First-principles approach to Mn-doped group IV semiconductors: comparison with experiments and outlook

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**Abstract.** We present an extensive theoretical and experimental study of the Mn-Ge dilute magnetic semiconductor, a material which - due to its high integrability with mainstream Si technology - may hold good promises for spintronic applications. *Ab-initio* calculations on several different systems containing isolated Mn impurities as well as small clusters (up to three Mn impurities) show that Mn has a tendency to segregate into the Ge matrix and to stabilize occupation of interstitial sites if these are coordinated with other Mn occupying substitutional sites nearby. Several different experimental characterizations (HRTEM, XRD, UPS, MOKE) performed on Mn ion-implanted systems are analyzed and discussed: a close comparison between experimental evidences and density functional calculations allows a full understanding of the sample properties and to disentangle the contributions coming from the diluted and segregated phases. The complexity of this system shows that much has to be done still to understand the physics of these materials and to undisclose all their possible applications.

**Introduction**

Spintronics based on diluted magnetic semiconductors (DMS) represents one of the most promising, challenging and exciting areas of current materials science. The possibility to combine storage and logic into a single device, in fact, has recently led to a burst of scientific activities into different fields that range from the design of devices based on the manipulation of the electron spin, to the controlled fabrication of suitable magnetic semiconductors. Fabrication of a material with the desired properties is, however, one of the most ambitious goals. Within DMS, the prototype material is by far GaMnAs [1] (usually grown by molecular beam epitaxy - MBE), with its ferromagnetic response reported up to a Curie temperature of about 170 K. However, in order to foresee large-scale production of such DMS in the near future, it is desirable to explore: new group-IV-based DMS (compatible with current Si based technology), and, at the same time, alternative DMS growth techniques, such as ion implantation. To this end, some attention has been paid recently to group-IV based DMS [2,3]. MBE grown Mn\(_x\)Ge\(_{1-x}\) alloys [2] showed Curie temperatures that increased linearly with Mn concentration up to about 120 K and possibly higher (~280K)[4]. However, it is by now generally agreed that MBE growth[5] (even if kept at rather low temperature, below 100°C) leads to phase precipitation into nano-crystallites of Mn-rich alloys (mainly Mn\(_5\)Ge\(_3\)) still at rather low Mn-doping concentrations (below 3%), thus severely hindering the highly desired Mn content within the Ge matrix.

Nevertheless, new and exciting reports [6] claim that novel techniques employing *subsurfactant* epitaxy are able to overcome the bottle-neck related to the low solubility of magnetic ions into the...
semiconductor matrix, thus allowing fabrication of DMS with ferromagnetic ordering exceeding room temperature. Therefore, it is extremely important to understand in detail both theoretical and experimental findings in order to fully assess the possible technological role that these materials might have.

In this paper we will revise some of the work that our group has been recently undertaking on Mn-Ge diluted systems and in particular the theoretical aspects of Mn in Ge from first-principles calculations, including bonding properties, carrier localization and magnetic properties, and the experimental evidences focusing on Mn-implanted Ge: an alternative and very promising technique to fabricate DMS. In particular, since the most important issue in these materials is to ascertain whether dilution of Mn dopants is achieved or rather competing segregated phases are formed, we will concentrate on the characterization of the samples and on the experimental abilities to distinguish the different contributions and fully characterize each phase, separately.

First of all, we will review the most important theoretical findings concerning the dilution of Mn into the Ge system and its tendency to form Mn-rich aggregates. Then, we will discuss experimental findings in comparison with theoretical predictions, where possible, and we will demonstrate that the cooperative interaction between the diluted and the segregated phase determines the overall magnetic properties of the samples.

The aim of the paper is to show that the synergy between computational and experimental techniques is able to deliver valuable and precious information that can not be obtained otherwise and that much has to be done still to fully understand the physics of these systems.

**Theory of Mn impurity in Ge**

*Ab-initio* calculations, within density functional theory using the VASP package[7] and PAW pseudopotentials, were performed for different transition metals (TM) at low concentrations (< 6.25 %), corresponding to unit cells containing 32 (64) atoms for the ferromagnetic (antiferromagnetic (AFM) and cluster structures) at the experimental Ge lattice constant ($a = 5.636$ Å), well reproduced within local density approximation (LDA) (within 0.1%) and less accurately within generalized gradient approximation (GGA) ($a = 5.776$ Å). The Irreducible Wedge of the Brillouin Zone was sampled with several different shells: good convergency was obtained with the (8,8,8) and (4,4,4) shell for the 32 and 64 atom cells, respectively, within the Monkhorst-Pack scheme.

The TM atom was considered to occupy the substitutional site (i.e. one of the diamond lattice sites) and the interstitial site of the diamond lattice tetrahedrally coordinated.

The other possible interstitial site (the one with hexagonal symmetry) was not considered since experimental evidences obtained in similar systems showed that the former site is always favored[8]. In the present work, only neutral states were considered for the impurity and this is of course expected to affect the final results; however, as shown in other works (see for example Ref.[9,10]) the neutral defect seems to be the lowest possible state for Mn in Ge[9] as well as for several TM impurities in GaAs[10].

We find that the substitutional state is favored over the interstitial one for all TM of the $3d$ series[11]. However, the heat of formation is rather large as in other DMS, (of the order of a few eV/atom) for all the species considered, showing that rather low dilution is expected for all the impurities considered. In addition, the trend of the heats of formation for both substitutional and interstitial
sites as a function of the TM atomic species is very similar: it decreases as the $3d$ shell becomes more and more occupied.

We here briefly recall the $p$-$d$ hybridization mechanism in DMS: TM $l=2$ states are split by the cubic crystal field into two-fold ($e$) and three-fold ($t_2$) states. $e$ states very weakly hybridize with host-like states, whereas $t_2$ states form bonding-antibonding ($b$-$ab$) pairs with anion $p$ states in each spin-channel.

As we analyze now the electronic properties, we can note that the symmetry-resolved TM $l=2$ contribution to the total density of states, plotted in Fig. 1, shows how the energy distance between majority and minority $e$ states, related to exchange interaction, increases from V to Mn and then rapidly decreases as soon as half-filling of the $d$ band is completed (from Fe to Ni), reaching its maximum in Mn, where the $e$ majority states are at energies very close to the bonding combination of $t_2$-like states. We find states within the semiconductor band-gap (see Fig. 1) in the case of Mn, Co, and Ni, corresponding to the anti-bonding combination of $p$-$d$ states. We remark here that a correct description of the $p$-$d$ hybridization requires treatment of the exchange-correlation interaction for localized states which goes beyond the Local Density Approximation: we will discuss the effect of correlation in Mn-Ge DMS later on in this paper as we compare with photoemission results.

The contribution to the density of states related to $p$ states of Ge nearest neighbours of the TM impurity is very similar to what found for Mn in Ge[3]: the larger hybridization between TM-$d$ and Ge-$p$ derived states occurs at lower binding energies (from -1 to -3 eV) and generally shifts towards lower energies as we move from V to Mn along the series, thus following the energy position of the TM $t_2$ states (not shown).

The magnetic properties of substitutional TM impurities in Ge can be easily inferred from their electronic properties as far as the main trends are concerned[11]. In fact, we would expect stable magnetic states with magnetic moments equals to 1, 2 and 3 $\mu_B$ for V, Cr, and Mn, respectively. This is, indeed, what we find, as shown in Fig. 2, where the calculated magnetic moments (total and on the TM atom) within GGA are reported. However, in order to more deeply understand the magnetic properties of these compounds, a more detailed study is needed. This concerns, in particular, the stabilization of antiferromagnetic versus ferromagnetic alignment in V and Cr impurities, both exhibiting $e$ states as the highest occupied states. For these two TMs, in fact, we find that the AFM state is energetically favored over the FM one by $\sim$30 and only 3 meV/TM-atom for V and Cr, respectively.

In these last two cases, in fact, the $e$ states are those closest to the Fermi level: these states are rather narrow in energy and quite spatially localized since symmetry forbids any hybridization with $p$-derived states. However, $e$ states interact with other $e$ states at different TM sites, resulting in the small broadening observed in their density of states (Fig. 1); these highly localized states have a very narrow band-width and would lead to an antiferromagnetic and insulating (as for the Cr case) ground state of the system: in the case of V, the $e$ states are doubly degenerate and only partially filled, resulting in an antiferromagnetic metallic behavior.

The magnetic moment induced on the Ge site which is closest to the TM impurity is always very small (not larger than -0.02 $\mu_B$) and negative: this is already well known in Ge as well as in GaAs and other DMS systems and is related to the $p$-$d$ hybridization and the antiferromagnetic coupling between localized magnetic moments and semiconducting holes[12]. A last interesting comment concerns the properties of the carriers eventually introduced upon TM doping in Ge. The density of states in Fig. 1 shows that the lowest unoccupied states are of the kind $e$ for V, and $t_2$ for Mn, Co and Ni, while we will not expect, within GGA, any carrier doping effect related to substitutions with Cr.

![Fig.2 Magnetic moment on the transition metal atom (in Bohr magneton $\mu_B$) for the TM considered.](image-url)
and Fe, both showing a semiconducting behavior. From this picture, it is clear that the most promising magnetic dopant in Ge is Mn with its high magnetic moment and nominally 2 spin-polarized holes in the delocalized $t_2$ majority states.

**Mn clusters in Ge**

Having established that Mn is the most promising transition metal among the entire 3d series to be used as possible magnetic dopant in Ge, we turn now to the study of clusters of Mn-impurities inside the Ge matrix. This is a very relevant issue since it has been shown that phase separation and segregation of Mn$_x$Ge$_{1-x}$ compounds cannot be inhibited in epitaxial growths at temperatures exceeding 80°C. A similar behavior was found in (Mn,Ga)As where, however, higher Mn-concentrations were successfully achieved reaching ferromagnetic ordering temperatures as high as 170 K. In this case, post-growth annealing was found useful to stabilize a more efficient ferromagnetic ordering, thus enhancing the Curie temperature, thanks to diffusion of interstitial Mn towards substitutional or surface sites.

Therefore, in the following we will investigate the energetics which governs the stability of dilution versus segregation of Mn in Ge. To this end, we performed *ab-initio* calculations of two and three Mn impurities in different configurations and evaluate the formation energies of the defective structures in each case and the corresponding magnetic properties. Since single impurities of all the TM species considered are energetically favored on substitutional sites rather than on interstitials[9], we start our analysis considering the formation energies of two TM impurities both occupying substitutional sites (SS) at different distances: nearest neighbours-dimer [positions at $a(0,0,0)$ and $a(1/4,1/4,1/4)$]; bridge [at $a(0,0,0)$ and $a(1/2,1/2,0)$] and at the largest distance compatible with the chosen cell (i.e. at $a(0,0,0)$ and $a(1,1,1)$). First of all, we stress that the Mn-Mn dimers (i.e. at first-neighbour zincblende substitutional sites) can be stabilized only at their ideal unrelaxed structure[2]. As full structural relaxation is allowed, the two magnetic impurities tend to come closer and closer and to align antiferromagnetically showing that, at equilibrium growth conditions, metallic AFM Mn-precipitates may form. However, in out-equilibrium growth conditions other configurations might be stabilized and these latter are the focus of the present investigation.

Our results are summarized in Fig. 3, where we show a comparison among the heat of formation of the most stable configurations at fixed number of substitutional/interstitial sites. For two substitutional impurities, we find that the most energetically convenient configuration is the one in which the two Mn's are in the bridge position and that the system gains energy in bringing the two impurities close to each other: the heat of formation for two substitutional impurities is in fact less than twice the value for the single isolated impurity (value at the left in Fig.3(a)). Surprisingly, as we allow occupation of a substitutional and an interstitial site, we find that the heat of formation becomes lower than in the two substitutional impurities case: although the energy cost for an isolated interstitial impurity is very high (∼1 eV higher than for the isolated substitutional site), one of the possible substitutional-interstitial dimers (with atomic positions: $a(0,0,0)$ and $a(-1/4,-1/4,-1/4)$ has formation heat about 0.5 eV lower than the substitutional-substitutional pair. This situation can be rationalized as follows: as the TM-$d$ states of the isolated interstitial impurity are in a non-bonding configuration, the interaction between impurities generates bonds which stabilize the complex: the values of the formation heats are
strongly reduced with respect to the bare sum of the single isolated impurities values (cfr. Fig. 3). Thus, interstitial impurities, although energetically expensive when isolated, can be more easily stabilized thanks to TM-TM interactions. Interestingly, the total magnetic moment ($\mu_T$), shown in Fig. 1 panel (b), for this latter structure is lower than in the two substitutional configuration: as the Mn impurities come in closer contact, $d-d$ hybridization tends to prevail thus inhibiting parallel spin-ordering. Occupation of the interstitial and the consequent clustering with substitutional sites apparently should not hinder the ferromagnetic behavior of the doped semiconductor. However, due to the formation of $d-d$ bonds between nearby sites, the SI Mn-complex results to be insulator with a rather large total magnetic moment: thus, the SI Mn-complex, although FM, does not provide the necessary polarized hole carriers to mediate FM alignment.

As we move to the three impurities case, we find that the presence of an interstitial site always lowers the heat of formation and at the same time depresses the total magnetic moment of the cell: the structure with all 3 Mn in substitutional sites (SSS) shows in fact a much larger formation energy (more than 1.5 eV/cell) than the one with two substitutional + one interstitial site (SIS), although it exhibits a rather large ferromagnetic coupling.

Starting from the SI Mn-complex, in fact, and adding one more substitutional Mn nearby, the interstitial site at $a(1/2,0,0)$ is energetically competing in such a way that direct bonds with the 2 equivalent Mn at $a(0,0,0)$ and $a(1/2,1/2,0)$ might be established and the $d-d$ hybridization favored. However, this configuration leads to an overall AFM alignment between the interstitial and each substitutional site resulting in only one magnetically active Mn per cell. It is clear, therefore, that Mn shows a very pronounced tendency towards segregation and cluster formation: although interstitial isolated impurities are always energetically costly with respect to substitutional ones, the formation of interstitial defects can be stabilized becoming energetically competitive, if clustering with other substitutional impurities occurs. This kind of mechanism leads to complexes that, at fixed impurity concentration, are always energetically favored over occupation of other possible substitutional sites; magnetism is not necessarily hindered by clustering effects: while full substitutional impurities lead to strong FM coupling among Mn, the presence of interstitial sites often generates AFM alignment between impurities. The AFM alignment between substitutional and interstitial defects, however, is not detrimental to the overall magnetic moment since the coupling with other substitutional impurities is always FM[13].

**Correlation effects and comparison with experiments**

Chemically cleaned intrinsic Ge(100) single crystal wafers were implanted with 100 keV Mn$^+$ ions at two different doses of $4 \times 10^{16}$ at./cm$^2$ and $2 \times 10^{16}$ at./cm$^2$. The samples were kept at 300 °C during the implantation to avoid sample amorphization. Ion implantation at a fixed beam energy produces films with non uniform concentration profiles, thus allowing investigations as a function of concentration on a single sample. Ion implanted Mn$_x$Ge$_{1-x}$ alloys ($0.01 < x < 0.15$) were investigated and characterized by means of X-ray diffraction (XRD) and photoemission spectroscopy. The coexistence of Mn rich precipitates with Mn diluted in the Ge matrix was demonstrated probing the samples at various Mn concentration as a function of the depth of the Mn ion projected range into the Ge matrix. XRD shows the presence of Mn$_2$Ge$_3$ clusters in the Ge matrix[14]. Correspondingly, photoemission shows spectral evidences of Mn phase separation but this occurrence is in competition, as the Mn concentration is diminished, with spectral features that can only be ascribed to a diluted phase. X-ray photoemission spectroscopy (XPS) depth profiles of samples showed no differences at the same doses after annealing at 400°C: thus, no Mn diffusion occurred even after annealing at a temperature 100°C higher than the implantation one. The results are thus focused on the as-implanted alloys. An accurate analysis of the XRD data in conjunction with TEM analysis allows to estimate the volume ratio of the clusters in the two implanted alloys which results to be $(8/12)^3 \sim 0.3$. This is significantly lower than the 1:2 ratio expected from the doubling of the Mn dose in the two alloys and indicates that, by halving the Mn dose in the implanted region, there is a less effective migration of Mn into the segregated phase. This evidence
of phase coexistence is clarified and strengthened by our valence band (VB) investigation. In this case we focused on the $4 \times 10^{16}$ at./cm$^2$ dose that allowed to span the larger concentration range.

Fig. 4 (a) reports, from bottom to top, the VB spectra obtained after seven subsequent sputter annealing cycles, each one stopped at the following estimated depths (i) 11 nm, (ii) 22 nm, (iii) 38 nm, (iv) 50 nm, (v) 63 nm, (vi) 77 nm, and (vii) 106 nm, with respect to the initial non sputtered surface, corresponding to Mn concentration values of: (i) 0.025, (ii) 0.08, (iii) 0.13, (iv) 0.15, (v) 0.12, (vi) 0.10, and (vii) 0.05%[12]. A spectral signature of Mn$_5$Ge$_3$ precipitates is given by the high spectral density at the Fermi level ($E_F$), due to Mn $d$-states, in all the spectra in Fig. 4(a)[15]. However, valuable spectral information regarding the Mn-content can be gained looking at the difference spectra as shown in panels (b) and (c) of this figure. Since the Ge matrix is common to all sampled regions, such spectra give an experimental estimate of the Mn projected density of states of the alloy. We find a clear increase (decrease) of the density of states at $E_F$ upon increasing (decreasing) x (cfr. Fig. 4(b),(c)) that can be ascribed to an increase (decrease) of the volume concentration of Mn$_5$Ge$_3$ crystallites in the host Ge matrix, in turn depending on the depth inside the sample. The same difference spectra are reported in the region between 2.0 and 6.0 eV below $E_F$ in Fig. 4(c): the three lowest difference curves, obtained increasing x, show a prominent feature centered at 4.8 eV, typical of the Mn$_5$Ge$_3$ phase. The difference curves obtained considering spectra related to a decrease in the Mn concentration show an additional positive peak at 4.0 eV below $E_F$. This new feature can not be explained if Mn were incorporated only as Mn$_5$Ge$_3$ precipitates: as x in the alloy decreases, there is an increase of the spectral weight related to features that are not typical of Mn$_5$Ge$_3$ precipitates but are rather signatures of a typical Mn-Ge diluted alloy. In fact, the experimental Mn PDOS, as appears in the curves (v)-(iv), (vi)-(v) in Fig. 4(c), are very similar to those obtained for MBE Mn-doped III-V compounds like Ga$_{1-x}$Mn$_x$As and In$_{1-x}$Mn$_x$As [16], where Mn dilution in substitutional sites is claimed.

In order to ascertain this point, accurate first-principles calculations have been performed within GGA, using the full-potential linearized augmented plane wave method (FLAPW)[17]. To simulate Mn-doped Ge, we considered different concentrations compatible with the experimentally accessible range ($x = 6.25\%$ and $12.5\%$, corresponding to a fcc 16-atoms and simple cubic 8-atoms cell, respectively), with Mn in the substitutional or interstitial site. Muffin-tin radii were set to 2.25 a.u. for all the atoms, a wave function cutoff of 3.6 a.u. was considered and a Brillouin zone sampling of up to 56 k-points (for the smaller 8-atoms cells) was considered. In Fig. 5 (top panel) we report the Mn partial density of states (PDOS) for the substitutional and interstitial case, respectively, at different Mn-concentrations with and without the introduction of Hubbard-like correlations (thin solid line), whereas, focusing on the substitutional case, the inset describes in detail the orbital and spin resolved Mn PDOS. As discussed previously, $e$ states very weakly hybridize with host-like states, whereas $t_2$ states form bonding-antibonding ($b$-$ab$) pairs with anion $p$ states in each spin-channel. Bonding states with a large weight on Mn are generally labeled[10] as crystal field resonances (CFR), whereas antibonding states mainly localized on the Mn nearest neighbours with small weight on Mn are labeled as dangling bond hybrids (DBH). This picture is
clearly illustrated in Fig. 5 for $x = 6.25\%$. Unoccupied d states ($e'$ and $t_{DBH}$) are not relevant on the photoemission framework. Noteworthy, Mn projected DOS spectra calculated with bare GGA are not reliable due to the inaccurate treatment of correlation effects[18], that in DMS cause a significant underestimate of the position of Mn 3$d$ states with respect to the Fermi level. Therefore, for Mn in Ge, there is an evident inadequacy of bare GGA in reproducing the VB spectra and a GGA+$U$ approach is needed[18]. Within GGA, $e'$ and $t_{b}'$ states are fully occupied and lie in a similar energy range ($\sim 2$ eV); the singly occupied $t_{ab}'$ crosses $E_F$ (giving rise to two holes), whereas $t_{b}'$ is just below $E_F$. Upon introduction of $U$, both $e'$ and $t_{b}'$ states are shifted towards higher binding energies, along with a remarkable energy localization: the $t_{b}'$ state appears as a peak as sharp as the non-hybridized $e$ state. In parallel, as $U$ is increased, the Mn weight on the $t_{ab}'$ state (and, as a consequence, on states close to $E_F$) is strongly reduced and the holes have larger Ge $p$ character. The Mn total magnetic moment changes from 3.2 $\mu_B$ to 3.8 $\mu_B$ with and without $U$, respectively, leading to a Mn electronic configuration $d^5 + 2$ holes in both cases. In a realistic description of a Mn-Ge DMS, $U$ cannot be arbitrarily varied, but can be estimated, within a recently proposed pseudopotential approach[19], in a range of about $U \sim 3$-4 eV[19]. Whether $U$ is constrained in the range above, a good qualitative agreement is found between the theoretical PDOS of Fig. 5 (a) with the experimental findings.

For $U \sim 3$eV the $t'$ peak of the Mn theoretical DOS is at slightly lower binding energy and it is sharper (0.3 eV) than the spectral feature (0.7 eV width) observed experimentally. Indeed, once the Hubbard parameter is set to $U = 4$ eV, an excellent agreement is found between theory and experiment (see Fig. Fig. 4 (c) and Fig.5 (a)) not only for the energy position of the experimental data, but also for the peak width. Namely, due to an energy resonance with the Ge 3$p$ states, the $e$-$t$ crystal field splitting spreads over 0.7 eV as in the experiment. This picture is kept upon variation of $x$: there are no basic differences in doubling (or halving, not shown) the transition-metal doping (see Fig. 5 (a)). Instead, similar GGA and GGA+$U$ calculations for Mn$_x$Ge$_{1-x}$ alloys with Mn in the interstitial do not produce a good agreement even upon the necessary introduction of $U$: however, they result in a more structured PDOS characterized by two peaks (at $\sim -5$ and $\sim -3.5$ eV) in a 3:1 intensity ratio.

**Magnetic Properties**

Having established that the Mn-ion implanted samples show a significant part of the implanted Mn in the form of a diluted MnGe alloy, we now investigate the magnetic properties of the same samples studied with photoemission spectroscopy, in order to assess the magnetic properties of such complicated materials. To this end, a thorough structural characterization by means of high-resolution transmission electron microscopy (HRTEM) joined by an electron energy loss spectroscopy (EELS) was undertaken. At the same time, a complete characterization of the magnetic properties was achieved by means of the magneto-optical Kerr effect technique (MOKE).
The HRTEM images reveal that the host matrix has a good overall crystallinity[20] and a fine dispersion of nanometer size particles embedded in the Ge matrix. The presence of the Moirè fringes in the HRTEM images indicates that the nanoparticles are in a crystalline phase. By increasing the Mn dose, an increase of the number of the particles with Moirè fringes is observed with a well defined orientation. This indicates that in average they are in the same register with the Ge matrix. Fast Fourier transform of the recorded signal, allows to establish that these particles have hexagonal structure and that can be recognized to be made of Mn₅Ge₃, having the lattice parameters perfectly matching with that compound. Further EELS analysis shows a population of dark spots dispersed in the brighter matrix. The size distribution of these dark spots allows us to make a one-to-one correspondence between these spots and the populations of the Mn₅Ge₃ particles observed in the HRTEM images. Consistently with this assignment, the particles are metallic (higher plasmon loss intensity). Beside the obvious high Mn content of the clusters, there is a significant Mn EELS signal also from the surrounding Ge matrix. Interestingly, close to the surface, where there is no efficient Mn implantation, the EELS image is dark. On the contrary, more deeply in the sample, there is a diffuse brighter background that can be assigned to Mn not belonging to precipitates. Thus, as shown by photoemission spectroscopy above, we have here a direct evidence of the coexistence of the Mn₅Ge₃ precipitates and diluted Mn in the host Ge matrix. Fig. 6 reports the magnetic characterization of the samples considered (at 2×10¹⁶ at./cm² and 4×10¹⁶ at./cm² doses, respectively). Both these samples show a rather high magneto-optical signal and a noticeable hysteresis loop (not shown). Comparison of the respective loops shows that the Kerr rotation scales approximately with the Mn content. For both samples the remanence and the coercivity remain up to almost room temperature. The values of $T_C$ estimated from the temperature dependence of these two parameters are about 255 K and 270 K for the samples with x = 6% and 12 %, respectively. The different magnetic behavior of the two samples, as far as the coercive field and the remanence are concerned, indicates a larger magneto-crystalline anisotropy of the more Mn concentrated sample, due to the larger size of its particles, to the higher relative amount of crystalline particles and to the higher overall Mn concentration. Moreover, the presence of the magnetic particles embedded in the DMS enhances the long-range magnetic order of the DMS matrix, increasing its Curie temperature and the squareness of the hysteresis loops. Clearly, the two phases have a single cooperative magnetic response. A similar interpretation was also given for the observed inhomogeneously distributed Mn in MBE grown Ge:Mn alloys[20].

In the top panel of Fig. 6 we also report the high temperature portion of the saturation. It is evident that the samples exhibit magnetic character above $T_C$ as well, up to about 300 K. This value is very close to the reported Curie temperature $T_C$ = 296 K of Mn₅Ge₃ [21], suggesting, for $T_C < T < T_{C*}$, the loss of strong interactions among the Mn₅Ge₃ particles, leaving them in a super-paramagnetic state. Unfortunately, the present study does not allow us to disentangle the contribution coming from the pure dilute Mn:Ge phase, since both phases, diluted and segregated, cooperatively determine the overall magnetic properties of the samples.
Conclusions

In summary, a joint theoretical and experimental study was presented on MnGe DMS. We showed that theory can be a valuable and enlightening tool to understand the physics of Mn-ion implanted Ge crystals. Our study shows that the implanted samples exhibit coexistence of a dilute and segregated phases that were distinguished by means of structural and photoemission characterizations. This is in agreement with first-principles calculations that predict the Mn tendency towards clustering and stress the relevance of correlation effects in these systems. However, the magnetic properties are clearly dependent on both phases since they are shown to jointly contribute to the overall magnetic response of the samples. Our investigation shows that these materials, as a matter of fact, possess very appealing properties: they keep their magnetic properties up to temperatures very close to room temperature; their morphology, as well as their magnetic response, can be tuned varying the implantation dose; effective dilution of Mn into the Ge matrix has been proved and could be further increased. Of course, the control of the other implantation parameters (energy, temperature, and rate) affects also greatly the resulting structural and magnetic properties of the compound, thus opening new opportunities for new investigations. In addition, the interaction between the diluted and the segregated phase has still to be undisclosed and may hold good promises for brand new physics and possible applications.

References


