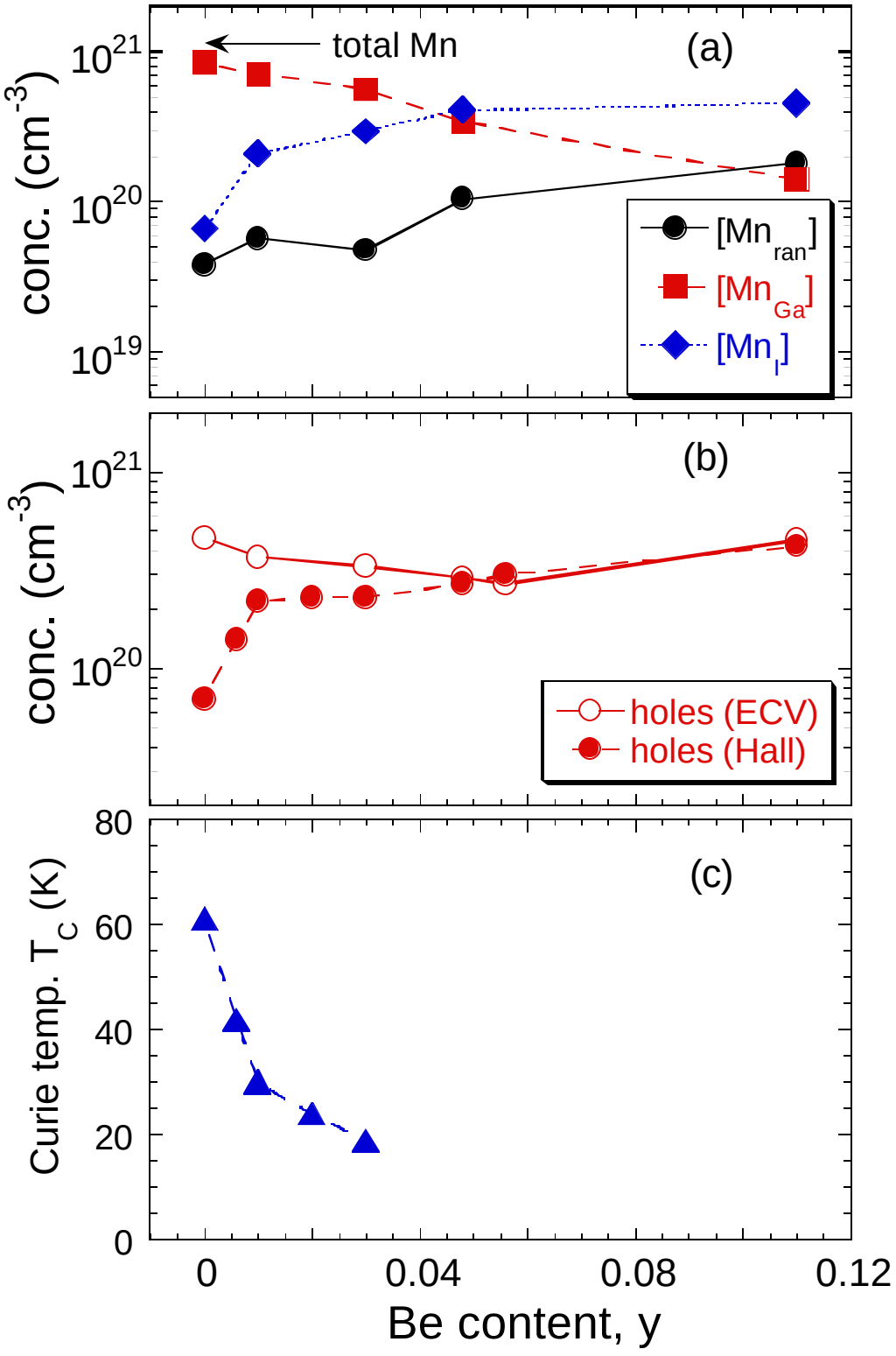
total Mn
(a)
conc. (cm^{-3})
10^{21}
10^{20}
10^{19}
[Mn$_{ran}$]
[Mn$_{Ga}$]
[Mn$_{I}$]
(b)
conc. (cm^{-3})
10^{21}
10^{20}
holes (ECV)
holes (Hall)
(c)
Curie temp. T_C (K)
80
60
40
20
0
0
0.04
0.08
0.12
Be content, y

Fig. 3