Spinodal nanodecomposition in magnetically doped semiconductors

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This review presents the recent progress in computational materials design, experimental realization, and control methods of spinodal nanodecomposition under three- and two-dimensional crystal-growth conditions in spintronic materials, such as magnetically doped semiconductors. The computational description of nanodecomposition, performed by combining first-principles calculations with kinetic Monte Carlo simulations, is discussed together with extensive electron microscopy, synchrotron radiation, scanning probe, and ion beam methods that have been employed to visualize binodal and spinodal nanodecomposition (chemical phase separation) as well as nanoprecipitation (crystallographic phase separation) in a range of semiconductor compounds with a concentration of transition metal (TM) impurities beyond the solubility limit. The role of growth conditions, co-doping by shallow impurities, kinetic barriers, and surface reactions in controlling the aggregation of magnetic cations is highlighted. According to theoretical simulations and experimental results the TM-rich regions appear either in the form of nanodots (the dairiseki phase) or nanocolumns (the konbu phase) buried in the host semiconductor. Particular attention is paid to Mn-doped group III arsenides and antimonides, TM-doped group III nitrides, Mn- and Fe-doped Ge, and Cr-doped group II chalcogenides, in which ferromagnetic features persisting up to above room temperature correlate with the presence of nanodecomposition and account for the application-relevant magneto-optical and magnetotransport properties of these compounds. Finally, it is pointed out that spinodal nanodecomposition can be viewed as a new class of bottom-up approach to nanofabrication.

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In this review we focus on the latest progress in clarifying the origin of high-\(T_c\) ferromagnetism in dilute magnetic semiconductors (DMSs), such as group III pnictides, e.g., GaAs and GaN), group II chalcogenides, e.g., ZnTe), and group IV elemental semiconductors, e.g., Ge) doped with transition metal (TM) ions, either Cr, Mn, or Fe. Recent comprehensive studies have pointed out that in these systems, except for Mn in II-VI compounds (Giebultowicz et al. 1993, Pajączkowska 1978), the fundamental premise of DMSs on the random distribution of magnetic ions over cation sites is often not valid. As described here, this striking conclusion, and its consequences for electronic and magnetic properties, have been drawn from state-of-the-art theoretical modeling and experimental investigations. More specifically, the present understanding of these systems has been built by combining:

- \textit{Ab initio} computational studies providing the magnitude of chemical interactions between magnetic cations depending on their distance, charge state, and location (surface vs. bulk); the interaction energies constitute the input parameters for kinetic simulations of spinodal nanodecomposition within the Monte Carlo method or by solving the relevant Cahn-Hilliard equation.

- Extensive epitaxy and post-growth processing protocols, including co-doping and annealing, allowing to establish the relationship between fabrication conditions and physical properties.

- Comprehensive nanocharacterization investigations employing ever improving methods of electron microscopy, synchrotron radiation, ion beams, and scanning probes that provide element-specific information on atom distributions, charge states, magnetic properties, and defects with spatial resolution down to the nm range.

Scrupulous magnetization and magnetic resonance studies involving also the extensive examination of reference samples containing nominally no magnetic ions but otherwise grown and processed in the same way as the films under investigation.

According to the results reviewed in this paper, the above methodology has made it possible to bring to light theoretically and experimentally a number of unanticipated properties of magnetically doped semiconductors. The new findings can be summarized as follows:

1. In DMSs, open orbitals of TM impurities not only provide localized spins but also, via \(p-d\) hybridization, contribute to the bonding, which usually results in attractive forces between magnetic cations and in a miscibility gap in the thermodynamic phase diagram of the alloy.

2. The actual TM distribution, for given fabrication conditions, post-growth processing, and epitaxial...
strain, is determined by a competition between attractive forces, entropy terms, and kinetic barriers at the growth surface or in the sample volume. This results in the co-existence of TM ions in random cation-substitutional positions and in regions with high concentrations of magnetic constituents, either commensurate with the host lattice (chemical phase separation) or in the form of precipitates (crystallographic phase separation). The process of TM aggregation is referred to as spinodal nanodecomposition though nucleation mechanisms (binodal decomposition) is involved in many cases.

3. The buried regions with high concentrations of magnetic constituents (called condensed magnetic semiconductors - CMSs, even if an insulator-to-metal transition occurred locally) appear as TM-rich nanodots (distributed randomly over the sample volume or clustered in defined planes) or in the form of TM-rich nanocolumns extending along specific crystal directions.

4. The incorporation and distribution of magnetic ions depend on co-doping by shallow impurities or electrically active defects, which rather than changing the carrier concentration alter the valence of the TM ions and, thus, the chemical forces and kinetic barriers controlling the aggregation of magnetic cations either at the growth surface or in the film volume.

5. Because of the bonding to host atoms and the effects of strains, the structural and magnetic properties of particular CMS nanocrystals (NCs) may not yet been listed in chemical compendia, and have to be assessed experimentally.

6. Depending on the predominant character of the exchange interactions, the spins within the individual CMS NCs exhibit FM, ferrimagnetic, or antiferromagnetic (AF) spin ordering that owing to the high concentrations of TM ions persists typically to above room temperature (RT). At the same time, local strains, the character of interfaces, internal spin-orbit interactions, and the shapes of TM-rich regions control the magnetic anisotropy of particular CMS NCs.

7. Samples of nominally the same DMS with a given average TM concentration, can show diverse structural and macroscopic magnetic properties, as the relative abundance of randomly distributed TM ions and NCs formed by various phase separation processes depends on fabrication conditions, co-doping, and defect content. Except for DMSs with a large concentration of holes, randomly distributed TM spins can order only at low temperatures, whereas the NCs can lead a FM, AF, and/or superparamagnetic behavior persisting up to high temperatures.

8. Due to the combine effects of magnetic anisotropy and dipole interactions, decomposed magnetic alloys rather than exhibiting superparamagnetic characteristics show typically temperature independent narrow and leaning magnetic hysteresis loops up to the ordering temperature of the relevant CMS (superferromagnetic characteristics), even if the diameters of TM-rich regions are in the sub 10 nm range. Ferromagnetic-like features can result also from uncompensated spins on the surface of AF NCs.

9. The outstanding structure of decomposed alloys points to novel functionalities compared to hole-mediated uniform dilute FM semiconductors. In particular, the magnetotransport and magneto-optical properties of such systems, while correlate usually with the magnetic characteristics, reveal specificities of the nanocomposite media, such as the mixing between diagonal and non-diagonal components of the conductivity tensors and the persistence of magneto-optical effects into the spectral region below the band gap.

10. Magnetic studies of thin epitaxial layers containing a small quantity of magnetic impurities are challenged by the uncontrolled contamination of samples by FM nano- and micro-particles.

Altogether, one can now obtain various semiconductors with spatial distributions of TM cations on demand. In particular, by selecting appropriate growth conditions, layers’ layout, co-doping, and/or processing protocols it becomes possible to fabricate either a uniform DMS or a decomposed alloy with a predefined (i) character of the phase separation (chemical vs. crystallographic); (ii) type of TM aggregation (nanodots vs. nanocolumns); (iii) plane at which nanodots assemble, and (iv) chemical and magnetic properties of the precipitates. This command over the structural and magnetic properties offers a spectrum of opportunities for the design and realization of modulated systems with properties and functionalities encountered neither in uniform DMSs nor in the case of self-assembled quantum dots or nanowires of non-magnetic semiconductors.

As seen in the Table of Contents, the main body of the present review consists of three major parts.

First, we discuss theoretical aspects of nanodecomposition in magnetically doped semiconductors (Sec. II). We start (Sec. II.A) by presenting first principles (ab initio) approaches and their applications (Sec. II.B) for determining the chemical forces between magnetic ions, either in bulk or at the growth surface, as well as their dependence on co-doping with shallow impurities. In Secs. II.C.1 and II.C.2 we describe Monte Carlo simulations of three-dimensional (3D) and two-dimensional (2D) spinodal decomposition, corresponding respectively to the spontaneous formation of TM-rich nanodots in the film volume and to the self-assembly of TM-rich
nanocolumns during the epitaxy. Next, in Sec. [VII] the computed phase diagrams of some binary alloy are presented, allowing us to recall the notions of miscibility gap, nucleation, and spinodal decomposition. We also emphasize the importance of kinetic barriers in the process of TM aggregation. These concepts make it possible to discuss, in Sec. [VIII], the Cahn-Hilliard equation quantifying the dynamics of spinodal decomposition. As a whole, theoretical modeling opens to the understanding of the physics of nanodecomposition for different combinations of hosts, TM ions, shallow impurities, and fabrication procedures.

Second, in Secs. [III],[VII] experimental studies of nanodecomposition in specific families of magnetically doped semiconductors are presented. Whenever possible the findings are discussed in the context of the theoretical predictions outlined in Sec. [I]. We start (Sec. [III]) with the model FM semiconductor (Ga,Mn)As. For this system pioneering works aiming at the fabrication of GaAs containing MnAs nanoprecipitates were carried out (Boeck et al., 1996; Shi et al., 1996). Furthermore, early ab initio studies of (Ga,Mn)As and related systems revealed the presence of strong attractive forces between TM cation pairs in DMSs (van Schilfgaarde and Mryasov, 2001). We describe the chemical and crystallographic phase separations occurring in (Ga,Mn)As under annealing or epitaxy at appropriately high temperatures. Structural information on Mn-rich (Mn,Ga)As NCs is linked to FM-like features as well as to device-relevant magnetic circular dichroism (MCD) and magnetotransport characteristics of this noncomposite system. The understanding of ferromagnetism in decomposed (Ga,Mn)As allows us to assess the origin of high-\(T_C\) in (Ga,Mn)P, (In,Mn)As, (Ga,Mn)Sb, and (In,Mn)Sb.

In Secs. [IV] and [V] we describe investigations of group III nitrides, doped with either Mn or Fe and, in some studies, co-doped with Si or Mg. In the case of (Ga,Mn)N (Sec. [IV]) a rich collection of magnetic properties at similar average Mn content is observed. The nanodecomposition scenario is confirmed by structural nanocharacterization demonstrating the correlation of high-\(T_C\) and low-\(T_C\) with respectively the presence and absence of a phase separation. Similar experiments point to spinodal decomposition, in the form of nanocolumns, in (Al,Cr)N (Gu et al., 2005). Section [V] is devoted to (Ga,Fe)N, the subject of particularly comprehensive structural and magnetic studies. The collected data provide evidences for spinodal decomposition as well as for the precipitation of various Fe-rich (Fe,Ga)\(_2\)N NCs whose composition \(x\) (and thus magnetic properties), abundance, and location in predefine planes can be controlled by growth conditions, co-doping by Si and Mg, and architecture.

Sections [VI] and [V] present the outcome of nanodecomposition studies on Mn- and Fe-doped Ge, respectively, in which the TM distribution is uniform or either chemical or crystallographic phase separation is observed depending on the growth temperature. In addition to detailed structural and magnetic investigations, comprehensive MCD and magnetotransport data are available for these systems. Particularly relevant are works on the formation of Mn-rich nanocolumns along the [001] growth direction in (Ge,Mn) deposited onto Ge(001) substrates.

As described in Sec. [VIII] in the case of (Zn,Cr)Te spinodal decomposition results in either Cr-rich nanodots or nanocolumns assuming a (111) orientation, even for epitaxy on (001) substrates. Despite chemical heterogeneity there is a strict correlation between magnetization, MCD, and anomalous Hall effect (AHE) in these alloys. Furthermore, nanodecomposition and, thus, other associated properties are strongly affected by changing the concentrations of donors or acceptors, either by manipulating with stoichiometry via altering the intensities of the molecular beams or by co-doping with I or N, respectively. Pioneering work drawing attention to the possibility of spinodal nanodecomposition in (Zn,Cr)Se (Karczewski et al., 2003) is also discussed.

In the third part of our review, Sec. [IX] we discuss application prospects of the remarkable properties revealed for decomposed magnetically doped semiconductors over the recent years. We emphasize the possibility of bottom-up nanotechnology based on the control of spinodal nanodecomposition (‘spinodal nanotechnology’). It is pointed out that decomposed magnetic alloys consisting, for instance, of a semiconductor with embedded NCs of a FM metal can exhibit functionalities that cannot be realized employing either uniform FM metal films or semiconductor quantum dot layers. Finally, in Sec. [X] we summarize the main conclusions stemming from studies of heterogeneous DMSs and present an outlook on open questions and challenges ahead. Furthermore, a list of abbreviations is provided.

As seen, the physics of high-\(T_C\) ferromagnetism in magnetically doped oxides (Coey et al., 2010; Fukumura and Kawasaki, 2013; Li et al., 2012; Sawicki et al., 2013), carbon derivatives (Kuzemsky 2013; Makarova, 2010), and some other systems (Nealon et al., 2012; Roever et al., 2011; Rytkov et al., 2012; Yao et al., 2012) is beyond the scope of this review. In particular, the question of ferromagnetism originating from spins residing on defects (Coey et al., 2010; Zhou, 2014) or on open p shells (Volianska and Boguslawski, 2010), or mediated by defects or by residual impurities like hydrogen (Li et al., 2012) is not addressed here. We only note that not only several authors have considered theoretically whether ferromagnetism would be possible without magnetic elements (Bouzerar and Ziman, 2006; Droghetti et al., 2006; Du et al., 2012; Elfimov et al., 2002; Ivanovskii, 2007; Kenmochi et al., 2004a, 2005, 2004b; Mavropoulos et al., 2009; Volianska and Boguslawski, 2010) but also the role of spinodal nanodecomposition was examined in this context (Seike et al., 2012; 2013a,b).

As emphasized in our survey, the recent progress in understanding high-\(T_C\) DMSs results, to a large extent, from the application of various powerful nanocharacterization tools. Nevertheless, we do not discuss in details relevant experimental techniques, as many of them were
recently reviewed in a collection [Bonanni 2011] that contains also useful information about the methodology of magnetic measurements on thin films employing superconducting quantum interference device (SQUID) magnetometry [Sawicki et al. 2011]. A related experimental challenge is the contamination by FM nano- and microparticles that already reside in the substrate or can be incorporated during the growth, annealing, etching, handling, or storing of particular samples. Some instructive examples were disclosed [Abraham et al. 2005; Grace et al. 2009; Makarova et al. 2006; Matsubayashi et al. 2002] but presumably much more cases, even if spotted, have not been published.

II. THEORY OF SPINODAL NANODECOMPOSITION

A. Ab initio materials design

Ideally, theoretical studies should predict the microscopic TM distribution—including the presence of chemical and crystallographic phase separations—and the corresponding electronic and magnetic properties at given growth conditions and co-doping by shallow impurities. As already reviewed elsewhere (Sato et al. 2010), first-principles methods for electronic structure calculations have played the important role in predicting various properties of homogeneous and heterogenous DMS without referring to any experimental parameters. This is mainly due to the success of the local density approximation (LDA) in the density functional theory (DFT) [Dreizler and Gross 1995; Hohenberg and Kohn 1964; Kohn and Sham 1965].

In the DFT, a many electron system is described by using the electron density $n(\mathbf{r})$, i.e., it is proven that the many electron wave function $\Phi$ and the expectation value of a physical quantity ($\langle A \rangle$) can be written as a functional of $n(\mathbf{r})$, such as $\Phi[n(\mathbf{r})]$ and $A[n(\mathbf{r})]$, respectively. In particular, one can search for the ground state by minimizing the total energy functional $E[n(\mathbf{r})]$ with respect to $n(\mathbf{r})$. In the Kohn-Sham scheme, the total energy functional is formulated by referring to a one-electron system and given as,

$$E[n(\mathbf{r})] = T_\text{op}[n(\mathbf{r})] + \int n(\mathbf{r})v(\mathbf{r})d^3r + \frac{1}{2} \int \int e^{-2n(\mathbf{r}) \cdot n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{xc}}[n(\mathbf{r})].$$

(1)

Here, $T_\text{op}[n(\mathbf{r})]$ is the electrons’ kinetic energy, the second term is the energy of the electrons in an external potential $v(\mathbf{r})$, the third term is the classical Hartree interaction energy and the last term, the exchange-correlation energy. For the exchange-correlation energy, a rigorous expression is not known and an efficient approximation is needed [Dreizler and Gross 1995].

The standard approximation is the LDA within which $E_{\text{xc}}$ is taken as the exchange-correlation energy of homogeneous electron gas [Ceperly and Alder 1980; Dreizler and Gross 1995; Perdew and Wang 1986]. Thus, within the LDA, $E_{\text{xc}}$ is calculated as a function of the local electron density, i.e., $E_{\text{xc}}[n(\mathbf{r})] \sim E_{\text{xc}}(n(\mathbf{r}))$. This approximation sounds inaccurate since the electron density distribution in a real material varies strongly depending on the position $\mathbf{r}$). Furthermore, the computations are carried out for supercells containing typically less than 100 atoms and assuming periodic boundary conditions. Actually, despite these approximations, the LDA, or its spin-polarized version, the local spin density approximation (LSDA), are accurate enough for explaining many physical properties of various materials [Martin 2004]. Recently, LDA, LSDA, and their modifications are used not only for understanding experimental results but also for designing new functional materials.

It is well known that the phase diagrams of a number of alloys exhibit a solubility gap in a certain concentration range. Particularly low is the solubility of TM impurities in semiconductors. An exception here is a large solubility of Mn in II-VI compounds, in which Mn atoms remain distributed randomly over the substitutional cation sites up to concentrations often exceeding 50% [Furdyna and Kossut 1988; Pajaczkowska 1978]. The large solubility of Mn in II-VI compounds can be assigned to the truly divalent character of Mn whose $d$ states little perturb the $sp^3$ tetrahedral $sp$ bonds as both the lower $d^0$ (donor) and the upper $d^6$ (acceptor) Hubbard levels are respectively well below and above the band edges [Dietl 1981; 2002; Zunger 1986].

We describe now two ab initio approaches that have provided quantitative information on the thermodynamic stability of particular DMS alloys $A_{1-x}TM_xB$ as well as input parameters (such as the pairing energy $E_d$ and mixing energy $\Delta E(x)$) for studies of decomposition dynamics by the Monte Carlo simulations and by the Cahn-Hilliard equation, respectively. Within the first method one evaluates a change of the system energy associated with bringing two or more TM ions to neighboring cation positions. If this pairing energy $E_d$ is negative, i.e., there is an attractive chemical force between TM ions, their distribution may not be random. The second approach involves the evaluation of the alloy energy in comparison to weighted energies of the end compounds. A positive value of this mixing energy $\Delta E(x)$ points to the instability of the alloy.

B. Pairing energy

The pairing energy $E_d$ (known also as heat of reaction or pair interaction energy) for a DMS alloy $(A,TM)B$ is evaluated from total energies $E$ corresponding to three different contents of TM cations in the supercell [van Schilfgaarde and Mryasov 2001],

$$E_d = E[(A_{N-2}, TM_2)B_N] + E[A_NB_N] - 2E[(A_{N-1}, TM)B_N].$$

(2)
where \( N \) is the total number of cations in the supercell. The magnitudes of \( E_d \) for TMs at the nearest neighbor cation positions were determined employing various DFT implementations for (Ga,Mn)As (Birowska et al., 2012; Mahadevan et al., 2005; Sato et al., 2005; van Schilfgaarde and Mryasov, 2001); (Ga,V)As, (Ga,Cr)As, and (Ga,Fe)As (Mahadevan et al., 2005); (Ga,Mn)N (Bo-oguslawski and Bernholc, 2006; Chan et al., 2008; Das et al., 2005; Gonzalez Szwacki et al., 2011; Raebiger et al., 2014; Sato et al., 2005) van Schilfgaarde and Mryasov, 2001; (Ga,Cr)N (Cui et al., 2005; Gonzalez Szwacki et al., 2011; Mahadevan et al., 2005; van Schilfgaarde and Mryasov, 2001); (Ga,Fe)N (Gonzalez Szwacki et al., 2011; Navarro-Quezada et al., 2011); (Ge,Mn,Cr,Co) (Continenza et al., 2006a); (Zn,Mn)Te (Kuroda et al., 2007), and (Zn,Cr)Te (Da Silva et al., 2008; Fukushima et al., 2006b) Kuroda et al., 2007; Raebiger et al., 2014.

In the case of the nearest neighbor Mn cations in ZnTe, \( E_d = 21 \text{ meV} \) (Kuroda et al., 2007), the result consistent with a large solubility of Mn in II–VI compounds, as mentioned above. In contrast, \( E_d = -160 \text{ meV} \) for Cr cations in Zn\(_{0.95}\)Cr\(_{0.05}\)Te (Fukushima et al., 2006b), which indicates that Cr cations should aggregate provided that diffusion barriers can be overcome at the growth or annealing temperature. Similarly, the pairing energy of Mn cation dimers was computed to be \( E_d = -120 \text{ meV} \) in GaAs and \( -300 \text{ meV} \) in GaN (van Schilfgaarde and Mryasov, 2001). Being determined by \( p-d \) hybridization, the magnitude of \( |E_d| \) decays quickly with the distance between TM cations, as shown in Fig. 1.

A number of experimentally relevant extensions of this approach has been proposed.

Beyond dimers: The formation of larger TM cation clusters than dimers were considered and their magnetic properties assessed (Cui et al., 2007; Das et al., 2003; Gonzalez Szwacki et al., 2011; Hynninen et al., 2006b; Mahadevan et al., 2005; Navarro-Quezada et al., 2011; van Schilfgaarde and Mryasov, 2001). In this case (van Schilfgaarde and Mryasov, 2001),

\[
E_d(n) = E([A_{N-n}, \text{TM}_n]B_N) + E[A_NB_N] - E([A_{N-n+1}, \text{TM}]B_N) - E([A_{N-1}, \text{TM}]B_N). \tag{3}
\]

This represents the energy change associated with the trapping of one more TM cation by a cluster consisting of \( n-1 \) TM cations. Early studies (van Schilfgaarde and Mryasov, 2001) suggested that \( E_d(n) \sim 0 \) for \( n = 3 \) in the case of (Ga,Mn)As, (Ga,Mn)N, and (Ga,Cr)N, i.e., that decomposition of these alloys into systems containing clusters with three TM cations is favored energetically. This conclusion is not supported by a more recent investigation indicating that \( E_d(n) \) remains strongly negative up to at least \( n = 4 \) (Gonzalez Szwacki et al., 2011), as shown in Fig. 2. This work pointed also out that coupling between pairs of Mn and of Cr ions is FM in wurtzite (wz) GaN, whereas the interaction between Fe ions is AF. These expectations are discussed in comparison to experimental results in Secs. IV and V.

![FIG. 1 Calculated pair interaction energies \( E_d \) as a function of the distance between TM pairs in (a) Ga\(_{1-x}\)Mn\(_x\)As (from Sato et al., 2005) and (b) Zn\(_{1-x}\)Cr\(_x\)Te (from Fukushima et al., 2006b) with various average concentrations \( x \) of TM ions.](image-url)
layer-by-layer epitaxy can result in the growth of TM-rich nanocolumns (Fukushima et al., 2006b). The resulting structure was named the 'konbu phase', where 'konbu' means seaweed in Japanese. The presence of the konbu phase was experimentally demonstrated in the case of (Al,Cr)N (Gu et al., 2005), (Ge,Mn) (Sec. VI), and (Zn,Cr)Te (Sec. VIII). Often, however, the TM-rich regions appear in the form of nano-dots, the case of, e.g., annealed (Ga,Mn)As (see Sec. III). Since the cross section looks then like a marble ('dairiseki' in Japanese), the decomposed state is referred to as the 'dairiseki phase' (Sato et al., 2005). Results of Monte-Carlo simulations designed to show the formation of either konbu or dairiseki phases are presented in Secs. II.C.1 and II.C.2.

Surface aggregation: Since the initial step of the TM aggregation is expected to occur on the epitaxial plane, paring energies of TM impurities residing on surfaces relevant to epitaxial processes were evaluated (Birowska et al., 2012). As presented in Fig. 2, $E_d$ values for Mn and Cr cation dimers on the (0001) wz-GaAs surface become positive ($E_d \approx 170$ meV and 280 meV, respectively), whereas $E_d$ remains negative for Fe pairs ($E_d = -120$ meV), favoring the formation of Fe-rich clusters during the epitaxy (Gonzalez Szwacki et al., 2011).

This explains a much smaller solubility limit of Fe compared to Mn in epitaxial films of wz-GaAs but does not elucidate why it is difficult to grow epitaxially (Ga,Cr)N with a large concentration of randomly distributed Cr ions (see, Secs. IV and V). Furthermore, a question was addressed how the spatial distribution of TM ions in epitaxial films could be affected by non-equivalence of certain crystal directions on the surface. It was found for (Ga,Mn)As deposited onto an unreconstructed surface of (001)GaAs that $E_d$ is by 1 eV smaller for Mn pairs residing along the [110] axis comparing to the [110] case (Birowska et al., 2012). Puzzling uniaxial anisotropies found in (Ga,Mn)As were explained by lowering of crystal symmetry associated with the non-random distribution of Mn dimer orientations, setting in during the epitaxy (Birowska et al., 2012).

Role of co-doping: It was suggested that co-doping of DMSs with shallow donors or acceptors constitutes an efficient method of controlling the TM aggregation (Dietl et al., 2006). This way of affecting the process of nanodecomposition operates if there are band gap states derived from TM $d$ orbitals that can trap carriers supplied by shallow impurities (for compilation of TM-related levels in various hosts see, e.g., Dietl and Ohno, 2003). The corresponding change in the charge state and valency of the magnetic ions modifies chemical and spin-dependent interactions between TM impurities. As an example, the energy of the screened Coulomb repulsion between two elementary charges residing on the nearest neighbor cation sites in the GaAs lattice is 280 meV. Accordingly, a surplus of charge on TM ions brought by co-doping with shallow dopants or by electrically active defects can overweight the gain of energy stemming from $p-d$ hybridization and impede the NC assembling (Boguslawski and Bernholt, 2006; Dietl, 2006; Ye and Freeman, 2006). This intuitive picture was checked by ab initio computations for (Ga,Mn)N (Boguslawski and Bernholt, 2006), (Ga,Fe)N (Navarro-Quezada et al., 2011), (Zn,Cr)Te (Da Silva et al., 2008), and (Ga,Cr)As (Da Silva et al., 2008). As shown in Fig. 3, the value of $E_d$ attains a minimum in ZnTe when the two Cr cations are in the $2^+$ charge state (Da Silva et al., 2008). However, the computation results shown in the same plot indicate that also in GaAs, $E_d$ goes through a minimum for the Cr$^{2+}$ case, rather than for the Cr$^{3+}$ pairs, as might be expected for III-V compounds. Experimental verifications of these ideas have been found for (Ga,Fe)N co-doped with Si (Sec. IV) and for (Zn,Cr)Te co-doped with I and N or deposited under growth conditions allowing to control the concentration of electrically active point defects (Sec. VIII). The effect of co-doping is also discussed theoretically in Sec. II.E exploiting the concept of the mixing energy.

Impurity and defect complexes: Electrically active impurities and defects not only alter the position of the Fermi level and, thus, the TM charge and spin state but can form with TM ions complexes characterized by specific structural and magnetic properties. Prompted by experimental results summarized in Secs. IV and V, farther investigations were performed for various complexes in wz-GaAs, including Mn-Mg$_k$ (Devillers et al., 2012) as well as Fe$_n$-Mg$_k$ and Fe$_n$-Si$_k$ in the bulk and at the surface (Navarro-Quezada et al., 2011). It was also established theoretically that Mn-D cation dimers, where D denotes either P, As, or Sb donor, allow to increase the

![Graph](image-url)
FIG. 3 Computed energy change resulting from bringing two Cr impurities to the nearest neighbor cation positions in ZnTe and GaAs depending on the charge state, i.e., the number of holes in the Cr d⁵ shell. Adapted from Da Silva et al. (2008).

C. Monte Carlo simulation of nanodecomposition

From paring energy considerations given in Sec. II.B, nanodecomposition is expected to occur in a number of DMSs. In order to predict the resulting TM distribution, it is relevant to simulate crystal growth. For this purpose, a hybrid method, combining ab initio and Monte Carlo simulations, was developed (Sato et al., 2005).

Within this method, the alloy is described by an Ising model with the Hamiltonian of the system is written as,

$$H = \frac{1}{2} \sum_{i \neq j} V_{ij} \sigma_i \sigma_j,$$

where $V_{ij}$ is the effective pair interaction energy between two TM cations at sites $i$ and $j$, $\sigma_i$ is the occupation index of the site $i$ by the TM ion, i.e., $\sigma_i = 1$ if site $i$ is occupied by a TM atom while $\sigma_i = 0$ if site $i$ is occupied by a host atom. The effective interaction is calculated as $V_{ij} = V_{AA} + V_{BB} - 2V_{AB}$ for a two component alloy AB, where $V_{AA}$, $V_{BB}$ and $V_{AB}$ are the potential energies for the sites $ij$ occupied by AA, BB, and AB atoms, respectively. The effective pair interactions $V_{ij}$ are evaluated for the medium obtained within the coherent potential approximation (CPA) by using the generalized perturbation method proposed by Ducastelle and Gautier (1976) in the formulation of Turchi et al. (1988).

The calculated effective pair interactions in (Ga,Mn)As and (Zn,Cr)Te have been plotted in Fig. 1 as a function of the pair distance. By definition of $V_{ij}$, a negative $V_{ij}$ indicates effective attractive interactions between the same kind of atoms and repulsive interactions between different kind of atoms. As shown in Fig. 1, pair interactions between magnetic impurities are effectively attractive.

Once the pair interactions in the Ising model are obtained, one can perform the Monte Carlo simulation of the Ising model to obtain the distribution of TM cations in a given semiconductor host at non-zero temperature. The Kawasaki dynamics is used to relax the system (Landau and Binder, 2000). First, a large supercell [typically $14 \times 14 \times 14$ face-centered cubic (fcc) conventional cubic cell] is considered and the magnetic cations are randomly distributed in the cell. Then, one pick up one host-TM pair and their position is exchange. When the change in the energy due to the exchange is negative, this process is allowed. When the energy is positive, it is decided whether this process is allowed or not by using the Metropolis criterion. This Monte Carlo step is repeated many times until the system reaches the thermal equilibrium. In the present study, a non-equilibrium states, namely the system is quenched within a very short time interval which is not sufficient for the complete relaxation of the impurity distribution and then frozen. This situation is simulated by interrupting the iteration after a certain number of Monte Carlo steps (Sato et al., 2005). This procedure assumes that $V_{ij}$ is the only relevant energy scale and, in particular, that there are no kinetic barriers for cation exchange and diffusion over the lattice.

FIG. 4 (Color online) Total energy for Mn₄N, GaMn₃N, and Mn₃N in different magnetic ordering configurations. From Miao et al. (2005).
FIG. 5 (Color online) Mn configuration in (Ga,Mn)N. (a) and (c) refer to completely random configurations, (b) and (d) after 100 Monte Carlo steps (decomposed phase). Mn concentrations are 5% for (a) and (b), and 20% for (c) and (d). Nearest neighbor MnMn pairs are connected by bars. From Sato et al. 2005.

sites. The role of such barriers is discussed in Secs. II.E and II.F.

1. Dairiseki phase

Figure 5 visualizes decomposition in (Ga,Mn)N, as revealed by Monte Carlo simulations. In the studied example, the average concentration of Mn in the simulation cell is 5% or 20% and 100 Monte Carlo steps per Mn site are performed at temperature \(k_B T_b / V_{01} = 0.5\), where \(V_{01}\) is the chemical pair interaction energy between the nearest neighbors. Due to the chemical pair interactions, the Mn atoms attract each other, which results in the formation of clusters. In each cluster, the Mn atoms occupy nearest neighbor sites in order to decrease the energy as much as possible. As seen in Fig. 5(b), the Mn concentration in the cluster is almost 100% and the shape of the cluster is nearly spherical. If the Mn average concentration is low, and the clusters are separated. For higher concentrations, average size of clusters becomes larger and at 20% the clusters are connected and percolate through the cell [Fig. 5(d)]. Since the cross section of the decomposed system looks like a marble, the decomposed state of magnetically doped semiconductors was named the ‘dairiseki phase’ (Sato et al. 2005), where ‘dairiseki’ means marble in Japanese.

As shown in the previous studies on ferromagnetism in DMSs with short range spin-spin interactions, at low concentrations \(T_C\) is suppressed (Sato et al. 2010, Stefanowicz et al. 2013). For example, below the percolation threshold (20% for the fcc structure (Stauffer and Aharony 1994)) \(T_C\) is 0 for systems with interactions only between the nearest neighbors. As shown in Fig. 5(d), owing to decomposition there are many percolating paths already at 20% and the decomposition should affect considerably the magnetic properties of the system. In order to see effects of decomposition, \(T_C\) values were calculated as a function of the Monte Carlo steps (Fukushima et al. 2006a). In order to include in the \(T_C\) calculations the distribution of magnetic impurities, the random phase approximation (RPA) proposed by Bouzerar et al. 2005 and Hilbert and Nolting 2004 was employed (Fukushima et al. 2006a). It is known that this method correctly reproduces the magnetic percolation effects and predicts reasonable \(T_C\) magnitudes, close to the exact Monte Carlo values. Figure 6 shows the calculated \(T_C\) of (Zn,Cr)Te within the RPA as a function of MC steps.

As shown in Fig. 6, at low concentrations the decomposition works to lower \(T_C\) values. Due to decomposition many spatially isolated clusters are formed, as shown in Fig. 5(b). Since the exchange interactions between TM atoms are short range in this case, there is strong FM coupling between TM moments in the cluster, but FM correlations between clusters are weak. This is why \(T_C\) of the whole system is suppressed by decomposition. In the case of (Zn,Cr)Te after 100 MC steps, non-zero values of \(T_C\) is predicted, and the system is FM. However when the exchange interactions are more short range, the system becomes superparamagnetic after the decomposition. For higher concentrations, because of the increase of the number of the nearest neighbor pairs, \(T_C\) increases as the decomposition proceeds. The increase of \(T_C\) is observed already at 15%, which is below the percolation threshold, thus it is found that the decomposition lowers the magnetic percolation threshold effectively.

FIG. 6 Calculated Curie temperature of (Zn,Cr)Te as a function of Monte Carlo steps in the simulation of decomposition. Curie temperatures are calculated by using the random phase approximation. From Fukushima et al. 2006a.
2. Konbu phase

In addition to growth temperature and TM concentration, one can control the dimensionality of the growth process. In the simulations presented in the previous subsection (Sec. II.C.1), the magnetic impurities can diffuse in any direction, therefore TM aggregation occurs in three dimensions. In actual experiments, molecular beam epitaxy (MBE) or metalorganic vapor phase epitaxy (MOVPE) are standard methods for crystal growth. On a surface with low coverage, the migration of atoms on the surface occurs relatively freely, but it is difficult to diffuse into the layers beneath, i.e., the diffusion is limited only to the uppermost layer. Thus under such crystal growth conditions, the dimensionality of the decomposition is automatically controlled. Since the decomposition occurs layer-by-layer and the exchange of atoms between layers is prohibited under this condition, one can expect anisotropic shape for the clusters formed by the decomposition. On the first layer, small clusters are formed due to the decomposition, then the impurity atoms deposited on the second layer gather around the nuclei in the first layer. This process is repeated for many times and finally clusters with elongated shape along the crystal growth direction are produced [Fukushima et al. 2006b].

In Fig. 7 results of Monte Carlo simulations are shown for the layer-by-layer growth of (Zn,Cr)Te with the average Cr concentration of 5%. The growth direction is from the bottom to the top of the cube. As expected, the Cr cations form clusters with columnar shape. This state was named the ‘konbu phase’ [Fukushima et al. 2006b], where ‘konbu’ means seaweed in Japanese. Apparently the size of the clusters is much larger than the clusters found in the dairiseki phase. In the konbu phase, the clusters are spatially well separated. The $T_C$ value of each cluster is expected as high as the one of CrTe in a zinc-blende (zb) structure, presumably close to RT. The $T_C$ magnitude of the konbu phase shown in Fig. 7(a) by using the RPA method is only 15 K. This low value is due to the absence of magnetic interactions between separated columnar structures. However, once the magnetic percolation paths are introduced between the structures, $T_C$ should increase considerably. To visualize this effect, delta doping of Cr for the first and the last layers was assumed in the simulations [Fig. 7(b)], leading to $T_C$ of 346 K [Fukushima et al. 2006b]. In reality, magnetization blocking phenomena brought about by magnetic anisotropy (see Sec. IIC.2) and long-range dipole interactions between clusters’ magnetizations and can lead to a large magnitude of apparent $T_C$.

D. Super-paramagnetic blocking phenomena

If we only focus on a thermodynamic quantity such as a $T_C$ value, there is not much difference between the dairiseki phase and the konbu phase for low average TM concentrations. For both phases as a result of decomposition, $T_C$ goes to 0 and the system becomes superparamagnetic, if the interactions are short range. On the other hand, if we look into the magnetization process, the dairiseki phase and the konbu phase behave very differently due to superparamagnetic blocking phenomena associated with shape anisotropy.

To reverse the magnetization direction of nanomagnets with in a single magnetic domain state, magnetic anisotropy energy should be overcome. For a system with uniaxial magnetic anisotropy, the magnetic anisotropy energy is $KV\sin^2\theta$, where $K$, $V$ and $\theta$ are anisotropy energy density, volume of the system, and angle between magnetization direction and magnetic easy axis, respectively. In general, shape and crystalline anisotropies contribute to the magnitude of $K$. The existence of the energy barrier between the easy directions results in a finite relaxation rate of the magnetization direction, $1/\tau \propto \exp(-KV/k_BT)$. Accordingly, for larger systems (but small enough to keep single domain nature), the relaxation time $\tau$ becomes longer and the magnetization direction is effectively fixed along the initial direction at low temperatures. This is the so-called superparamagnetic blocking phenomenon [Aharoni 1996].

In the present cases of decomposed systems, the columnar structure contains high concentration of magnetic impurities. Due to the FM exchange interactions between magnetic impurities, the self-assembled structure with a high TM concentration behaves as a nanomagnet. The radius of the columnar structure is a few nanometers and within this length scale, we can expect that the structure contains a single magnetic domain.

As shown in the previous subsections (Secs. II.C.1 and II.C.2), it is possible to control the volume of the clusters formed by decomposition and, hence, sample magnetization via the superparamagnetic blocking phenomenon. In order to demonstrate this idea, the magnetization process was simulated by the Monte Carlo technique [Sato and Katayama-Yoshida 2007] employing the method elabo-
the external magnetic field. Above the blocking temperature, the direction of the magnetization flips and the system becomes higher for the dairiseki phase, and the konbu phases.

In order to determine the temperature and TM concentration range corresponding to nanodecomposition, a lattice model, originally developed by Flory and Huggins for the polymer-mixing problem (Flory, 1941; Huggins, 1942; Rubinstein and Colby, 2003), was adapted for DMSs (Chan et al., 2008; Hai et al., 2011; Sato et al., 2007). Within this approach, the free energy $F(x) = E(x) - TS(x)$ of a random alloy $A_{1-x}TM_xB$ is described by the mixing energy $E(x)$ and the entropy $S(x)$ per one cation of the form

$$\Delta E(x) = E(A_{1-x}TM_xB) - (1-x)E(AB) - xE(TM)B;$$

$$S(x) = -k_B[x \ln x + (1-x) \ln(1-x)].$$

If $\Delta E(x) > 0$, the alloy is unstable against decomposition into the end compounds but at $T > 0$ a tendency to randomization described by the entropy term becomes important. Figure 8 shows schematically the behavior of $F(x)$ for a convex function $\Delta E(x) > 0$ and $T > 0$. It is seen that for such a case $F(x)$ there are two points $B_1$ and $B_2$ at compositions $x_1$ and $x_2$, between which $F(x) > F(x_1) + F(x_2)$. Hence, for $x_1 < x < x_2$ the thermal equilibrium state corresponds to the binodal decomposition, i.e., in the case of DMSs, to the nucleation of TM-rich NCs of content $x_2$ in the TM-poor matrix of the concentration $x_1$. The region $x_1 < x < x_2$ corresponds to the miscibility gap at given temperature $T$.

Often, however, the alloy in some range between $x_1$ and $x_2$ is stable against small fluctuations $\pm \Delta x$ of local composition. Since changes in the local free energy density integrated over the volume encompassing many fluctuations is proportional to $(\Delta x)^2 \partial^2 F / \partial x^2$, the alloy can remain in a metastable state as long as $\partial^2 F / \partial x^2 > 0$, i.e., in the composition range, in which $F(x)$ is a concave function. In contrast, in the region between the points $S_1$ and $S_2$ in Fig. 8, where $\partial^2 F / \partial x^2 < 0$, there is no thermodynamic barrier separating the homogenous and non-uniform alloy.

The resulting spontaneous up-hill diffusion process, called spinodal decomposition, leads to a system that is structurally homogenous but shows a modulation of the

![FIG. 8](Color online) Superparamagnetic blocking phenomenon in (Ga,Mn)N according to Monte Carlo simulations. Left-hand panels: Magnetization as function of temperature starting from parallel or antiparallel configurations of initial magnetization to the external field. Right-hand panels: Magnetization as a function of external field. The simulations are performed for the uniform Mn distribution (a) and (d), the dairiseki phase (b) and (e), and the konbu phase (c) and (f). The insets in the lower panels show snapshots of the Mn distribution in (Ga,Mn)N for the respective phases. Temperature $k_B T$ and the external magnetic field are scaled by the strength of the nearest-neighbor exchange energy $J_{01}$. From Sato et al., 2007.
TM concentration. This mechanism of chemical phase separation is suitable for fabricating a NC system with rather uniform NC size and inter-NC distance (Jones 2002). An ordering in NC positions can be enhanced further on by strain, similarly to the case of self-assembling quantum dots in semiconductors (Stangl et al. 2004). As discussed in Secs. [III] and [VI] a periodic-like arrangement of TM-rich NCs has been found in Mn-doped GaAs and Mn-doped Ge, respectively.

The CPA approach (Sato et al. 2007) and a cluster expansion method (Chan et al. 2008) were employed to evaluate from first principles the energy $E(A_{1-x}TM_xB)$ and, thus, the mixing energy $\Delta E(x)$ of DMSs containing randomly distributed substitutional TM cations. The CPA is particularly suitable for electronic structure calculations in the case of substitutional alloys (Akai 1989; Akai and Dederichs 1993; Shiba 1971), such as DMSs. It is most efficiently combined with the Korringa-Kohn-Rostoker (KKR) method for the band structure calculation, particularly employing the MACHIKANEYAMA package (Sato et al. 2010) developed by Akai (Akai 2002). Within the CPA, a configuration average of the alloy electronic structure is calculated by using a mean-field like procedure. In a first step one considers a hypothetical atom that describes the averaged system. The crystal of hypothetical atoms constitutes an effective CPA medium. By using the multiple scattering theory the scattering path operator of the host and of the impurity atoms in the CPA medium is determined. The weighted average of these scattering path operators with respect to the concentration should be equal to the scattering path operator of the hypothetical atom itself. This is the self-consistent equation to be solved by an iterative method for determining the CPA medium, providing electronic density of states and the total energy $E$ of the system. A more detailed explanation and practical formulation is provided by Gonis 2000.

The CPA method was employed to evaluate $\Delta E(x)$ for $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$, $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, $\text{Ga}_{1-x}\text{Cr}_x\text{N}$, and $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ assuming zb structure and the experimental values of the lattice constants (Sato et al. 2007). The convex form of $\Delta E(x)$ demonstrated that spinodal decomposition can appear in these systems. A similar conclusion was derived from cluster expansion studies of zb-$\text{Ga}_{1-x}\text{Mn}_x\text{N}$ (Chan et al. 2008). Figure 10 shows, as an example, $F(x)$ for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ at various temperatures (Sato et al. 2007), which allows to determine the spinodal line, i.e., the position of $S_1$ and $S_2$ points as a function of temperature. Such a spinodal line is presented in Fig. 11 for in zb-$\text{Ga}_{1-x}\text{Mn}_x\text{N}$ (Chan et al. 2008). It is seen that the upper critical solution temperature, above which the alloy is miscible for any $x$, is as high as 3 000 K in this case. Hence, within the temperature range relevant for epitaxial growth and post-growth annealing, the DMSs in question can undergo spinodal decomposition.

According to Figs. [9][11] the range of compositions, at which alloy decomposition could appear, diminishes with increasing temperature. This is in qualitative disagreement with the long staying experimental observations which imply that lowering of epitaxy temperature is necessary for obtaining a uniform DMS (Munekata et al. 1989), whereas annealing at high temperatures allows to generate phase separation (Boeck et al. 1996). This apparent contradiction, i.e., the existence of lower critical solution temperature, points to the importance of diffusion (kinetic) barriers precluding aggregation of TM cations if growth or annealing temperature is too low even if there is no thermodynamic barrier for spinodal decomposition. To our knowledge, in the case of DMSs, only the barrier height for diffusion of interstitial Mn and Li ions in GaAs has so far been evaluated theoretically (Bergqvist et al. 2010; Edmonds et al. 2004). At

FIG. 9 Typical dependence of DMS free energy $F$ on TM concentration $x$. Binodal decomposition can occur between points $B_1$ and $B_2$, the ends of the common tangent segment of $F(x)$ (dashed line). Spinodal decomposition occurs between points $S_1$ and $S_2$ corresponding to $\partial^2 F/\partial x^2 = 0$. From [Hai et al. 2011].

FIG. 10 Computed free energy $F(x)$ for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ at various temperatures. As shown schematically in Fig. 9 this plot allows to determine composition ranges corresponding to binodal and spinodal decompositions at particular temperatures. From [Sato et al. 2007].

\[ \text{Ga}_{1-x}\text{Mn}_x\text{As} \]
FIG. 11 Computed spinodal line for zinc-blende Ga$_{1-x}$Mn$_x$N. In the range of compositions $x$ between the lines at a given temperature $T$ the alloy can undergo spinodal decomposition, so that at, e.g., 1000 K Ga$_{1-x}$Mn$_x$N decomposes into compounds with $x = 0.03$ and 0.45. From Chan et al. 2008.

The same time, a phenomenological Cahn-Hilliard theory of spinodal decomposition, presented in Sec. II.F, was employed to describe properties of phase separation in DMSs (Hai et al. 2011). The influence of growth and processing conditions on nanodecomposition is discussed from the experimental perspective in Secs. III–VIII.

Another important ingredient that has not been taken into account by the approaches leading to the results presented in Figs. 10 and 11 is the omission of interfacial energies. In particular, the comparison of free energies corresponding to the random alloy and the decomposed case has referred to the thermodynamic limit, i.e., energies of TM ions at interfaces between TM-rich and TM-poor phases have been disregarded. In general, energy lowering associated with the TM aggregation is smaller for interfacial ions comparing to the ions inside the cluster. This promotes the Oswald ripening, i.e., the formation of larger clusters at the expense of smaller ones. In extreme cases, small clusters, up to the so-call nucleation radius, are energetically unstable, which imposes a barrier for the nucleation process. Such a barrier can be lowered at crystal defects acting as nucleation centers or diffusion channels. According to the discussion of the pairing energies in Sec. II.B, even small clusters of TM cations are stable in a number of semiconductor compounds.

As already mentioned in Sec. II.B, according to ab initio studies, co-doping of DMSs by electrically active impurities or defects affects considerably the TM pairing energies. This conclusion is supported by studies of the mixing energy $\Delta E(x)$ of (Ga,Mn)As (Bergqvist et al. 2010), (Ga,Mn)N, (Ga,Mn)Cr, and (Zn,Cr)Te (Sato and Katayama-Yoshida 2007) co-doped with donors. In particular, the mixing energies of (Ga,Mn)As with interstitial impurities acting as donors, such as Li (Li$_{\text{int}}$) and Mg (Mg$_{\text{int}}$), were computed (Bergqvist et al. 2010). As shown in Fig. 12 the effect of co-doping is dramatic and the the mixing energy is significantly modified. Particularly at low concentrations of Mn, a negative and concave region is found in the calculated values of $\Delta E(x)$. This means that even at thermal equilibrium homogeneous doping of Mn is possible over a wide $x$ range. Similar effects were also found for other combinations of the host semiconductors and different substitutional donor impurities (Sato and Katayama-Yoshida 2007).

The advantage of interstitial impurities (particularly Li$_{\text{int}}$) over the substitutional ones is that interstitials can easily be removed by post-growth annealing. To check the effectiveness of this process, Monte Carlo simulations of diffusion of interstitial impurities in (Ga,Mn)As were performed (Bergqvist et al. 2010). The results imply that since the binding energy between Mn$_{\text{int}}$ and Mn$_{\text{Ga}}$ is much greater than in the case of Li$_{\text{int}}$, the low temperature annealing more effectively wipes away Li$_{\text{int}}$ than Mn$_{\text{int}}$ in (Ga,Mn)As.

F. Cahn-Hilliard theory of spinodal decomposition

One of the goal of decomposition theory is to describe spatial and temporal evolution of the local composition $x(\vec{r},t)$ at a surface or in a volume of the alloy containing initially randomly distributed TM cations of the concentration $\bar{x}$. While it is rather difficult to determine $x(\vec{r},t)$
in the nucleation regime, there exists a time-honored Cahn and Hilliard [1958] theory of spinodal decomposition, discussed also in the context of phase separation in DMSs (Hai et al., 2011). This approach exploits the Ginzburg-Landau theory of the continuous phase transitions, taking \( u(\vec{r}, t) = x(\vec{r}, t) - \bar{x} \) as an order parameter. Furthermore, the interfacial effects are included to the lowest order in the gradient in the TM concentration \( x(\vec{r}) \). Under these assumptions the functional of the free energy assumes the form,

\[
F_{\text{tot}}[u(\vec{r})] = N_0 \int d\vec{r} F[u(\vec{r})] + \frac{1}{2} \kappa |\nabla u(\vec{r})|^2. \tag{7}
\]

where \( N_0 \) is the cation density and \( F(x) \), in addition to the contributions given in Eqs. 5 and 6 can contain a term \( ku^2(\vec{r}, t)/2 \) describing an increase of the system energy associated with strain that builds in a decomposed system if the lattice constant depends on \( x \). Along with the mixing energy \( \Delta E(x) \), \( \kappa \) and \( k \) are parameters of the model, which in principle can be determined experimentally or by ab initio methods.

The distribution \( u(\vec{r}) \) under conditions of thermal equilibrium is provided by the variational minimization of \( F_{\text{tot}}[u(\vec{r})] \), \( \delta F_{\text{tot}}[u(\vec{r})]/\delta u(\vec{r}) \) at 0 with the constraint, imposed by the mass conservation, that \( u(\vec{r}) \) integrated over the relevant crystal surface or volume vanishes. This procedure implies that (i) the decomposition occurs at temperatures below the critical temperature \( T_c \), where \( \partial^2 F(u, T)/\partial u^2 \biggr|_0 < 0 \); (ii) the compositions of TM-rich NCs and TM-poor matrix are determined from \( \partial F(u) - u(\partial F/\partial u) \biggr|_0 / \partial u = 0 \) and (iii) the spatial width of the transition region between these two domains scales with \( \kappa^{1/2} \).

However, from the experimental viewpoint particularly relevant is the evaluation of \( u(\vec{r}, t) \) during the early stage of decomposition, i.e., far from thermal equilibrium. The starting point is the continuity equation,

\[
\partial N_0 u(\vec{r}, t)/\partial t = -\nabla \cdot \vec{j}(\vec{r}, t), \tag{8}
\]

where the current of TM cations \( \vec{j}(\vec{r}, t) \) is driven by the gradient in the chemical potentials \( \mu \),

\[
\vec{j}(\vec{r}, t) = M \nabla \mu(\vec{r}, t). \tag{9}
\]

Here, \( M \) is the TM mobility, one more material parameter. Since the chemical potential corresponds to a change of the free energy by adding or removing one atom, its local non-equilibrium value is given by a variational derivative,

\[
\mu(\vec{r}, t) = -\delta F_{\text{tot}}[u(\vec{r}, t)]/\delta u(\vec{r}, t), \tag{10}
\]

with the constrain \( \int d\vec{r} u(\vec{r}, t) = 0 \). This variational derivative and, thus, the chemical potential is not zero as \( u(\vec{r}, t) \) does not yet correspond to the thermal equilibrium distribution. Inserting Eq. 10 into Eq. 9 and then Eq. 9 into 8, one obtains the Cahn-Hilliard equation in the form

\[
\partial u(\vec{r}, t)/\partial t = M \nabla^2 \partial [F(u) - u(\partial F/\partial u) \biggr|_0] / \partial u - \kappa \nabla^2 u. \tag{11}
\]

There is a comprehensive literature devoted to mathematical aspects of this differential equation [see, e.g., Novick-Cohen, 2008]. It is convenient to write its solution \( u(\vec{r}, t) \) as a Fourier transform of a function \( A(\vec{q}, t) \). If only the two lowest order terms are retained in the Taylor expansion of \( F(u) \), a justified approximation at the early stage of decomposition, then

\[
A(\vec{q}, t) = A_0(\vec{q}) \exp[R(\vec{q})t], \tag{12}
\]

where the aggregation rate

\[
R(q) = -M[\partial^2 F(u)/\partial u^2]_0 + \kappa q^2 \biggr|_{q}. \tag{13}
\]

This formula shows that \( R \) is positive, at least for sufficiently small \( q \) values, in the spinodal decomposition range, \( \partial^2 F(u)/\partial u^2 \biggr|_0 < 0 \). In such a case, \( R \) is governed by the cation mobility \( M \) which, because of diffusion barriers, decreases strongly on lowering temperature. This explains why low-temperature epitaxy can result in a metastable state corresponding to a DMS with a uniform distribution of magnetic ions. However, growth or annealing at appropriately high temperatures, or the presence of lattice defects, can enhance \( M \) and promote TM aggregation.

Because of the interfacial energy, on approaching thermal equilibrium conditions, the size of TM-rich NCs should increase whereas their concentration decrease. However, the formation of a periodic structure by spinodal decomposition at early times may render the Oswald ripening a prohibitively slow process, particularly in DMSs with \( x \ll 1/2 \). In contrast, both NCs and the surrounding matrix can attain uniform TM concentrations, \( x_2 \) and \( x_1 \), respectively, corresponding to the binodal points, \( B_2 \) and \( B_1 \) in Fig. 9 or even a transformation of TM-rich NCs to another crystallographic phase can take place. In either case, by determining \( q_c \) that maximizes \( R(q) \) one can evaluate the expected distance \( \lambda_c = 2\pi/q_c \) between TM-rich NCs,

\[
\lambda_c = 4\pi [\kappa/2\partial^2 F(u)/\partial u^2]\biggr|_0^{1/2}, \tag{14}
\]

where \( \kappa \), representing the interfacial energy, is of the order of \( |E_d|/a^2 \) and \( a \) is the lattice parameter. Since the magnitudes of pairing energy \( E_d \) and \( \partial^2 F(u)/\partial u^2 \biggr|_0 \) are similar (cf. Figs. 1 and 10), the distance between TM-rich NCs is expected to set at about 10 lattice constants, the value in reasonable agreement with experimental results collected in Secs. IV-VI. Simple geometrical considerations provide an average radius of NCs at given \( x \), \( x_1 \), and \( x_2 \), and \( \lambda_c \).

Another interesting aspect is the dependence of \( R(\vec{q}) \) on the crystallographic direction of \( \vec{q} \) brought about by the elastic term \( 1/2ku^2 \) in \( F(u) \) (Hai et al., 2011). According to theory developed for cubic crystals (Cahn, 1962), if elastic moduli fulfill the relation \( 2C_{44} - C_{11} + C_{12} > 0 \),
the spinodal decomposition is predicted to proceed along ⟨100⟩ cubic directions. This inequality is obeyed in zb compounds of interest, GaAs, Ge, and ZnTe. Similarly to the case of self-assembling semiconductor quantum dots obtained in the Stranski-Krastanov heteroepitaxy regime (Stangl et al. 2004), strain minimization can govern the NC arrangement.

Typically, the TM concentration of the host containing TM-rich NCs is non-zero, \( x_1 > 0 \). Accordingly, the magnetic response of decomposed alloy shows characteristics of the uniform DMS with TM content \( x_1 \) superimposed on magnetism of a system of NCs with the TM concentration \( x_2 \). Since the crystallographic and chemical structure of the NCs is usually imposed by the host, magnetic properties of the individual NCs may not be listed in the existing materials compendia. Furthermore, magnetism of the NC ensemble is strongly affected by their distribution and coupling, either dipole-dipole type or mediated by strain and/or spins in the host.

III. SPINODAL NANODECOMPOSITION IN (Ga,Mn)As

It is well known that (Ga,Mn)As containing uniformly distributed magnetic atoms has become a model system for the entire class of dilute FM semiconductors (Dietl and Ohno 2014; Jungwirth et al. 2014; Tanaka et al. 2014). Similarly, the decomposed (Ga,Mn)As system, consisting of MnAs or Mn-rich (Mn,Ga)As NCs embedded in Mn-poor (Ga,Mn)As, since its first fabrication (Boeck et al. 1996; Shi et al. 1996), has revealed properties relevant to the whole family of high Tc semiconductors. For instance, both crystallographic (Boeck et al. 1996) and chemical (Moreno et al. 2002) phase separations were put into the evidence, depending on fabrication and processing conditions. Furthermore, despite a small diameter down to 2 nm, the ensemble of zb Mn-rich NCs shows FM-like features persisting up to 360 K (Moreno et al. 2002), to be compared to \( T_C \) of 318 K specific to free standing samples of MnAs that crystallizes in a hexagonal NiAs-type structure. Enhanced magneto-optical response was found in decomposed films of (Ga,Mn)As (Akinaga et al. 2000a; Shimizu et al. 2000).

A. Fabrication methods and nanocomposite structure

Various methods were found to provide decomposed (Ga,Mn)As. It can be obtained by MOVPE (Krug von Nidda et al. 2006; Lampalzer et al. 2004) or MBE at sufficiently high substrate temperatures (Hai et al. 2011) or by post-growth annealing of either GaAs implanted with Mn (Ando et al. 1998; Chen et al. 2000; Shi et al. 1996; Wellmann et al. 1997) or fabricated by low-temperature (LT) MBE (Boeck et al. 1996; DiPietro et al. 2010; Kwiatkowski et al. 2007; Moreno et al. 2002; Rench et al. 2011; Sadowski et al. 2011; Shimizu et al. 2001; Yokoyama et al. 2005).

At the growth temperature specific to MOVPE, 500–600°C, one observes assembling of hexagonal MnAs NCs and their segregation towards the layer surface (Krug von Nidda et al. 2006). They have typically elongated shape in the growth direction and their length reaches 100 nm.

According to the MBE growth diagram of Ga\(_{1-x}\)Mn\(_x\)As (Dietl and Ohno 2014; Hayashi et al. 1997; Matsuura et al. 2002; Ohno et al. 1996), at temperatures above 350°C at \( x = 1 \% \) and above 200°C at \( x = 10 \% \) an onset of TM aggregation is observed. Growth temperatures below 200°C are required for maintaining 2D growth of (Ga,Mn)As incorporating more than 10% of uniformly distributed Mn cations (Chiba et al. 2007; Mack et al. 2008; Ohya et al. 2007; Wang et al. 2008). Results of detailed investigation by reflection high-energy electron diffraction (RHEED) of temperature \( T_B(x) \) at which 2D growth disappears entirely, i.e., RHEED stripes transform into dots, are shown in Fig. 13 (Hai et al. 2011). As seen, \( T_B(x) \) decreases monotonously with \( x \) reaching 270°C for \( x = 6.7 \% \) at which \( T_B \) abruptly rises to 320°C, the effect accompanied by a step-like increase in the in-plane lattice constant. For \( x > 6.7 \% \) a gradual decrease of \( T_B \) continues down to about 300°C at \( x = 0.15 \% \). This behavior, may indicate that zb-MnAs or Mn-rich (Mn,Ga)As NCs prevail for \( x < 6.7 \% \), whereas at higher \( x \) hexagonal MnAs NCs nucleate at \( T \) \( \geq T_B \) on the growth surface.

High annealing temperatures, typically 500–700°C, are required to promote (Ga,Mn)As decomposition in films grown by low-temperature MBE (Boeck et al. 1996; DiPietro et al. 2010; Kwiatkowski et al. 2007; Moreno et al. 2002; Rench et al. 2011; Sadowski et al. 2011; Shimizu et al. 2001; Yokoyama et al. 2005), although at onset of Mn aggregation was already noted in films annealed at 400°C (Sadowski et al. 2011). Similar or higher temperatures were employed to fabricate decomposed
(Ga,Mn)As out of Mn-implanted GaAs (Ando et al., 1998; Chen et al., 2000; Shi et al., 1996; Wellmann et al., 1997). These temperatures, significantly surpassing $T_B$, of Fig. 13, collaborate the fact that aggregation of Mn cations is kinetic-limited (see, Sec. II.F), as at given temperature atom diffusion is slower in the bulk than on the growth surface.

Depending on the magnitudes of the initial Mn concentration and annealing temperature, either hexagonal MnAs NCs with an NiAs structure and diameter ranging from 5 nm to 500 nm precipitate usually with no dislocations and with orientation MnAs(0001) || GaAs(111)B (crystallographic phase separation) (Ando et al., 1998; Boeck et al., 1996; Chen et al., 2000; Krug von Nidda et al., 2006; Moreno et al., 2002; Rench et al., 2011; Shi et al., 1996; Wellmann et al., 1997; Yokoyama et al., 2005) or zb Mn-rich (Ga,Mn)As NCs aggregate (chemical phase separation) (Kwiatkowski et al., 2007; Moreno et al., 2002; Yokoyama et al., 2005), according to high-resolution transmission electron microscopy (HRTEM), as shown in Fig. 14. A comprehensive x-ray diffraction (XRD) (Moreno et al., 2003; 2005) and extended x-ray absorption fine structure (EXAFS) studies (Demchenko et al., 2007) of hexagonal MnAs buried in the GaAs lattice provided detailed information on the magnitude of strain in reference to free-standing MnAs. The zb NCs can assume either tetrahedral (Moreno et al., 2002) or spherical form (Kwiatkowski et al., 2007; Sadowski et al., 2011; Yokoyama et al., 2005) with diameter typically from 2 to 6 nm; they are not stable against a transformation to the hexagonal phase for diameters exceeding 15 nm (Sadowski et al., 2011). Hexagonal and cubic zb NCs coexist in annealed (Ga,Mn)As with Mn content of 2% and smaller (Sadowski et al., 2011). It appears that main features of decomposed (Ga,Mn)As and (Ga,Mn)As:Be (Rench et al., 2011) are similar.

The exact relative concentrations of Mn and Ga in the cubic NCs is barely known and may depend on details of the fabrication protocols; the Mn concentration as low as 20% was suggested (Lawniczak-Jablonska et al., 2011). Under some processing conditions the obtained nanoparticles were found to be structurally disordered (Kwiatkowski et al., 2007; Moreno et al., 2002). In certain cases, presumably if growth of (Ga,Mn)As results in a substantial concentration of As antisites, hexagonal MnAs NCs obtained by annealing are accompanied by As precipitation and voids (Kovács et al., 2011).

From application viewpoint particularly relevant is the preparation of magnetically active NCs that reside in a pre-define plane. This can be achieved by growing appropriately thin (Ga,Mn)As layers, in which Mn-rich NCs gather after annealing below 600°C (Sadowski et al., 2013; Shimizu et al., 2001), as shown in Fig. 15.

Furthermore, according to results presented in Fig. 16, rectangular-like distribution of MnAs NCs with a narrow dispersion of diameters was obtained by using the phase decomposition diagram of the (Ga,Mn)As alloy and spinodal decomposition induced by annealing.

More recently, the influence of laser irradiation on the self-assembly of MnAs NCs was investigated (Hai et al., 2012). It was found that laser irradiation suppresses the temperature-induced transformation of small zb NCs into larger hexagonal MnAs NCs, and that the median diameter $D_1$ in the size distribution of small NCs depends on the incident photon energy $h\omega$ following $D_1 \sim \omega^{-1/5}$. This behavior was explained by the desorption of Mn atoms from small NCs due to energy gain from optical transitions between their quantized energy levels.
FIG. 16 (Color online) Periodic arrangement of MnAs NCs in GaAs. (a) Plain-view TEM image of hexagonal MnAs NCs fabricated using spinodal decomposition of a 5 nm-thick Ga$_{0.8}$Mn$_{0.2}$As layer. (b) Fourier transform of the contrast of a 0.36 × 0.36 µm$^2$ TEM image. A ring structure with a radius of 0.063 nm$^{-1}$ corresponding to a period of 16 nm is observed. The inset shows the pattern of the ring structure after applying a step-like high pass filter, revealing four fold symmetry, that is, rectangular lattice structure. Adapted from Hai et al., 2011.

B. Magnetic properties

Figures 17(a,b) show magnetization loops at various temperatures for (Ga,Mn)As samples with hexagonal and cubic NCs, whose micrographs have been displayed in Figs. 14(a,b), respectively. As seen in 17(a), square hystereses pointing to the $T_C$ value specific to bulk MnAs, $T_C \simeq 318$ K are observed for the film with hexagonal NCs (Moreno et al., 2002), the finding reported also by others (Ando et al., 1998; Rench et al., 2011; Wellmann et al., 1997; Yokoyama et al., 2005). The data indicate that superparamagnetic blocking temperature $T_b$ exceeds $T_C$, the conclusion consistent with an expected magnitude of the NC anisotropy energy, $E_a = VK$, for the large NCs in question.

In contrast, the behavior of magnetization in the case of the sample with cubic NCs [Fig. 17(b)] is intriguing and reveals surprising but generic aspects of decomposed magnetically doped systems:

- Despite a rather small size of zb NCs, even at high temperatures magnetization loops are opened and weakly temperature dependent. This indicates that $M(H,T)$ cannot be modeled by the Langevin function describing superparamagnetic systems above $T_b$, the conclusion emerging also from other studies of decomposed (Ga,Mn)As (Sadowski et al., 2011; Yokoyama et al., 2005). Given the NC volume $V$, this FM-like behavior points to a rather large magnitude of $K$ or to a significant role played by spin-dependent interactions between the NCs (Hai et al., 2007). For specific spatial distributions and densities of FM nanoparticles, long-range dipole interactions and/or exchange coupling lead to the so-called superferromagnetic phase (Bolei et al., 2012; Morup et al., 2010; Panov, 2012), whose characteristics are consistent with the data displayed in Fig. 17(b). In particular, a smaller magnitude of low temperature magnetization, as compared to the value expected from spin counting, is consistent with the superferromagnetic scenario.

- This set of data points to $T_C \gtrsim 360$ K, for zb Mn-rich (Mn,Ga)As stabilized by the GaAs host (Moreno et al., 2002; Sadowski et al., 2011; Yokoyama et al., 2005), the value substantially higher than $T_C \simeq 318$ K of free standing MnAs that crystallizes in the hexagonal structure. This $T_C$ enhancement can be assigned to higher crystal symmetry, which typically leads to greater density of states at the Fermi level and, hence, to elevated $T_C$.

- While decomposed films discussed above show superferromagnetic features, in some other samples, containing similar NCs according to TEM studies, a standard superparamagnetic behavior was found (DiPietro et al., 2010; Rench et al., 2011; Sadowski et al., 2011). Differing properties of nominally similar samples imply that magnetic characteristics of decomposed systems are rather sensitive to pertinent details of the system fabrication and the resulting morphology, including:
  - the chemical structure and composition of...
the individual NCs (i.e., TM concentration), which determine the electronic structure (e.g., the itinerant vs. localized character of d electrons) and, thus, magnetic characteristics such as the magnitude of $T_C$, magnetic moment, and energy of bulk and interfacial magnetic anisotropy

- the spatial distribution and density of the NCs’ ensemble, which underlines the magnetic ground state originating from long-range dipole interactions
- the nature of host-mediated spin coupling among the NCs, which can depend on strain and interface between NCs and the host as well as on the TM, carrier, and defect concentrations in the host.

- Si co-doping enhances the formation of bigger MnAs nanoclusters (Shimizu and Tanaka, 2002b).

In the case of superparamagnetic samples, the temperature dependence of zero-field cooled magnetization demonstrates that the distribution of NCs’ size is log-normal (DiPietro et al., 2010; Rench et al., 2011). At the same time, characteristics of magnetization relaxation are consistent with the superparamagnetic scenario and allow excluding spin-glass freezing as an origin of the magnetization maximum as a function of temperature (Sadkowski et al., 2011).

In general, magnetic response of decomposed (Ga,Mn)As contains contributions from both NCs with a high Mn concentration and (Ga,Mn)As with lower Mn content. In the cases discussed above, the NCs dominate magnetic response in the entire temperature range. However, for (Ga,Mn)As grown by MBE under conditions corresponding to the onset of phase separation, FM response of the (Ga,Mn)As host can prevail at low temperatures. Here, the NCs lead to pinning of domain walls and to enhancement of the coercive force (Wang et al., 2006). Only at high temperatures, above $T_C$ of the host, magnetization is dominated by the NCs (Wang et al., 2006). Similar situation takes place in magnetic resonance studies: FM resonance of MnAs NCs dominates at high temperature, whereas a signal of dilute Mn ions takes over at low temperatures (Krug von Nidda et al., 2006).

C. Magneto-optical phenomena

One of the attractive aspects of decomposed semicon-
ductor alloys is that they show FM characteristics to above RT and at the same time they can be easily inte-
grated with existing semiconductor devices. For in-
estance, one can envisage magneto-optical insulators and modulators that would exploit a large magnitude of the Kerr effect characterizing FM metals and weak optical losses specific to semiconductors. Indeed, the giant Faraday effect and magnetic circular dichroism was found in GaAs with hexagonal metallic MnAs NCs at RT (Aki-
naga et al., 2000a). The Faraday rotation angle of the GaAs:MnAs layer reached about $0.2^\circ/\mu\text{m}$ at 0.98 $\mu\text{m}$.

Optical reflectivity of GaAs with hexagonal MnAs and zb-(Mn,Ga)As NCs is similar to that of the host GaAs matrix (Yokoyama et al., 2005). However, magneto-
optic spectra and intensities are different in these two kinds of decomposed (Ga,Mn)As; the intensity is weaker in the case zb NCs.

While the magnitude of the Verdet constant (i.e., the normalized Faraday rotation) is attractive and compar-
able or larger that the one characterizing magnetic mate-
rials employed in commercial optical insulators, it is hard to obtain a GaAs:MnAs layer thick enough to insure the required angle of polarization rotation, $45^\circ$. However, it is possible to enhance the rotation angle by extend-
ing the effective optical path length through a magnetic layer by using multiple reflections. By inserting a 140-
nm thick GaAs:MnAs film in-between distributed Bragg reflectors (DBR) of GaAs/AlAs, the Faraday rotation an-
gle was enhanced sevenfold at a wavelength of 970 $\text{nm}$ at RT (Shimizu et al., 2001). The MCD signal at RT as a function of the magnetic field showed saturation at about 1 kOe, the dependence corresponding to magnetization of GaAs:MnAs system. Furthermore, a similar structure showed the Kerr rotation of $1.54^\circ$ at the designed wave-
length of 980 $\text{nm}$ under a relatively low magnetic field at RT (Ueda et al., 2003). Theoretical modeling of optical and magneto-optical properties of these magneto-
photonic structures properly describes the experimental data.

As a further step, in order to reduce transmission losses associated with large MnAs NCs, the central GaAs:MnAs layer was replaced by a superlattice (SL) consisting of 2.8 $\text{nm}$ thick AlAs and 5 $\text{nm}$ thick GaAs:MnAs formed by annealing of (Ga,Mn)As with Mn content of $x = 0.047$ (Shimizu and Tanaka, 2001). In this way, the trans-
mssion coefficient at a local maximum at 990 $\text{nm}$ was 30%, greatly improved from 2% in the previous multilayer without a SL. However, in this case, the enhancement in the Faraday rotation per unit magnetic layer thickness, compared to the GaAs:MnAs/AlAs SL structure without DBR, is only 3.3, presumably because of lower structural quality.

Another interesting structure, presented in Fig. 18, was optimized for the photon wavelength of $1.55\mu\text{m}$ (Shimizu and Tanaka, 2002b). Here, the central 230 nm thick layer consisted of GaAs:MnAs decomposed film co-doped with Si donors in order to reduce optical absorption associated with holes delivered by residual Mn ions in the GaAs host. The figure of merit (FOM), which is defined by the ratio of Faraday ellipticity (shown in Fig. 18) to optical losses, is 0.074$^\circ$/dB at the wavelength of 1.54 $\mu\text{m}$, which is twice as large as the FOM of 0.037$^\circ$/dB at 0.98 $\mu\text{m}$ obtained in the studies (Shimizu et al., 2001) referred to above.

At the same time, properties of waveguide-type optical insulators based on higher losses of backward propagat-
FIG. 18 An optimized structure with MnAs NCs for optical isolation. (a) A cross-sectional micrograph taken by scanning electron microscope of a Si-doped GaAs:MnAs layer placed between DBRs whose operational wavelength was set at 1.55 µm. Solid lines in (a,b,c) show respectively optical transmission $T$; Faraday ellipticity $\eta_f$ (transmission MCD) and Faraday rotation $\theta_f$ at room temperature in the magnetic field of 1 T perpendicular to the plane of the sample shown in (a). Spectra of a Si-doped GaAs:MnAs single layer (200 nm) having the same Mn and Si concentration are also plotted as references (dotted lines). From Shimizu and Tanaka, 2002b.

D. Magnetoresistance

1. Films

Transport phenomena in granular metals exhibit a number of outstanding properties (Beloborodov et al., 2007) that can be enriched by spin phenomena in decomposed magnetically doped semiconductors (Binns et al., 2005; Michel et al., 2008).

Magnetoresistance (MR) properties of GaAs/MnAs granular hybrid structures consisting of FM MnAs clusters within a paramagnetic GaAs:Mn host differ considerably from those of paramagnetic and FM (Ga,Mn)As alloys. According to experimental studies of decomposed samples obtained by various methods, giant positive MR dominates at high temperatures (typically above ~ 30 K) whereas negative MR takes over at low temperatures (Akinaga et al., 2000b; Michel et al., 2005; Wellmann et al., 1998; Ye et al., 2003). Large positive MR was also observed at RT in the impact ionization regime (Yokoyama et al., 2000).

The positive MR effect is similar to the giant MR found in other metal-semiconductor hybrid systems (Akinaga et al., 2000b; Solin et al., 2000; Sun et al., 2004). One of the relevant mechanisms could be an admixture to the longitudinal voltage of the field-dependent Hall voltage, possibly enhanced by the AHE, a well known phenomenon in other heterogeneous systems (Solin et al., 2000). A strong decrease of the positive MR for the in-plane magnetic field (Ye et al., 2003) supports this scenario.

Two quantum mechanisms, considered widely in the case of homogeneous DMSs (Dietl, 2008b), can contribute to negative MR: (i) an orbital effect originating from the influence of the magnetic field upon interferences of self-crossing trajectories in either diffusing or hopping regime; (ii) a spin effect brought about by a destructive effect of the magnetic field upon spin-disorder scattering that controls interference of carrier-carrier interaction amplitudes in disordered systems. At the same time, giant MR (GMR) or tunneling MR (TMR) effects associated with the field-induced ordering of NCs’ magnetic moments or spin-splitting of host’s bands produced by stray fields can contribute to the magnitude of MR (Michel et al., 2005). Furthermore, independently of the dominating MR mechanism, the spatial distribution of magnetic NCs is a factor affecting substantially the magnitude of MR and allowing its control (Michel et al., 2008).
2. Spin-valve structures

The decomposed (Ga,Mn)As layers containing MnAs NCs with diameter of 10 nm were also formed in the fully epitaxial magnetic tunnel junctions (MTJs), GaAs:MnAs/Al(Ga)As/MnAs, in which a 20 nm MnAs layer constituted the second FM electrode and the barrier was either of AlAs [Hai et al., 2006] or of GaAs [Hai et al., 2008]. The magnitude of tunneling magnetoresistance (TMR) was examined as a function of temperature and the barrier thickness attending, at 7 K, 17% for \( d_{\text{AlAs}} = 2.9 \) nm [Hai et al., 2006] and 8% for \( d_{\text{GaAs}} = 10 \) nm [Hai et al., 2008]. The observed oscillatory behavior of the TMR ratio with the increasing AlAs barrier thickness was explained by quantum interference of two X-valley related wave functions in the AlAs barrier. The ensemble of the results demonstrates that GaAs:MnAs layers can act as an efficient spin injector and a spin detector at low temperatures.

Figure 19(a,b) presents micrographs of a lateral nanodevice patterned of a MnAs/GaAs/GaAs:MnAs MTJ, which allowed to study TMR in the limit of tunneling across a single MnAs NC [Hai et al., 2010]. Sizable oscillations in differential conductance \( \frac{dI}{dV} \) demonstrated that the Coulomb blockade regime was achieved at 2 K. As shown in Fig. 19(c), clear oscillations were also detected in TMR, defined as a relative difference in the resistance values without an external magnetic field (antiparallel arrangement of magnetization in the MnAs contacts) and in the magnetic field of 1 T (parallel magnetizations across the device). Modeling of the TMR results by the theory of Barnaš and Fert, 1998 led to the spin relaxation time \( \tau_s \) of carriers in MnAs NCs as long as 10 \( \mu \)s. The enhancement of \( \tau_s \) was assigned to dimensional quantization of electronic states specific to nanoparticles [Hai et al., 2010].

On the other hand, the magnetizing process of zb-MnAs NCs incorporated into tunnel junctions was found to generate a voltage and a huge magnetoresistance effect, which lasted for a time scale of \( 10^2 \)–\( 10^3 \) s [Hai et al., 2009]. This spin-motive force was explained by the transformation of magnetic energies of the NCs into the electric energy of the electron system in the Coulomb blockade regime. A similar long-living spin-motive force was observed by [Miao et al., 2014] in tunnel junctions with EuS barriers and Al nanoparticles. However, an external energy, brought about by, e.g., thermal or electromagnetic noise, should be provided to these systems to maintain such a long-living spin-motive force [Miao et al., 2014; Ralph, 2011]. The problem of spin-motive force and magnetotransport in nanoscale magnetic systems remains an outstanding experimental and theoretical topic in spinodal-decomposed magnetic semiconductors.

E. Spinodal nanodecomposition in other magnetic III-V compounds

Several properties outlined above for decomposed (Ga,Mn)As have been found in other III-V semiconductors doped with TM ions. These systems, if fabricated under specific growth conditions, show FM-like features with \( T_C \) magnitudes independent of an average Mn concentration but virtually identical to values characterizing relevant Mn pnictides, i.e., \( T_C \) of 291, 318, 573 K, for MnP, MnAs, and MnSb, respectively. To this category belong (Ga,Mn)P [de Andrés et al., 2011], (In,Ga,Mn)As/InP [Hara and Fukui, 2006; Hara and Kuramata, 2005], (In,Mn)As [Khodaparast et al., 2013], and (In,Mn)Sb [Lari et al., 2012] grown by MOVPE as well as (Ga,Sb)Mn [Abe et al., 2000] obtained by MBE and GaP:C implanted with Mn [Theodoropoulou]
IV. SPINODAL NANO DECOMPOSITION IN (Ga,Mn)N

A. A controversial system

Various contradicting information about magnetism of (Ga,Mn)N has been reported in the literature.

Fabrication of single crystalline Ga$_{1-x}$Mn$_x$N epitaxial films with an experimentally documented random distribution of Mn cations and a small concentration of donor-like defects or residual impurities (Bonanni et al. 2011a, Kunert et al. 2012, Sarigiannidou et al. 2006, Stefanowicz et al. 2010) pointed to the presence of low-temperature ferromagnetism (Sarigiannidou et al. 2006). Sawicki et al. 2012, Stefanowicz et al. 2013). In such samples the Fermi level is pinned by the mid-gap Mn$^{2+}$/Mn$^{3+}$ impurity band (Dietl and Ohno 2014) in (Ga,Mn)N (Dietl 2000). In other series of Ga$_{1-x}$Mn$_x$N samples (Dhar et al. 2003b), pointed also to the AF character of the spin interactions. The presence of spin-glass freezing at $T_\text{f}$ between 3 and 4.4 K was revealed for these samples (Dhar et al. 2003b). The nature of compensating donors providing electrons to Mn ions has not yet been firmly established.

Surprisingly, the appearance of FM-like features in (Ga,Mn)N, persisting up to temperatures well above 300 K, was announced by quite a few groups (Liu et al. 2005, Earle et al. 2005, Pearton et al. 2003), and assigned to double exchange that may appear when Mn$^{3+}$ and Mn$^{2+}$ ions coexist (Reed et al. 2005, Sonoda et al. 2007). In view of the technological importance of group III nitrides in today’s photonics and electronics, the fabrication of a GaN-based functional FM semiconductor would constitute a major breakthrough. Since, however, neither spintronic devices nor phase diagram $T_C(x)$ have so far been reported in this case, it is tempting to assume that the high-temperature ferromagnetism in question is not under control. It is probable that spinodal nanodecomposition was involved. Theoretical aspects of nanodecomposition, for which (Ga,Mn)N has often served as a model system, are addressed in Sec. IV. No magneto-optical effects associated with high-$T_C$ ferromagnetism have been detected in (Ga,Mn)N (Ando 2006).

B. Experimental evidences for spinodal nanodecomposition in (Ga,Mn)N

The FM response persisting at elevated temperature and in the absence of carriers mediating the interaction between magnetic ions, is presently widely recognized to originate in TM-doped semiconductors from regions of spinodal nanodecomposition in the form of either coherent chemical separation or crystallographic phase precipitation. In the case of (Ga,Mn)N the inclusion of FM NCs with different transition temperatures, such as Mn$_4$N ($T_C=784$ K) (Pop et al. 1994), Mn$_{3-x}$Ga ($T_C=765$ K) (Nida et al. 1996), or Ga$_{0.8}$Mn$_{0.2}$N ($T_C=235$ K) (Garciá 1985) has been identified.

As the appearance and the form of spinodal nanodecomposition depends sensitively on fabrication conditions, co-doping by shallow impurities, defect concentration, and post-growth processing, the detection of the subtle presence of phase separation requires a thorough characterization of individual samples with a combination of both local—high resolution TEM (HRTEM), 3D atom probe (3DAP),... —and averaging—SQUID magnetometry, synchrotron-based XRD (SXRD), x-ray XMCD, magnetotransport,... —techniques.

Early examples of extended characterization of (Ga,Mn)N and detection of crystallographic phase separ-
FIG. 20 XRD pattern of (Ga,Mn)N grown by the am-
onothermal method with low (a) and high (b) Mn content. 
The Miller indices of the GaN crystal lattice planes are given 
for each diffraction line and arrows indicate diffraction lines 
originating from the Mn$_3$N$_2$ phase. From Zajac et al. [2001].

ration are found in works reporting on samples fabricated 
by means of the ammonothermal technique with 0.25% 
of Mn [Zajac et al. 2001]. Here, the formation of a 
Mn$_3$N$_2$ was detected through XRD analysis, as reported 
in Fig. 20 and diffraction measurements as in Fig. 21 al-
lowed also to identify GaMnN phases in MBE layers 
containing more than 2% Mn (Giraud et al. 2004; Yoon 
et al., 2006).

FIG. 21 Determination of NCs’ structure in (Ga,Mn)N. (a) 
XRD patterns of (Ga,Mn)N epilayers. For a 18% Mn-doped 
GaN epilayer: presence of oriented clusters with perovskite 
structure. (b) X-ray absorption: the perovskite clusters at 
Mn contents larger than 2% are identified as GaMn$_3$N NCs. 
From Giraud et al. 2004.

Furthermore, through TEM bright-field micrographs 
it has been possible to recognize the presence of not 
better identified secondary phases in MBE (Ga,Mn)N 
grown onto a GaN buffer and employing specific growth 
conditions [Kim et al. 2012]. or onto 4H-SiC(0001) 
substrates and containing 13.7% of Mn ions, as seen 
in Fig. 22, where the comparison between TEM micro-
graphs from samples with respectively 7.6% (left panel) 
and 13.7% (right panel) is given [Dhar et al. 2003a]. 
From this work, the magnetization of the sample with 
the highest Mn concentration as a function of tempera-
ture and the magnetic field is reported in Fig. 23. Always 
worth to underline is that the measured magnetization of 
phase separated (Ga,Mn)N—and generally (Ga,TM)N—
consists of different components, as exemplified in Fig. 24 
and particular caution has to be given to discriminating 
between the various contributions, to the correct sub-
traction of the signal from the substrate and to possible 
Sources of contamination [Bonami et al. 2007; Hwang 
et al., 2007; Ney et al. 2008].

As already mentioned, synchrotron radiation-based 
characterization techniques can supply precious informa-
tion when standard methods, such as, e.g., conventional 
XRD, fail to provide the necessary sensitivity to the pres-
ence of spinodal nanodecomposition in the investigated 
materials [Navarro-Quezada et al. 2010]. An example 
is given by the application of synchrotron radiation mi-
croprobe to the identification and study of Mn-rich inter-
metallic Mn-Ga NCs in MBE (Ga,Mn)N with 11% of Mn 
(Martinez-Criado et al. 2005). A combination of fluores-
cence mapping with spectroscopic techniques allowed to 
examine the composition of the clusters and their crys-
FIG. 24 Evidence for various contributions to (Ga,Mn)N magnetization. (a) Magnetization as a function of the magnetic field for several temperatures. (b) Schematic of the total magnetization (PM + FM) decomposition into paramagnetic (PM) and ferromagnetic (FM) contributions. From Zajicek et al., 2003.

tallographic orientation, as summarized in Fig. 25.

FIG. 25 (Color online) Decomposition of (Ga,Mn)N with an average Mn concentration of 11% studied by x-ray fluorescence mapping. Mn Kα, Ga Kα fluorescence line, and inelastic (Compton) scattering signal, are shown. Ga and Mn profiles along the dotted scan line are presented in the lower panel indicating the formation of Mn-rich intermetallic Mn-Ga NCs. From Martinez-Criado et al., 2005.

It has been reported that by employing H₂/N₂ instead of mere N₂ during the plasma-assisted MBE (PAMBE) of (Ga,Mn)N the solubility limit of Mn can be enhanced and the formation of secondary Mn-rich phases hindered (Cui and Li, 2002). Furthermore, again during a PAMBE process, it has been shown that by switching from N-rich to Ga-rich conditions the efficiency of Mn incorporation is diminished, while the crystalline quality is improved and the presence of mixed domains wz-zb is suppressed (Han et al., 2007). The amount of Mn likely to be incorporated without precipitation has been found to depend critically in MBE on the growth temperature T_g (Kondo et al., 2002) and above a critical value of the Mn ions supply, GaMn₃N NCs are found to form on the samples surface (Kocan et al., 2006), as exemplified in Fig. 26.

The role of defects in the aggregation of Mn has been also taken into account (Larson and Satpathy, 2007) and, e.g., from x-ray absorption spectroscopy (XAS) and XMCD data complemented by ab initio calculations it has been concluded that Mn in GaN preferentially occupies Ga sites neighboring N split interstitial defects (Keavney et al., 2005). The to-date literature lacks of a systematic study on the possible role of threading dislocations—especially in a system based on GaN—as preferential site for the aggregation of Mn. Energy filtered TEM (EFTEM) experiments should be considered, in particular in the perspective of identifying coherent regions (not crystallographically phase separated) with enhanced Mn concentration.

The high magnetic moment of Mn and its low solubility limit into GaN—common to all TMs—has prompted to optimize and exploit also Mn-induced phases onto a GaN surface: e.g., magnetic MnGa can grow with an abrupt interface and with a defined epitaxial orientation on wz-GaN, developing an ideal magnetic/semiconductor bilayer (Lu et al., 2006). Furthermore, well ordered Mn submonolayers have been deposited onto wz-GaN by evaporation (Chinchore et al., 2008) and (Ga,Mn)N nanostructures, though with a not-investigated structure and actual composition, and grown by MOVPE onto GaN are reported (Gupta et al., 2006). A combined study by scanning tunneling microscopy (STM) and first-principles analysis states the feasibility of ordered Mn-induced nanostructures onto GaN(0001) at elevated temperatures, while the growth at RT leads to disordered phases (Qi et al., 2010).

FIG. 26 Cross section HRTEM of a NC in a (Ga,Mn)N layer with nominal 33% Mn. From Kocan et al., 2006.

C. Co-doping with shallow impurities and δ-doping in (Ga,Mn)N

As mentioned above (Sec. IV.A), the charge state of a magnetic impurity in a semiconducting matrix, which can
be altered in GaN by co-doping with electrically active impurities, is crucial for the magnetic properties of the material. Moreover, as discussed in Sec. II.H engineering of the Fermi level position by co-doping can serve to modify the lattice position (e.g., interstitial vs. substitutional) and the distribution of magnetic impurities over cation sites (Dietl, 2006; Ye and Freeman, 2006).

In addition to infrared and magnetic-resonance spectroscopy (see, Bonanni et al., 2011; Graf et al., 2003; Wołos and Kamińska, 2008), x-ray absorption near-edge spectroscopy (XANES) is a widely employed method to determine the valence state of Mn in GaN (Biquard et al., 2003; Bonanni et al., 2011; Sato et al., 2002; Titov et al., 2005; Wei et al., 2006). As summarized in Fig. 27 from the analysis of the absorption-edge pre-peaks it is possible to infer the charge state of the TM ions. Furthermore, a careful modeling of the total signal can give information on the presence and nature of phase separation (Biquard et al., 2003; Sato et al., 2002; Titov et al., 2005; Wei et al., 2006). Another sensitive method is x-ray emission spectroscopy (XES) that was exploited to determined the evolution of Mn oxidation state with the Mg concentration in (Ga,Mn)N:Mg (Devillers et al., 2012).

The tuning of the Fermi level through co-doping with acceptors or donors is expected (Dietl, 2006)—and in other systems proven (Bonanni et al., 2008; Kuroda et al., 2007)—to affect the aggregation of TM ions in a semiconducting host and therefore the onset of spinodal nanodecomposition. In (Ga,Mn)N the modulation of the Mn charge state has been mainly considered in relation to its possible effect on the magnetic response. However, the reports are highly controversial: e.g., in some works the reduction from the neutral state Mn$^{3+}$ to Mn$^{2+}$ has been found to decrease the FM response of (Ga,Mn)N layers (Yang et al., 2008), while elsewhere it has been argued that paramagnetic (Ga,Mn)N with a majority of Mn$^{3+}$ can be rendered FM via double-exchange mechanisms if Mn$^{3+}$ and Mn$^{2+}$ coexist in the same sample (Sonoda et al., 2007). Furthermore, co-doping with acceptors (Mg) is even reported to act not univocally, but depending on the quality of the matrix to either enhance or quench the FM response (Reed et al., 2005). Again a hint of the crucial importance is a characterization of the material at the nanoscale, as co-doping often controls the formation of Mn-rich NCs that can dominate magnetic properties, especially at high temperatures.

Actually, it was demonstrated that co-doping of GaN with Mn and Mg during the MOVPE growth leads to the formation of Mn-Mg$_k$ impurity complexes, where $k$ increases up to $k = 3$ with the ratio of Mg to Mn concentration according to the binomial distribution (Devillers et al., 2012). These complexes show appealing optical properties, particularly broad-band infrared emission persisting up to RT (Devillers et al., 2012).

Interestingly, MBE $p$-(Ga,Mn)N spinodally decomposed in regions of GaMn$_3$N is seen to have an enhanced conductivity (Kim et al., 2003) that could make this phase-separated system promising for functional effects.

While thermodynamically stable (Ga,Mn)N crystallizes in the wz-structure, it has been reported that MBE
layers can be locally stabilized by Mn δ-doping in the zb-phase (Lazarov et al., 2008), as evidenced in Fig. 28. Furthermore, the energetics of cubic and hexagonal (Ga,Mn)N arrangements has been studied with ab initio pseudo-potential calculations and indeed δ-doping has resulted likely to stabilize the zb phase (Choi et al., 2006).

V. SPINODAL NANO DECOMPOSITION IN (Ga,Fe)N

A. Diluted Ga,Fe)N: current status

While extensive studies have been conducted on (Ga,Mn)N (Bonanni et al. 2007, Dietl 2004, Graf et al. 2003, Liu et al. 2005, Pearton et al. 2003) as promising workbench for future applications in spintronics, until very recently, only little was known about (Ga,Fe)N. Formerly, and to a broad extent still now, this system is being widely considered as semi-insulating substrate for high frequency devices, as AlGaN/GaN high-mobility transistors (Heikman et al., 2003, Kashiwagi et al. 2007, Kubota et al. 2009, Lo et al. 2006, Muret et al. 2007). In this context and generally in relation with a use of this material system in reliable devices, careful studies of the electronic structure of (Ga,Fe)N have been carried out and especially the knowledge of the exact position of the Fe$^{3+}$/2+ acceptor level within the band gap—used to predict band offsets in heterostructures on the basis of the internal reference rule (Langer and Heinrich, 1985)—has been considered of great importance. Furthermore, the behavior of d$^5$ and d$^6$ level systems in a trigonal crystal field of C$_{3v}$ symmetry is of interest for general aspects of group and crystal-field theory (Lo et al., 2006, Malguth et al., 2008).

Furthermore, GaN doped with Fe impurities substitutional of Ga in their Fe$^{3+}$ d$^5$ configuration (Baur et al., 1994, Bonanni et al. 2007, Malguth et al. 2006a, 2008) attracted considerable attention as an ideal system for the study of the p–d exchange interaction in the strong coupling limit (Pacuski et al., 2008). Indeed, magnetically-doped II-VI oxides and III-V nitrides, due to their small bond length and, thus, strong p–d hybridization, are expected to give rise to large values of the exchange energy $N_0|\beta|$, a prediction supported by photoemission experiments (Hwang et al., 2005). Surprisingly, however, anomalously small field-induced exciton splittings in paramagnetic (Zn,Co)O (Pacuski et al. 2006), (Zn,Mn)O (Pacuski et al. 2011, Przedziacka et al. 2006), and (Ga,Mn)N (Pacuski et al. 2007) Sufczynski et al. (2011) were reported. It was suggested (Dietl 2008a) that due to the strong p–d coupling, the molecular and virtual crystal approximations fail in oxides and nitrides, making the apparent exchange splitting the valence band, quantified by $N_0|\beta|^{(app)}$, reduced in absolute value and of opposite sign than expected, and observed in other II-VI DMSs. In this context, measurements of magnetization and magnetoreflectivity in the free exciton region for (Ga,Fe)N epilayers were reported (Pacuski et al., 2008, Rousset et al., 2013), and the obtained values for $N_0|\beta|^{(app)}$ supported the theoretical expectations (Dietl 2008b).

Moreover, recently reported DFT calculations supporting the notion that the spin-spin coupling in dilute (Ga,Fe)N is AF, while it becomes ferrimagnetic when holes are introduced into the system, have reignited the discussion on the nature of the magnetic interactions in TM-doped DMS (Dalpian et al., 2009). Additionally, DMSs in general and (Ga,Fe)N in particular, have become model systems to test various implementations of the DFT to disordered strongly correlated systems (Cui et al. 2006, Mirbt et al. 2002, Sanyal et al. 2003, Sato and Katayama-Yoshida, 2002).

![Fig. 29 Room temperature conversion electron Mössbauer spectroscopy spectra of a 4 × 10$^{16}$ cm$^{-2}$ Fe-implanted GaN sample: (i) as-implanted, annealed at 750°C, (iii) annealed at 850°C. From Talut et al. 2006](image)

B. Fabrication and properties of spinodally decomposed (Ga,Fe)N

Both the above considerations and the search for high-$T_C$ DMSs (Dietl et al., 2000) impelled the research in various TM-doped GaN, and the Fe-doping has been pursued through a vast palette of fabrication techniques with variegated results. (Ga,Fe)N grown by means of radio-frequency plasma-assisted MBE (RF-MBE) at 800°C and with a Fe concentration up to 5 × 10$^{21}$ cm$^{-3}$ was shown to have superparamagnetic behavior and HRTEM images gave hints of some inhomogeneity in the layers (Kuwabara et al. 2001b).

The same system fabricated by the ammonothermal technique (Dwiliński et al., 1998, Gosk et al. 2003) and by a chemical transport method (Gosk et al. 2003) re-
FIG. 30 GaN sample implanted with $4 \times 10^{16}$ cm$^{-2}$ Fe ions and annealed at 800°C: left panel - HRTEM: Fe clusters in the implanted region of the sample; right panel - selected area diffraction pattern of the same region. From [Talut et al., 2006].

FIG. 31 HRTEM of (Ga,Fe)N showing (a) dilute case; (b) coherent spinodal decomposition (chemical phase separation), and (c) crystallographic phase separation. From [Bonanni et al., 2007].

revealed the coexistence of paramagnetic and FM contributions (see Sec. V.F), but the origin of this latter component was not investigated. The magnetic properties of nominally undoped and p-doped GaN implanted with Fe ions were reported, evidencing a FM response characterized by magnetization hysteresis loops persisting—depending on the provided dose (Pearton et al., 2002)—up to RT (Shon et al., 2004; Theodoropoulou et al., 2002a).

The full width at half maximum (FWHM) of the GaN(0002) XRD rocking curves peaks acquired on Fe implanted GaN was found to increase as a function of the Fe dose, though without further analysis guiding to the presence of decomposition (Shon et al., 2006). The emission channeling technique applied to Fe-implanted (Fe dose up to $10^{19}$ cm$^{-3}$) GaN samples confirmed the presence of a high percentage of TM ions (up to 80%) occupying substitutional Ga sites of the host crystal (Wahl et al., 2001). Moreover, GaN films doped with Fe, with concentrations up to $3 \times 10^{19}$ cm$^{-3}$ were fabricated by MBE at growth temperatures ($T_g$) ranging from 380°C to 520°C directly on sapphire (0001) and FM behavior with $T_C = 100$ K was observed only in the samples grown at 400°C (Akinaga et al., 2000c).

Films of (Ga,Fe)N (Fe density up to $6 \times 10^{21}$ cm$^{-3}$) fabricated by means of MBE at $T_g = 500 - 800$°C showed a superparamagnetic behavior (Kuwabara et al., 2001a,b) assigned to Ga-Fe and/or Fe-N inclusions. EXAFS analysis suggests that the decrease of $T_C$ is caused by a structural transition from wz to zb, and this transition was related to the origin of FM in Fe-doped GaN films (Ofuchi et al., 2001).

C. Fe distribution from nanoscale characterization

Especially the need to gain insight into the origin of the puzzling FM signatures detected in GaN upon doping with Fe and persisting up to above RT, has prompted lately a considerable experimental effort in the characterization of the system at the nanoscale. As discussed in this section, (Ga,Fe)N represents an interesting case, in which, for specific growth conditions, NCs formed by spinodal nanodecomposition gather in planes perpendicular to the growth direction.

Early steps were undertaken in the understanding of, e.g., the behavior of Fe-implanted GaN, where a combination of Mössbauer spectroscopy and HRTEM revealed the precipitation of Fe during implantation (Talut et al., 2006). There, $^{57}$Fe was employed as an atomic sensitive probe to investigate the local environment of Fe by Mössbauer spectroscopy and to study the precipitation at very early stage. MOVPE p-type Mg doped $10^{17}$ cm$^{-3}$ wz-GaN(0001) films about 3 µm thick grown onto sapphire (0001) substrates were analyzed. The samples were implanted with 200 keV $^{57}$Fe ions with fluences between...
A series of works with a first systematic study of the (Ga,Fe)N system fabricated by means of MOVPE from the impurity limit until the phase separation, was carried out \cite{Bonanni2007, Bonanni2008, Kowalik2008, Pawlowski2008, Przybylinska2006, Rovezzi2009}. It was shown that by controlling the growth parameters it is possible to incorporate the magnetic ions in different fashions, giving rise to respectively: (i) a DMS phase with Fe substitutional of Ga, in the charge state Fe$^{+3}$ and responsible for the paramagnetic response of the samples; (ii) a system with spinodal decomposition (chemical phase separation) in Fe-rich regions structurally coherent with the matrix; (iii) a crystallographic phase-separated material consisting of Fe$_{x}$N NCs embedded in the GaN host and likely to account for the FM signatures, as discussed in Sec. V.E.

The mentioned different arrangements are evidenced by the HRTEM images in Fig. 31, where (a) dilute, (b) chemically separated, and (c) crystallographically separated (Ga,Fe)N are, respectively, reported. Energy dispersive x-ray spectroscopy (EDS) measurements could confirm the enhanced concentration of Fe both in the coherent regions (b) and in the incoherent precipitates (c) \cite{Bonanni2007}.

While often laboratory XRD does not evidence any phase separation in (Ga,Fe)N samples giving a FM response—an example is given in Fig. 32—where MOVPE (Ga,Fe)N with 0.7% Fe ions does not show diffraction peaks from secondary phases—XRD measurements on MOVPE (Ga,Fe)N with more than 0.4% Fe, reveal the presence of diffraction peaks identified as the (002) and (111) of the phase ε-Fe$_{3}$N—as reported in Fig. 33—a compound known to be FM with $T_C = 575$ K.

The solubility limit in (Ga,Fe)N was found to be around 0.4% of the Fe ions under the optimized MOVPE growth conditions \cite{Bonanni2007}. As discussed in Sec. IV.B, an order of magnitude lower solubility limit of Fe comparing to Mn (see Sec. IV) under similar growth conditions is to be linked to a different sign of chemical forces between TM adatoms on the (0001)GaN surface during the epitaxy: according to \textit{ab initio} studies the pairing interaction that is repulsive for surface cation Mn dimers, becomes attractive in the case of Fe ions \cite{Gonzalez-Swaacke2011}. Actually, a reduced magnitude of FM response with increasing the growth rate \cite{Bonanni2008} and lowering growth temperature \cite{Navarro-Quezada2010} constitutes an experimental hint about the importance of aggregation at the growth surface in the formation of Fe-rich NCs in (Ga,Fe)N.

An interesting aspect of spinodal nanodecomposition in (Ga,Fe)N was discovered by HRTEM \cite{Navarro-Quezada2011} and confirmed by x-ray photoemission electron microscopy (XPEEM) and XAS \cite{Kowalik2012}. It was found that Fe-rich NCs tend to accumulate in a plane adjacent to the film surface. This observation allowed to develop a method of controlling the NCs’ position \cite{Navarro-Quezada2012}. As shown in Fig. 34, it was demonstrated that for an employed growth mode, the NCs gathered in a plane at which the Cp$_2$Fe source flow was interrupted, i.e., at the interface between the (Ga,Fe)N layer and the GaN cap. This means that Fe-rich regions move together with the growth front as long as Fe is supply, reemphasizing the notion that the aggregation of TM ions occurs at the growth surface.

The command over the location of the NC array is obviously a major step toward applications of decomposed systems. Furthermore, a highly non-random distribution of NCs over the film volume indicates that the visual-
FIG. 34 Control over the spatial distribution of Fe-rich nanocrystals (NCs) in (Ga,Fe)N. (a) Schematic layout of the structure; (b) cross-sectional TEM: magnification of the region containing the array of NCs for the sample reported in (c); (c) and (d) cross section TEM images of the samples, showing the spatial distribution of the NCs into a planar array perpendicular to the growth direction and located at the interface to the cap layer, 500 nm and 150 nm below the sample surface, respectively; (e) plane-view TEM image of the sample in (c), giving the in-plane distribution of NCs. From Navarro-Quezada et al. 2012).

......

D. Phase diagram of the spinodal decomposition in (Ga,Fe)N

It is known that the increase of \( T_g \) promotes the aggregation of the TM ions incorporated in the semiconductor host and brings therefore the system far from the dilute state. Moreover, various Fe\(_x\)N phases with specific magnetic and structural properties are expected to be stable up to different temperatures. The MOVPE (Ga,Fe)N material system was studied as a function of \( T_g \) in the range between 800 and 950°C and for samples with a total concentration of Fe ions in the range \( 1 - 4 \times 10^{20} \text{ cm}^{-3} \) (Navarro-Quezada et al. 2010). In that work, SXRD, EXAFS and XANES, combined with HRTEM and SQUID magnetometry permitted to detect and to identify particular Fe\(_x\)N phases in samples fabricated at different \( T_g \), as well as to establish a correlation between the existence of the specific phases and the magnetic response of the system. It was found that already a 5% variation in the growth temperature is critical for the onset of new Fe\(_x\)N species and it could be confirmed that an increase in the growth temperature promoted the onset of spinodal decomposition, resulting in an enhanced density of Fe-rich NCs in the matrix and in a consequent increase of the FM response of the system.

In Fig. 36, SXRD spectra for (Ga,Fe)N samples grown at different temperatures, are reported. For layers fabricated at 800°C there is no evidence of secondary phases and only diffraction peaks originating from the sapphire substrate and from the GaN matrix are revealed, in agreement with HRTEM measurements showing no crystallographic phase separation. Moving to a \( T_g \) of 850°C different diffraction peaks belonging to secondary phases become evident, giving proof that at this \( T_g \) and at the given growth parameters the system undergoes spinodal decomposition and is phase separated. It was reported (Bonanni et al. 2007) that when growing (Ga,Fe)N at this temperature, one dominant Fe-rich phase is formed, namely Wz \( \varepsilon \)-Fe\(_3\)N, for which two main diffraction peaks are identified, corresponding to the (002) and the (111) reflexes, respectively. A closer analysis of the (111)-related feature and a fit with two gaussian curves centered at 35.2° and 35.4°, gives evidence of the presence of the (110) reflex from cubic metallic \( \alpha \)-Fe. Moreover, the broad feature appearing around 38° is associated to the (200) reflex of fcc \( \gamma' \)-Fe\(_4\)N, that crystallizes in an inverse perovskite structure (Jack, 1952).

As the growth temperature is increased to 900°C there is no contribution left from the (110) \( \alpha \)-Fe phase, and the signal from the (111) of \( \varepsilon \)-Fe\(_3\)N is significantly quenched, indicating the reduction in either size or density of the specific phase. Furthermore, an intense peak is seen at 34°, corresponding to the (121) contribution from orthorhombic \( \zeta \)-Fe\(_2\)N. This phase crystallizes in the \( \alpha \)-PbO\(_2\)-like structure, where the Fe atoms show a slightly distorted hexagonal close packing (hcp), also found for \( \varepsilon \)-Fe\(_3\)N (Jacobs et al. 1995). At a growth temperature of 950°C the diffraction peak of (200) \( \gamma' \)-Fe\(_4\)N recedes, indicating the decomposition of this fcc phase at temperatures above 900°C, in agreement with the phase diagram for free standing Fe\(_3\)N (Jacobs et al. 1995), reporting cubic \( \gamma' \)-Fe\(_4\)N as stable at low temperatures. Only the
FIG. 36 Color online) SXRD spectra for (Ga,Fe)N layers deposited at different growth temperatures. Inset: peak at 35.3° deconvoluted into two components assigned to diffraction maxima (111) of ε-Fe$_3$N and (110) of α-Fe [experiment (dotted line) and fit (smooth line)]. From [Navarro-Quezada et al., 2010]

(002) ε-Fe$_3$N- and the (121) ζ-Fe$_2$N-related diffraction peaks are preserved with a constant intensity and position with increasing temperature, suggesting that at high $T_g$ these two phases and their corresponding orientations, are noticeably stable.

Following a procedure based on the Williamson-Hall formula method [Lechner et al. 2009; Williamson and Hall 1953], the approximate average NCs size is obtained from the FWHM of the diffraction peaks in the radial $(ω/2θ)$ scans. The FWHM of the (002) ε-Fe$_3$N, of the (200) γ'-Fe$_4$N, and of the (121) ζ-Fe$_2$N diffraction peaks are comparable for samples grown at different temperatures, indicating that the average size of the corresponding NCs is also constant, as summarized in Fig. 37.

FIG. 37 (Color online) Average size vs. growth temperature $T_g$ of nanocrystals in the different Fe$_x$N phases, as determined from SXRD. From [Navarro-Quezada et al., 2010]

By summing up the SXRD, EXAFS, and HRTEM findings, a phase diagram of the Fe-rich phases formed in (Ga,Fe)N as a function of the growth temperature has been constructed and reported in Fig. 35, showing the dominant phases for each temperature interval. Moreover, according to the Fe vs. N phase diagram the orthorhombic phase (ζ-Fe$_2$N) contains a higher percentage of nitrogen [Jack 1952] compared to the hexagonal one (ε-Fe$_3$N), and this guides to conjecture that the higher the growth temperature, the more nitrogen is introduced into the system. Furthermore, similarly to the case of (Ga,Mn)As (III) and (Ga,Mn)N (IV), NCs in (Ga,Fe)N can be built from compounds containing Ga. The presence of planar arrays of Ga$_x$Fe$_{4−x}$N NCs was evidenced in a recent work [Navarro-Quezada et al., 2012].

E. Co-doping with shallow impurities in (Ga,Fe)N

Remarkably, HRTEM, SXRD, and SQUID data reveal that the aggregation of Fe ions in a GaN host, and therefore the onset of spinodal decomposition, can be affected by co-doping with shallow impurities, Si donors and Mg acceptors [Bonanni et al., 2008, Navarro-Quezada et al., 2011].

In Fig. 38 HRTEM images data for the two relevant spinodally decomposed initial regimes, namely (i) (Ga,Fe)N with embedded Fe-rich NCs [Fig. 38(a)] evidenced by Moiré fringes contrast and (ii) (Ga,Fe)N showing coherent chemical separation [Fig. 38(c)] generating mass contrast show the reduced aggregation of the Fe-rich regions as a consequence of co-doping with Si donors [Fig. 38(b),(d)].

This effect is further confirmed by the SXRD results given already in Fig. 37, where the introduction of shallow donor impurities is found to hamper efficiently the precipitate aggregation, so that the SXRD diffraction
peaks corresponding to $\varepsilon$-$\text{Fe}_3\text{N}$ are suppressed in the case of the co-doped samples \cite{Bonanni et al. 2008}. The quenching of the FM contribution in the co-doped layers is further validated by the reduced number of average Fe ions involved in the FM response in co-doped (Ga,Fe)N samples.

In order to explain these key findings, it was noted, as discussed theoretically in Sec. IIB that except for Mn in II-VI compounds \cite{Kuroda et al. 2007}, owing to the presence of the open $d$ shells in the vicinity of the Fermi level, the nearest neighbor pair of TM cations in semiconductors shows a large binding energy that promotes the magnetic ions aggregation. However, as also elaborated in Sec. IIB from a theoretical perspective, if carriers introduced by co-doping can be trapped by these ions, the pair binding energy will be altered, usually reduced by the corresponding Coulomb repulsion between charged TM impurities \cite{Dietl 2006, Ye and Freeman 2006}.

While the effect of shallow Si donors on the Fe aggregation and consequently on the onset of spinodal decomposition in (Ga,Fe)N is quite clear, since the presence of the mid-gap electron trap, i.e., the Fe$^{3+}$/Fe$^{2+}$ state, is well established in GaN \cite{Malguth et al. 2008}. It was found that the Fe K-edge probed by the XAS shifts under Si doping from a position expected for the Fe$^{3+}$ oxidation state towards that specific to the Fe$^{2+}$ configuration \cite{Rovezzi et al. 2009}, as evidenced by the XANES spectra in Fig. 39.

In contrast, the role of additional acceptors (Mg) is more complex in (Ga,Fe)N. The level Fe$^{3+}$/Fe$^{4+}$ is expected to reside rather in the valence band \cite{Malguth et al. 2008}, but it was suggested that the potential introduced by a TM ion in GaN (and ZnO) is deep enough to bind a hole \cite{Dietl 2008a}, shifting the Fe$^{3+}$/Fe$^{4+}$ up to the GaN band gap \cite{Pacuski et al. 2008}. If this is the case, Mg co-doping could also hamper Fe aggregation.

It was found experimentally that the influence of Mg depended crucially on the way it was introduced to the system: uniform Mg co-doping reduced incorporation of Fe, diminishing in this way the NC abundance \cite{Navarro-Quezada et al. 2011}. In contrast, co-doping of Mg in the $\delta$ fashion enhanced the NC formation, the effect discussed theoretically in terms of pairing energies of clusters containing different numbers of Fe and Mg cations in GaN \cite{Navarro-Quezada et al. 2011}. The influence of Mg co-doping on magnetic properties is discussed below (Sec. V.F).

Significantly, based on these results, the previously observed effect of co-doping on ferromagnetism in (Ga,Mn)N, and assigned to the dependence of the double exchange mechanisms of the spin-spin coupling on the position of the Fermi level with respect to the center of the $d$ band \cite{Reed et al. 2005}, has to be reconsidered.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig39}
\caption{(Color online) XANES spectra of (Ga,Fe)N and (Ga,Fe)N:Si. The region marked by the dashed box is expanded in the inset. Here the experimental data (lines) after a background subtraction are compared to the fitted values (dots). In addition to the peak at 7114.3 $\pm$ 0.1 eV assigned to the Fe$^{3+}$ charge state, a shoulder at 7112.7 $\pm$ 0.1 eV is visible in the Si-doped sample pointing to the reduction of a part of the Fe ions to the Fe$^{2+}$ charge state by Si doping. From Bonanni et al. 2008.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig40}
\caption{Magnetization of (Ga,Fe)N bulk crystals obtained by a chemical transport method showing a non-saturating linear in field component assigned to a Van Vleck-type paramagnetism of Fe$^{3+}$ ions, together with a high-$T_c$ ferromagnetic contribution visible in weak fields. From Gosk et al. 2003.}
\end{figure}

\section{F. Magnetic properties of (Ga,Fe)N}

Comprehensive nanocharacterization of (Ga,Fe)N has allowed to put on a more firm basis the origin of a complex magnetic response reported repetitively for this system. Two examples are given in Figs. 40 and 41 in which various contributions to magnetization are clearly seen. The richness of magnetic response correlates with the multi-phase character of (Ga,Fe)N with Fe concentrations beyond the solubility limit, as discussed above (Secs. V.C-E).

In general, according to studies of magnetization (Bonanni et al. 2007, Gosk et al. 2003, Navarro-Quezada et al. 2011, 2010), electron paramagnetic resonance (EPR) \cite{Bonanni et al. 2007, Malguth et al. 2006a}, ferromagnetic resonance (FMR) \cite{Grois et al. 2014}, infrared spectroscopy \cite{Malguth et al. 2006b}, magne-
to optical, X-ray magneto-optics (Pacuski et al., 2008; Rousset et al., 2013), and XMCD (Kowalk et al., 2012) Fe dopants appear in distinct magnetic phases in (Ga,Fe)N, whose relative importance depends on growth conditions, Fe concentration, and codoping by donors or acceptors.

**Brillouin paramagnetism** of Ga-substitutional Fe$^{3+}$ ions: Because of a non-zero but relatively low solubility limit, a paramagnetic contribution from diluted Fe$^{3+}$ ions is always present (provided that density of compensating donors is sufficiently small), as confirmed by a quantitative interpretation of EPR spectra in terms of weakly interacting localized spins $S = 5/2$ occupying Ga-substitutional sites (Bonanni et al., 2007; Malguth et al., 2006a). These spins give rise to the Brillouin-like dependence of magnetization on the magnetic field and temperature visible in magneto-optical (Pacuski et al., 2008; Rousset et al., 2013) and magnetization measurements (Bonanni et al., 2007, 2008; Navarro-Quezada et al., 2010; Pacuski et al., 2008).

**Van Vleck paramagnetism due to Fe$^{2+}$ ions:** In addition to the Brillouin-like term described above, a term linear in the magnetic field was found to contribute to (Ga,Fe)N magnetization, and assigned to the Van Vleck paramagnetism of Fe$^{2+}$ ions that can be present in (Ga,Fe)N due to residual or purposely introduced donors (Bonanni et al., 2007; Gosk et al., 2003; Malguth et al., 2006a).

**High-$T_C$ ferromagnetism:** A FM-like contribution to magnetization of (Ga,Fe)N, dominating at high temperatures, shows characteristics specific to the whole family of high-$T_C$ DMSs and dilute magnetic oxides (Coey et al., 2010; Sawicki et al., 2013). As presented in Fig. 42, for any temperature and orientation of the magnetic field magnetic hysteresis loops $M(H,T)$ are leaning and narrow, so that the magnitude of spontaneous magnetization $M_s(T)$ is much smaller than the saturation magnetization $M_{Sat}$. Remarkably, $M_s(T)$ persists up to above RT and the values of normalized magnetization are approximately described by a temperature independent Langevin function $M(H)/M_{Sat} = \tanh(H/H_0)$, where in the case under consideration $H_0 \approx 800$ Oe.

This behavior is in contrast to a square-like shape and strong temperature dependence of hystereses in, e.g., dilute ferromagnetic semiconductors, such as (Ga,Mn)As. At the same time, if interpreted in terms of superparamagnetism it indicates that, for some NCs, the blocking temperature $T_b$ is higher than RT. This conclusion was confirmed via zero-field cooled (ZFC) and field cooled (FC) SQUID magnetometry measurements at a low magnetic field of 50 Oe (Bonanni et al., 2007), as shown in Fig. 43. However, the high magnitudes of $T_b$ were surprising in view of relatively small values of NC diameters, collected in Fig. 37.
It was suggested that dipole-dipole interactions between densely packed magnetic constituents may lead to a magnetization that can be parametrized by a temperature-independent Langevin-type function \( C_0 \) (Coey et al., 2010), a behavior refer to as superferromagnetism (Sawicki et al., 2013). According to TEM (Navarro-Quezada et al., 2010) and XPEEM (Kowalik et al., 2012), NCs tend to aggregate in planes perpendicular to the growth direction in the case of (Ga,Fe)N, which increases density of NCs and thus supports the superferromagnetism scenario (Navarro-Quezada et al., 2011).

The above interpretation requires also that \( T_C \) of individual NCs is well above RT. According to results presented in Fig. 14, the value of \( M_{sat} \) determined from Arrott plots as a function of temperature for the same type of samples, pointed to a \( T_C = 575 \) K. This value is in accord with the identification of the dominant secondary phases via SXRD and TEM as \( \varepsilon\)-Fe\(_2\)N in samples under consideration (Bonanni et al., 2007). According to the phase diagram discussed in Sec. VI.D the abundance of ferromagnetic NCs (\( \varepsilon\)-Fe\(_2\)N, \( \gamma'\)-Fe\(_3\)N, \( \alpha'\)-Fe, and their derivatives) increases with lowering the epitaxy temperature.

Recently, FMR was detected at RT in spinodally decomposed (Ga,Fe)N in which Ga\(_x\)Fe\(_{4-x}\)N NCs formed a planar array (Grois et al., 2014). The magnetic anisotropy was found to be primarily uniaxial with the hard axis normal to the NCs plane and to have a comparably weak in-plane hexagonal symmetry.

**Antiferromagnetic contribution:** According to the phase diagram discussed in Sec. VI.D an increase in the epitaxy temperature results in the formation of NCs with a higher degree of nitridation, for which AF coupling can prevail. In particular, \( \gamma'\)-GaFe\(_3\)N exhibits a weak AF coupling with a Curie-Weiss temperature of \(-20\) K (Houwen et al., 2009), whereas orthorhombic \( \xi\)-Fe\(_2\)N is AF below \( 9K \) (Hinomura and Nasu, 1996). Furthermore, it is also possible that wz-FeN NCs formed by chemical phase separation exhibit AF properties, as according to theoretical predictions presented in Sec. II.B coupling between Fe cation pairs is AF in GaN. These considerations led to the conclusion that weakly saturating component of magnetization visible in Fig. 41 rather than resulting from a Van Vleck paramagnetism could originate from antiferromagnetically ordered Fe-rich NCs (Navarro-Quezada et al., 2010).

The presence of various Fe-rich phases with peculiar magnetic properties has been proven, but now it is mandatory to explore the routes that can lead to a single-phase system, especially in the perspective of exploiting hybrid AF/FM systems for, e.g., AF spintronics (Shick et al., 2010).

VI. SPINODAL NANODECOMPOSITION IN (Ge,Mn)

A. Mn dilution in germanium

Almost all the theoretical predictions on the magnetic properties of magnetic semiconductors rely on the ideal dilution of magnetic TM atoms substituting the semiconducting host. \( d \) levels of Mn atoms in a tetrahedral environment are split into two energy levels: \( e_g \) (twice degenerated) and \( t_{2g} \) (three times degenerated) levels. In germanium, \( t_{2g} \) orbitals strongly hybridize with \( p \) orbitals in the germanium valence band forming bonding and anti-bonding states. The resulting magnetic moment per Mn atom is 3 \( \mu_B \) and two holes (when activated) are created in the germanium valence band. *Ab initio* calculations have further shown that exchange coupling between Mn atoms mediated by holes oscillates following the Rudermann-Kittel-Kasuya-Yoshida (RKKY) magnetic interaction (Continenza et al., 2006b; Zhao et al., 2003). Among all TM atoms, Mn is the only one to provide both ferromagnetism and high localized spin moments in germanium. The Zener model complemented with mean field approximation further predicts \( T_C \) as high as 80 K in Ge\(_{0.975}\)Mn\(_{0.025}\) with a hole density of 3.5\times10^{20} \text{ cm}^{-3} (Dietl et al., 2000). However exchange coupling was shown to be highly anisotropic, i.e., to depend on the crystal orientation between two Mn atoms (Continenza et al., 2006b). Hence, for high Mn concentrations (up to few percents), the relative position of Mn atoms in the germanium crystal lattice should be known in detail to understand magnetic properties. Finally, from band structure calculations, Mn dilution in germanium is more favorable than in silicon to induce half-metallic character (100% spin polarization at the Fermi level) (Stroppa et al., 2003). To conclude about theoretical works, (Ge,Mn) might be a very promising candidate as a DMS in future spintronic devices compatible with mainstream silicon technology.

Surprisingly, only few works have been published on ferromagnetism in TM-doped germanium until 2002. The evidence of FM order in an epitaxial layer of Mn-

FIG. 44 (Color online) Saturation magnetization determined from the Arrott plots as a function of temperature for spinodally decomposed (Ga,Fe)N: the evaluated \( T_C \) of 575 K corresponds to the Curie temperature of \( \varepsilon\)-Fe\(_2\)N. Adapted from Bonanni et al., 2007.

\[ M_5(T) \text{ (emu/cm}^3\text{)} = 0.8 \]

\[ C_0 \text{ (emu/cm}^3\text{K}) = 0.6 \]

\[ H_{\text{eff}}(T) \text{ (emu/cm}^3\text{)} = 0 \]

\[ T_C \text{ (K)} = 575 \]

\[ C_0 \text{ (emu/cm}^3\text{)} = 0.8 \]
doped germanium was first reported in 2002 by Park et al. [2002]. Ge_{1−x}Mn_{x} (0.6 < x < 3.5%) films were grown by LT-MBE on Ge(001) and GaAs(001) substrates. They exhibit p-type doping with hole densities up to \(10^{19}−10^{20}\) cm\(^{-3}\) and \(T_c\) increases linearly with Mn concentration from 25 K up to 116 K. Moreover, they could demonstrate the interplay between band carriers and Mn spins by measuring AHE as shown in Fig. 45(a). They could further modulate AHE by the application of a gate voltage as low as 0.5 V. However, the magnetic moment per Mn atom (1.4-1.9 \(\mu_B\)) was much less than the expected value for Mn substituting Ge (3 \(\mu_B\)) and the authors reported the presence of small unidentified precipitates. Mn dilution in germanium can thus be questionable.

B. From Mn dilution to phase separation

Considering the very low solubility of Mn in germanium (\(10^{-6}\%\)) [Woodbury and Tyler 1955], out-of-equilibrium growth techniques are required to dope germanium films with few \% of Mn. Indeed, according to the binary phase diagram [Massalski 1990] and DFT calculations [Arras et al. 2011], the stable (Ge,Mn) alloy with the lowest Mn content is Ge_{0.8}Mn_{0.2} and contains 57.9 at.\% of Mn. Since the 1980’s, seven stable (Ge,Mn) alloys have been synthesized: \(\epsilon\)-Ge_{0.9}Mn_{0.1} [Ohoyama et al. 1961], \(\epsilon\)-Ge_{0.8}Mn_{0.2} [Olaba et al. 1987], \(\kappa\)-Ge_{0.7}Mn_{0.3} [Ohoyama 1961], GeMn_{2} [Ellmer 1980] and Ge_{0.9}Mn_{0.11} [Olba et al. 1984]. Although some of them are FM, they all exhibit a metallic character that makes them poor candidates for spin injection in non-magnetic semiconductors due to conductivity mismatch [Fert and Jaffres 2001]. Other (Ge,Mn) alloys could be prepared by melting Ge and Mn under very high pressure (\(\geq 4.6\) GPa) by Takizawa. Metastable alloys such as Ge_{0.8}Mn_{0.2} [Takizawa et al. 1987], GeMn [Takizawa et al. 1988], Ge_{0.9}Mn [Takizawa et al. 1990] or Ge_{0.8}Mn_{0.2} [Takizawa et al. 2002] could be obtained. All these (Ge,Mn) alloys are Ge-rich and thus can exhibit a semiconducting character required for direct spin injection in semiconductors. At this stage, it should be noted that low temperature MBE could also allow to grow metastable (Ge,Mn) alloys thanks to high epitaxial strain.

The very low solubility of Mn in Ge was further theoretically demonstrated using \textit{ab-initio} calculations. For instance, in order to increase Mn concentration, mixing substitutional and interstitial Mn in germanium lowers the free energy of the system [Arras et al. 2012, Continenza et al. 2007]. At last, except in the work by Zeng et al. [2008], most groups have experimentally observed inhomogeneous Mn-doped germanium films. Inhomogeneities can be either secondary phase precipitates such as Ge_{3}Mn_{5} clusters or Mn-rich nanostructures due to spinodal decomposition. Indeed spinodal decomposition leads to the formation of Mn-rich nanometer sized areas (either a metastable (Ge,Mn) alloy or Ge lattice with high Mn content) surrounded with an almost pure germanium matrix. In the next section, we make a thorough review of the results obtained on the (Ge,Mn) material.

1. Review of experimental results

As already mentioned, in order to prevent the formation of stable metallic (Ge,Mn) phases, out-of-equilibrium growth techniques are required. In the following, we summarize Mn implantation in germanium and MBE growth of thin (Ge,Mn) films. Ottaviano et al. [2006] first performed Mn implantation in germanium (up to 4\%) at 240\degree C and 270\degree C substrate temperatures. Before and after annealing (to improve the crystalline quality) Mn-rich precipitates are observed by TEM. These precipitates are amorphous before annealing and Ge_{3}Mn_{5} clusters after annealing. In addition, x-ray absorption measurements showed that Mn-rich precipitates only form in the deeper part and substitutional Mn are detected close to the film surface [Ottaviano et al. 2007]. Ferromagnetic behavior was further observed by magneto-optical Kerr effect measurements up to 270 K (before annealing) and 255 K (after annealing). However, the magnetic signal clearly arises from many different magnetic phases including Ge_{3}Mn_{5}. Passacantando et al. [2006] found similar results using different implantation doses in germanium wafers. At low implantation dose, Mn-rich precipitates are amorphous whereas they form Ge_{3}Mn_{5} clusters at higher implantation doses as shown in Fig. 45(b). The second technique widely used to grow Mn-doped Ge films is low temperature MBE. Following the first results published by Park et al. [2002b], many groups have attempted to dilute large amounts of Mn in Ge in order to raise \(T_C\) up to RT. D’Orazio et al. [2004] investigated the magnetic and electrical properties of thin epitaxial Ge_{1−x}Mn_{x} films (0.027 < x < 0.044) exhibiting ferromagnetism up to 250 K. Pinto et al. [2005] and Morresi et al. [2006] interpreted experimental observations in the framework of magnetic polaron excitation. However, further structural characterizations showed that (Ge,Mn) epilayers contained Ge_{3}Mn_{5} clusters surrounded with germanium containing almost 1.5\% of substitutional paramagnetic Mn atoms. Similar results were also reported by others (Bihler et al. 2006, Padovani et al. 2007, 2008). Finally, using high resolution TEM and energy dispersive x-ray spectroscopy, Sugahara et al. [2005] could show the phase separation between Mn-rich amorphous clusters and a pure Ge matrix in thin epitaxial (Ge,Mn) films [see Fig. 45 c)].

The second metallic (Ge,Mn) phase that usually forms during MBE growth is Ge_{4}Mn_{1}. This phase exhibits two magnetic transitions at 150 K (AF/FM) and \(T_C = 285\) K (FM/paramagnetic). Ge_{8}Mn_{11} precipitates were observed by Park in thin Ge_{1-7}Mn_{x} films (0 < x < 0.12) epitaxially grown between 250\degree C and 300\degree C [Park et al. 2001]. Using different methods to grow bulk single crys-
Since 2005, many groups have indeed reported the absence of any secondary phase precipitation in (Ge,Mn) films epitaxially grown at low temperature (<100°C). However, due to the very low solubility of Mn in Ge, the formation of Mn-rich nanostructures seems unavoidable mostly as a result of spinodal nanodecomposition. These nanostructures are so hard to detect that only highly sensitive techniques such as TEM with nanoscale chemical analysis, 3DAP or XRD/XAS using synchrotron radiation can be used. From the low temperature MBE growth of Ge_{0.93}Mn_{0.06} films, Sugahara et al. [2005] found elongated Mn-rich amorphous precipitates surrounded with pure germanium. These precipitates exhibit ferromagnetism up to 100 K as given by MCD measurements. Their diameter is close to 5 nm and the Mn content in between 10% and 20%. Using almost the same growth conditions, Ahlers et al. [2006], Bougeard et al. [2006], 2009 observed the formation of Mn-rich cubic clusters coherently strained on the Ge matrix in addition to the precipitation of Ge_{3}Mn_{5} clusters. Assuming zero Mn content in the Ge matrix, the maximum Mn content in the clusters is close to 15%. Their diameter is slightly less than 5 nm. Moreover they exhibit superparamagnetic behavior and a T_C value close to 200 K. Still using low temperature MBE growth and according to magnetic measurements only, Jaeger concluded that Ge_{1-x}Mn_{x} films (x=0.04 and 0.2) contain two clusters populations (undefined Mn-rich precipitates and Ge_{3}Mn_{5} clusters) along with diluted Mn atoms in the germainium matrix (Jaeger et al. [2006]). The overall population of Mn-rich precipitates behaves as a spin glass. The freezing temperatures are 12 and 15 K in Ge_{0.98}Mn_{0.02} and Ge_{0.95}Mn_{0.05} films, respectively. Finally Li also found elongated Mn-rich precipitates but coherently strained on the surrounding Ge matrix (Li et al. [2007]). In as-grown Ge_{0.95}Mn_{0.05} samples, these precipitates show ferromagnetism at low temperature: remanence vanishes above 12 K. Post-growth annealing at 200°C leads to a rather substantial improvement in magnetic and electrical properties by converting interstitial Mn into substitutional Mn. They exhibit remanence up to 125 K, the magnetic moment per Mn atom reaches 1.5 μ_B instead of 1.0 μ_B in as-grown samples. Moreover, annealing triggers strong positive MR and AHE in (Ge,Mn) films.

To summarize, the key issue of (Ge,Mn) material is Mn-dilution: the very low solubility of Mn in Ge always results in Mn segregation and in the formation of Mn-rich precipitates. Low temperature growth techniques favor the formation of metastable (Ge,Mn) phases. As a consequence, slight differences in growth parameters can result in much different magnetic and electrical properties. In the following sections, we show how to control spinodal nanodecomposition in (Ge,Mn). The structure, magnetic and electrical properties of (Ge,Mn) films with spinodal nanodecomposition are reviewed.
C. Growth and structure of thin (Ge,Mn) films with spinodal decomposition

1. Sample preparation

Growth was performed using solid sources MBE by co-depositing Ge and Mn evaporated from standard Knudsen effusion cells [Devillers et al., 2007a, 2006, 2007b; Jamet et al., 2006]. The deposition rate was kept constant and quite low (≈ 0.2 Å.s$^{-1}$). Germanium substrates were epi-ready Ge(001) wafers with a residual n-type doping and resistivity of 10$^{15}$ cm$^{-3}$ and 5 Ωcm respectively. After thermal desorption of the surface oxide, a 40 nm thick Ge buffer layer was grown at 250°C, resulting in a 2 × 1 surface reconstruction as observed by RHEED (see Fig. 46). Next, 80 nm thick Ge$_{1-x}$Mn$_x$ films were subsequently grown at low substrate temperature (between $T_g$ = 80°C and $T_g$ = 200°C). Mn content has been determined by x-ray fluorescence measurements performed on thick samples (≈ 1 μm thick) and complementary Rutherford back scattering (RBS) on thin Ge$_{1-x}$Mn$_x$ films grown on silicon. Mn concentrations range from 1% to 11% Mn.

![Ge buffer](image)

**FIG. 46** RHEED patterns recorded for different growth temperatures of Ge$_{1-x}$Mn$_x$. Adapted from Devillers et al., 2007a.

For Ge$_{1-x}$Mn$_x$ films grown at substrate temperatures below 180°C, after the first monolayer (ML) deposition, the 2 × 1 surface reconstruction almost totally disappears. After depositing few MLs (corresponding almost to 5 nm), a slightly diffuse 1 × 1 streaky RHEED pattern and a very weak 2 × 1 reconstruction (Fig. 46) indicate the predominantly 2D growth of a single crystalline film exhibiting the same lattice parameter as the Ge buffer layer. Increasing the layer thickness leads to an amplification of the surface roughness which is expected for the low temperature epitaxial growth of germanium [Charbon et al., 1989; Venkatasubramanian and Dorsey, 1993]. For growth temperatures above 180°C additional spots appear in the RHEED pattern during the Ge$_{1-x}$Mn$_x$ growth (Fig. 46). These spots correspond to the formation of very small Ge$_3$Mn$_5$ crystallites.

2. Morphology of (Ge,Mn) films

From TEM images, vertical elongated nanostructures, i.e., nanocolumns, were observed as shown in Fig. 47(a). These observations are in very good agreement with the theoretical predictions of Sec. II. The formation of the konbu phase as a consequence of 2D spinodal decomposition in (Ge,Mn) is clearly demonstrated here as well as in (Zn,Cr)Te in Sec. VII. Similar elongated nanostructures were also obtained in (Ge,Mn) by several groups in comparable growth conditions [Fig. 47(b-e)]. Nanocolumns span the entire Ge$_{1-x}$Mn$_x$ film thickness. Whatever the growth temperature and Mn concentration (except 0.1%) are, Ge$_{1-x}$Mn$_x$ films always exhibit the presence of nanocolumns with their axis along the growth direction [001]. Depending on growth conditions, the average columns diameter and density range between 2 and 7 nm, and between 10000 μm$^{-2}$ and 40000 μm$^{-2}$, respectively.

Further evidence of 2D spinodal nanodecomposition was provided by analyzing the periodic structures of the nanocolumns [Hai et al., 2011; Yada et al., 2011]. Figure 48(a) presents a plain-view TEM image showing that the nanocolumns are uniform in diameter (≈ 3 nm), and form either rectangular or triangular lattice structures, as indicted by thin dashed lines in Fig. 45(a). According to the Fourier transform of the TEM image, depicted in Fig. 48(b), the average distance between the nanocolumns is ≃ 9 nm.

The morphology of Ge$_{1-x}$Mn$_x$ films was further investigated using grazing incidence small angle x-ray scattering (GISAXS) from synchrotron radiation and atomic force microscopy (AFM), as depicted in Fig. 49.

As shown in Fig. 49(a), in addition to the specular reflection peak in the GISAXS spectrum, two pairs of correlation peaks were observed. The first one at large $q_z$ value corresponds to a correlation length of ≃ 10 nm which is the average distance between nanocolumns. The oscillations along $q_z$ are thickness oscillations and stand for the finite thickness of the Ge$_{1-x}$Mn$_x$ film. It demonstrates that nanocolumns span the entire film thickness. Furthermore there is a sizeable contrast of electronic density between nanocolumns and the surrounding matrix. At low $q_z$ value, a second pair of correlation peaks corresponds to a distance of almost 50 nm. Moreover these peaks are much more elongated along $q_z$ which is characteristic of a surface effect. Indeed, correlations are no more related to the presence of nanocolumns but to the surface roughness, as shown in Fig. 49(b). In order to investigate the columns chemical composition, electron energy loss spectroscopy (EELS) has been performed in cross section and plane view. The corresponding energy filtered TEM (EFTEM) images close to the Mn $L_{2,3}$ edge are displayed in Fig. 50 along with the corresponding Mn chemical profiles.
FIG. 47 (Color online) Characterization of Ge$_{1-x}$Mn$_x$ thin films grown by LT-MBE. (a) TEM plane view (up) and cross section (down) images of Ge$_{0.9}$Mn$_{0.1}$ containing Mn-rich nanocolumns. From Devillers et al., 2007a. (b) TEM cross section images of films with $x = 2.5, 4, 5.5, 7$, and 12% from top to bottom. The morphology of Mn-rich nanocolumns evolves from tadpole-like to cylinders when increasing Mn content. From Wang et al., 2010. (c) and (d) TEM images of Ge$_{0.93}$Mn$_{0.07}$ (from Li et al., 2007) and Ge$_{0.94}$Mn$_{0.06}$ (from Le et al., 2010), respectively showing the presence of nanocolumns. (e) Vertical self-assembly of roughly spherical Mn-rich clusters: TEM cross section image in dark field with $x = 7.3$% (left) and APT data for $x = 2$% (right). From Bougeard et al., 2009.

From EFTEM images, one can conclude that nanocolumns are Mn-rich and surrounded with an almost pure Ge matrix. The Mn signal in the Ge matrix is indeed below the resolution limit of EELS spectroscopy estimated to be around 1%. The most appropriate technique to estimate with more accuracy the Mn content in the Ge matrix is 3DAP. It leads to an average Mn concentration inside the Ge matrix below 0.05% (Mouton et al., 2012). As a consequence, the Mn concentration in the nanocolumns shown in Fig. 50 is close to 30%. Hence the composition of nanocolumns is close to Ge$_2$Mn. Depending on the growth conditions, nanocolumns with Mn concentrations between 5 and 50% could be grown, all of them exhibiting FM properties (Devillers et al., 2007a).

3. Lateral and vertical control of nanocolumns

In order to achieve lateral control of nanocolumns (size and density), the growth temperature and Mn concentration were varied to study their respective influence. For this purpose, two series of Ge$_{1-x}$Mn$_x$ films were grown at two different growth temperatures: $T_g = 100^\circ$C and $T_g = 150^\circ$C. In each case, the Mn concentration $x$ was varied between 1 and 11%. All the samples were then observed by TEM in plane view: they all exhibit Mn segregation in Mn-rich nanocolumns surrounded with an almost pure Ge matrix. The results are shown in Fig. 51.
FIG. 50 (Color online) Characterization of a Ge$_{0.94}$Mn$_{0.06}$ film grown at 130°C. (a) and (b) Cross sectional and plane view EFTEM images. (c) and (d) 3DAP reconstructed 3D images. From Mouton et al., 2012. Below EFTEM images are the corresponding Mn chemical profiles (bright areas are Mn-rich). From Jamet et al., 2006.

For samples grown at 100°C with Mn concentrations below 5% the nanocolumns mean diameter is 1.8 ± 0.2 nm. For higher Mn concentrations, it only slightly increases up to 2.8 nm at 11.3%. The evolution of columns density as a function of Mn concentration is also reported in Fig. 51. By increasing the Mn concentration up to 7% a significant increase of the columns density from 13000 to 35000 µm$^{-2}$ was observed. Then the density seems to reach a plateau corresponding to almost 40000 µm$^{-2}$. For Mn concentrations higher than 7%, the density slightly increases up to 40000 µm$^{-2}$.

Hence, increasing Mn concentration in samples grown at 100°C allows to control the columns diameter while keeping their density constant around 10000 µm$^{-2}$. To summarize, by combining two growth parameters (temperature and Mn concentration), it is possible to control independently the diameter and density of nanocolumns. This ability is of great importance from a fundamental point of view to characterize nanocolumns but also for potential applications in spintronic devices. In Fig. 51 the volume fraction occupied by the columns in the film is reported as a function of Mn concentration showing a clear linear dependence for Mn contents up to almost 7%. The non-linear behavior above 7% can indicate that the mechanism of Mn incorporation is different in this concentration range, leading to an increase of Mn concentration in the columns and/or in the matrix.

Considering the vertical geometry of nanocolumns and the Mn concentration contrast between the columns and the Ge matrix, vertical transport will mainly take place through nanocolumns. Since nanocolumns are FM (see Sec. VI.D), they could be used as conduction channels for spin injection in non-magnetic semiconductors such as Si and Ge. The vertical control of nanocolumns is thus an important issue from a fundamental point of view as well as for potential applications in spintronics. For this purpose, (GeMn/Ge) superlattices have been grown using different growth conditions. The (GeMn/Ge)$_4$ superlattice in Fig. 52(a) was grown in standard conditions (0.2 Å/s, 6% of Mn, $T_g = 100^\circ$C) leading to the formation of small nanocolumns with no vertical self-organization. The superlattice in Fig. 52(b) was grown at higher temperature (140°C) using a lower growth rate (0.13 Å/s) in order to favor the surface diffusion of Mn. Moreover the Mn content was increased up to 10% to grow larger Mn concentration in samples grown at 150°C allows to control the columns diameter while keeping their density constant around 10000 µm$^{-2}$. To summarize, by combining two growth parameters (temperature and Mn concentration), it is possible to control independently the diameter and density of nanocolumns. This ability is of great importance from a fundamental point of view to characterize nanocolumns but also for potential applications in spintronic devices. In Fig. 51 the volume fraction occupied by the columns in the film is reported as a function of Mn concentration showing a clear linear dependence for Mn contents up to almost 7%. The non-linear behavior above 7% can indicate that the mechanism of Mn incorporation is different in this concentration range, leading to an increase of Mn concentration in the columns and/or in the matrix.

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FIG. 52 (Color online) HRTEM images of (GeMn/Ge)₄ superlattices observed along the [110] crystal axis. From Devillers, 2008. In (a), no vertical correlation is observed whereas in (b) the vertical positions are clearly correlated and columns well aligned. In both cases, the germanium spacer is 5 nm thick.

columns. Assuming that the lattice parameters within the columns and the Ge matrix are different, larger columns lead to an enhanced residual strain field which favors the nucleation of nanocolumns on top of each other as in quantum dots superlattices (Tersoff et al., 1996). By this method, the vertical self-organization of nanocolumns could be achieved (Wang et al., 2011). Since the interface between nanocolumns and Ge spacer are quite abrupt, the diffusion of Mn along the growth direction is limited and then restricted to the top surface layer as discussed in the next section.

4. Two-dimensional spinodal decomposition

In order to understand the growth mechanism of nanocolumns, the first growth stage of (Ge,Mn) films on Ge(001) were investigated. For this purpose, scanning tunneling microscopy (STM) images have been recorded after depositing 0.44 Å of Mn on Ge(001) at 80°C [Fig. 53(a)].

They show the formation of self-assembled nanoislands. Their size and density are further comparable to the size and density of nanocolumns in as-grown (Ge,Mn) films [Fig. 53(b)]. Therefore, nanoislands are most probably Mn-rich nuclei at the origin of the formation of nanocolumns. Accordingly, this observation implies that the columns size and density are fully determined at the first growth stage. This growth mode leading to the formation of the konbu phase is summarized in Sec. II. It results from 2D spinodal decomposition due to Mn-Mn chemical pair attraction followed by layer-by-layer growth (Fukushima et al., 2006b; Zheng et al., 2010). The expected scenario for the growth of Mn-rich nanocolumns is thus illustrated in Fig. 54.

As a consequence, nanocolumns will always grow perpendicular to the initial surface. Therefore, they will exactly follow the initial surface roughness or facets (Fig. 54). In order to support this conclusion, thin (Ge,Mn) films were grown in standard growth conditions on a rough GaAs(001) surface as well as on a faceted Ge surface (Yu et al., 2010, 2011).

The resulting (Ge,Mn) films were then observed by TEM in cross section (Fig. 55). On GaAs(001), Mn-rich nanocolumns are clearly bent following the ini-
Fig. 55 (Color online) (a) Low and (b) HRTEM cross section images of a 80 nm thick Ge$_{0.9}$Mn$_{0.1}$ film grown at 100°C on GaAs(001). Before the growth, the native oxide layer was first thermally removed from the GaAs(001) substrate at 600°C leading to a rough Ga-rich surface. (c) AFM image and RHEED pattern of a faceted Ge surface obtained after anisotropic chemical etching revealing {113} facets. (d) TEM cross section image of a 80 nm thick Ge$_{0.94}$Mn$_{0.06}$ film grown at 100°C on the faceted Ge surface. After Yu et al. 2010.

5. Crystal structure of nanocolumns

The crystalline structure of (Ge,Mn) films was investigated using high resolution TEM observations as well as XRD and XAS. High resolution TEM observations in cross section show that Ge$_{1-x}$Mn$_x$ films grown below 180°C are single crystalline in epitaxial relationship with the substrate [Fig. 56(a)]. Furthermore nanocolumns can hardly be distinguished. The interface between the Ge buffer layer and the Ge$_{1-x}$Mn$_x$ film is flat and no defect propagates from the interface into the film. Diffraction scans performed in θ/2θ mode were acquired on a high resolution diffractometer using synchrotron radiation. The scans only reveal the (004) Bragg peak of the germanium crystal, confirming the good epitaxial relationship between the layer and the substrate, and the absence of secondary phases to a good accuracy proven by a high ratio of the main peak intensity to noise, of the order of 10$^7$ [inset in Fig. 56(a)].

Fig. 56 (Color online) (a) HRTEM image of a 80 nm thick Ge$_{0.94}$Mn$_{0.06}$ sample grown at 130°C. Inset: XRD showing the single (004) Bragg peak of pure Ge. (b) (h,k,0) map of the reciprocal space performed on a Ge$_{0.94}$Mn$_{0.06}$ film grown at 150°C. Adapted from Tardif et al. 2010b.

In order to get further insight into the crystalline structure of nanocolumns, grazing incidence SXRD was studied. The reciprocal space of a Ge$_{0.94}$Mn$_{0.06}$ film grown at 150°C [Fig. 56(b)] was mapped. In addition to the (400) and (220) Bragg peaks of germanium, two additional features were found: a broad (130) peak (which is forbidden in the diamond lattice) and a diffuse line connecting (400) and (220) Bragg peaks. At this stage, none of them could be related to the crystalline structure of nanocolumns (Tardif et al. 2010b). (220) and (400) Bragg peaks further exhibit correlation rings related to anisotropic elastic strain in the germanium matrix between nanocolumns (Tardif et al. 2010b). Since the internal crystalline structure of nanocolumns could not be resolved using XRD, three conclusions can be drawn: (i) nanocolumns exhibit the same diamond lattice as germanium with high Mn content, (ii) they are made of a metastable (Ge,Mn) phase showing a diffraction pattern similar to that of pure germanium and (iii) they are amorphous. In the following, the decisive role of the growth temperature on the columns crystalline structure is discussed.

High resolution TEM observations in plane view clearly demonstrate an evolution of the columns structure with growth temperature (Fig. 57). For $T_g = 100°C$, small nanocolumns are fully strained on the surrounding Ge matrix and clearly exhibit a perfect cubic crystal. For $T_g = 130°C$, crystalline columns were still observed. However, performing (220) and (220) Bragg filtering of diffraction spots, a pair of dislocations at the interface between the column and the Ge matrix is clearly visible. That leads to a lattice expansion of almost 4% in the column. Nanocolumns are thus only partially strained. For $T_g = 150°C$, nanocolumns are amorphous.
Finally, for samples grown at $T_g > 180^\circ$C or annealed at high temperature, nanocolumns have collapsed into stable Ge$_3$Mn$_5$ clusters. For annealed samples, these clusters are further well buried inside the germanium film away from the surface.

Since magnetic properties highly depend on the relative position of Mn atoms in the nanocolumns, the local chemical environment of Mn atoms was probed by EXAFS measurements (Rovezzi et al., 2008). By fitting EXAFS oscillations, the chemical environment of Mn atoms in the nanocolumns was found very similar to that of a Mn atom in an elementary tetrahedron of the Ge$_3$Mn$_5$ unit cell. This elementary tetrahedron corresponds to the building block of nanocolumns. However, at this stage, the structure of crystalline columns grown at low temperature still remains unknown. Nevertheless, a possible phase which exhibits a crystalline structure and composition compatible with the experimental findings was proposed by Arras et al. (2012). This phase is called the $\alpha$-phase and corresponds to a new class of materials based on the insertion of Mn atoms into a simple cubic crystal of Ge. Arras has shown that the incorporation of this phase (with a Mn content ranging from 10 to 50%) in the form of nanocolumns into the pure Ge matrix is energetically favorable (Arras et al., 2012).

D. Magnetic properties

In this section, the magnetic properties of four different Ge$_{1-x}$Mn$_x$ films grown at different temperatures are investigated: crystalline columns with and without partial relaxation through the formation of a pair of dislocations, amorphous nanocolumns and Ge$_3$Mn$_5$ clusters. For this purpose, highly sensitive SQUID magnetometry as well as electron paramagnetic resonance (EPR) were thoroughly used.

1. Crystalline (Ge,Mn) nanocolumns / Ge(001)

Magnetic measurements on diluted Ge$_{0.999}$Mn$_{0.001}$ films grown at 100°C are first reported. Only a paramagnetic signal at low temperature by SQUID and the 6 isotropic hyperfine absorption lines characteristic of paramagnetic Mn atoms in EPR spectra (not shown) could be measured. This result is in good agreement with TEM observations and EXAFS measurements. Indeed the absence of any contrast in TEM images rules out the presence of nanocolumns and EXAFS oscillations could be fitted with a single substitutional environment.

[FIG. 58 (Color online) Magnetic characterization of a Ge$_{0.9}$Mn$_{0.1}$ film grown at 100°C. (a) Temperature dependence of the saturation magnetization (in $\mu_B$/Mn). The applied field is 5 T. (b) Magnetization curves for different temperatures and (c) ZFC-FC measurements, pointing to with $T_C$approx 150 K of nanocolumns. The in-plane applied field is 0.015 T. Inset: magnetic remanence after maximum field cooling under 5 T. (d) ZFC measurements performed with the field parallel and perpendicular to the film plane. From Jain et al., 2010.]

For more concentrated films grown at $T_g = 100^\circ$C, small nanocolumns spanning the whole film thickness are observed by TEM. Moreover they are well crystalline and in perfect epitaxial relationship with the Ge matrix (see Fig. 57). Assuming that the Mn concentration in the Ge matrix below 0.05%, the resulting Mn content in the columns is close to 50%. SQUID measurements performed on a Ge$_{0.9}$Mn$_{0.1}$ film are reported in Fig. 58. Two different contributions in Fig. 58(a) can be identified: a paramagnetic signal from isolated Mn atoms and the FM nanocolumns. It has been shown recently that the paramagnetic Mn atoms are located within a thin shell around nanocolumns (Prestat et al., 2014). The $T_C$ magnitude of the columns is of the order of 150 K, according to Figs. 58(b,c) (Jain et al., 2010). In Fig. 58(b), magnetization curves are reversible above 15 K, also confirmed.
by ZFC-FC curves and dependence of remanence with temperature [Fig. 58(c)]. These nanocolumns are super-paramagnetic with a blocking temperature of 15 ± 5 K. Moreover the narrow shape of the ZFC peak is related to the narrow size distribution of nanocolumns grown in this temperature range (see Fig. 51). To determine the magnetic anisotropy of these columns, ZFC-FC measurements were performed with the field parallel and perpendicular to the film plane. The susceptibility perpendicular to the plane seems slightly higher than that in the plane but a strong diamagnetic signal from the substrate and paramagnetic signal from diluted Mn atoms makes it difficult to quantify precisely this anisotropy.

Moreover the narrow shape of the ZFC peak is related to isolated paramagnetic Mn atoms and a blocking temperature of 15 ± 9 K. The angle is defined between the [110] and [001] crystal axes respectively. For this purpose, it is assumed that nanocolumns are non-interacting and single domain at 5 K. The magnetic anisotropy energy of a single nanocolumn is written as:

$$K_2 = \frac{\mu_0 H_a}{4} \approx -0.11 \text{T for the fourth order with } \gamma/\gamma_e \approx 1.07$$

(where $\gamma$ is the gyromagnetic ratio of a free electron). Hence, the nanocolumns exhibit a perpendicular uniaxial anisotropy and a cubic anisotropy with easy axis along [111]. The presence of cubic anisotropy supports the crystallinity of nanocolumns. Also, cubic anisotropy and uniaxial anisotropy constants are of the same order of magnitude making the two crystal axes [110] and [001] close in energy. It thus explains the small difference between the ZFC curves for the field parallel and perpendicular to the film plane in the SQUID measurements of Fig. 58(d). Considering the saturation magnetization of these small nanocolumns $M_S = 140 \pm 20 \text{ kA/m}$, the uniaxial anisotropy constant can be calculated: $K_2 \approx -0.63 \times 10^4 \text{ J/m}^3$ which nicely corresponds to shape anisotropy $\mu_0 M_a^2/4 \approx 0.62 \times 10^4 \text{ J/m}^3$ assuming that nanocolumns are infinite cylinders (Aharoni 1996).

EPR technique is hence used to differentiate the FM signal of nanocolumns from the paramagnetic diluted Mn atoms and estimate magnetic anisotropy (Jain et al., 2010). The EPR spectra are observed as a function of the angle of applied magnetic field. The field is applied out-of-plane from the direction [110] to direction [110] passing through the [001] direction. In Fig. 59(b) the EPR spectra of a Ge$_{0.9}$Mn$_{0.1}$ film with crystalline nanocolumns exhibit the hyperfine Mn lines corresponding to isolated paramagnetic Mn atoms and also a weak FM line attributed to nanocolumns. The angular dependence of the resonance field in Fig. 59(b) is fitted using the Smit-Beljers formalism (Smit and Beljers, 1953). For this purpose, it is assumed that nanocolumns are non-interacting and single domain at 5 K. The magnetic anisotropy energy of a single nanocolumn is written as:

$$F = K_2 m_x^2 + K_4 (m_x^2 m_y^2 + m_x^2 m_z^2 + m_y^2 m_z^2)$$

where $x$, $y$, and $z$ are the [100], [010] and [001] crystal axes respectively. $m_x$, $m_y$, and $m_z$ are the coordinates of a unit vector along the column magnetization direction, $K_2$ and $K_4$ are second and fourth order magnetic anisotropy constants. Anisotropy fields are thus defined as: $\mu_0 H_{a2} = 2K_2/M_S$ and $\mu_0 H_{a4} = 2K_4/M_S$.

From EPR data, the anisotropy fields can be deduced from EPR data: $\mu_0 H_{a2} = -0.09 \text{T for the second order and}$

Finally in order to verify that the magnetic signal detected by SQUID magnetometry really comes from Mn-rich nanocolumns. For this purpose, XMCD measurements were carried out at the Mn $L_{2,3}$ edge. Data were acquired in the total electron yield mode. Measurements were performed on a Ge$_{0.9}$Mn$_{0.1}$ film grown at 100°C exhibiting different surface states: non-oxidized, partially oxidized and oxidized. The spectra are shifted vertically for the sake of clarity. The XMCD signal recorded at the Mn $L_3$ edge is then compared with the SQUID signal at 5 K. Both XMCD and SQUID signals are normalized to their maximum value. Adapted from Gambardella et al., 2005.)
addition, two positive MR contributions were observed: the first one arises from ordinary or Lorentz MR and the second one was attributed to geometrically enhanced MR as a consequence of the conductivity contrast between the nanocolumns and the matrix (Solin et al. 2000). Then AHE was demonstrated at low temperature but the interpretation of magnetotransport in such inhomogeneous system clearly remains a challenging task (Yu et al. 2011).

2. Crystalline (Ge,Mn) nanocolumns with partial relaxation / Ge(001)

$\text{Ge}_{0.94}\text{Mn}_{0.06}$ films grown in a narrow temperature range around 130°C exhibit partial lattice relaxation (see Fig. 57) and ferromagnetism above RT up to 400 K as shown in Fig. 61 (Jamet et al. 2006). This high-$T_C$ FM behavior was also observed in nanowires and quantum dots (Cho et al. 2008b; Kazakova et al. 2005; van der Meulen et al. 2009; Xiu et al. 2010a).

FIG. 61 (Color online) Magnetic characterization of $\text{Ge}_{0.94}\text{Mn}_{0.06}$ films grown around 130°C. (a) Temperature dependence of the saturation magnetization measured at 2 T. The inset shows the extrapolated matrix signal at low temperature after subtracting the nanocolumns magnetic signal. (b) ZFC-FC measurements performed at 0.01 T. Both curves superimposed. (c) Magnetization loops at 5, 100, and 400 K, after subtracting the diamagnetic contribution from the substrate. The inset demonstrates the easier saturation in-plane at 250 K. (d) Coercive field ($\mu_0H_C$) and remanent magnetization ($M_r/M_S$) versus temperature. $\mu_0H_C$ and $M_r/M_S$ are given with a precision of the order of 10%. From Jamet et al. (2006).

Figure (61a) shows the temperature dependence of the magnetization at 2 T, measured by SQUID magnetometry. The magnetic moment per Mn atom is 4.7 $\mu_B$ at 3 K. This value is close to 5 $\mu_B$ expected for isolated Mn$^{2+}$ ions according to Hund’s rule. The large magnetization at high temperature is consistent with a FM phase with $T_C > 400$ K. ZFC-FC curves superimpose from 3 to 300 K [Fig. 61(b)], thus ruling out the presence of superparamagnetic particles except if their blocking temperature exceeds 300 K. Considering the Mn distribution in the GeMn films, this high $T_C$ FM phase can be attributed to the nanocolumns. In the low temperature range, the magnetization increases when decreasing the temperature [inset in Fig. 61(a)]. The corresponding saturation magnetization is small ($\approx 9$ kA/m) and the additional susceptibility is described by a Curie-Weiss temperature between 10 and 15 K. A similar behavior was reported for a strongly diluted Ge$_{1-x}$Mnx layer. Assuming that isolated Mn atoms are present in the film, all magnetically active with a magnetic moment of 3 $\mu_B$ (Schulthess and Butler 2001), the Mn concentration in the nanocolumns reaches 33.7% (their composition is close to Ge$_2$Mn$_3$). The magnetic moment per Mn atom is close to 4.9 $\mu_B$ from the saturation magnetization $\approx$680 kA/m. Magnetization loops [Fig. 61(c)] all exhibit a pronounced S-shape, a low remanent magnetization and a low coercive field [Fig. 61(d): in-plane and out-of-plane directions act as hard magnetic axes. The saturation is easier with the field applied in-plane [inset in Fig. 61(c)].

Nanocolumns are very close to each other and a strong magnetostatic or carrier mediated coupling is expected. Energy calculations using Fourier formalism (Beleggia et al. 2004) were performed for an infinite square lattice of nanocolumns defined by the average experimental parameters (spacing 10 nm, diameter 3 nm and height 80 nm), taking into account the long range dipolar interaction and dipolar self energy of the nanocolumns. Three configurations have been tested: saturated out-of-plane (↑↓), saturated in-plane (→→) and anti-parallel out-of-plane with $M = 0(↑↓)$. Results are given in units of $\mu_0M_V^2V/2$ where $V$ is the volume of the nanocolumns and $M$ is their magnetization at saturation. The smallest energy, $E_{↑↓} \approx 0.01$, corresponds to the anti-parallel out-of-plane configuration: dipolar interactions favor an antiparallel arrangement of first neighbor nanocolumns. This finding is in good agreement with the low remanent magnetizations, low coercive fields and S-shaped in-plane and out-of-plane magnetization curves measured by SQUID. In real samples, the remanent magnetization is not zero because nanocolumns are randomly distributed, leading to many frustrated magnetic configurations. The model however fails to predict the right saturated configuration: we calculate $E_{↑↓} = 0.46$ and $E_{↑↑} = 0.08$, while experimentally the magnetization is easier to saturate in-plane ($E_{→→} < E_{↑↓}$). Thus an additional in-plane magneto-crystalline anisotropy has to be considered, competing with shape anisotropy, which favors the in-plane saturated state. This behavior has previously been observed in arrays of electrodeposited cobalt nanowires (Darques et al. 2004). In (Ge,Mn) nanocolumns, this magneto-crystalline anisotropy ori-
nates from the broken in-plane cubic symmetry (columns are fully strained in only one direction) leading to a natural uniaxial anisotropy combined with large magnetoelastic effects (columns are 4% contracted). This feature also explains the very high (at least higher than 400 K) blocking temperature of nanocolumns. As previously discussed in III-V and II-VI FM semiconductors (Dietl et al., 2001; Kossacki et al., 2004), strain can modify the valence band dispersion and induce a large magnetic anisotropy. Carrier mediated FM coupling between the nanocolumns would also favor an in-plane saturated state. It should also be noted in calculating the self-energy that the column aspect ratio can be overestimated since the columns are not perfect cylinders. Finally, these (Ge,Mn) films grown on Ge exhibit huge positive MR attributed to geometrically enhanced MR (Solin et al., 2000) and more importantly AHE that might be attributed to the spin polarization of holes (Jamet et al., 2000). That makes this system a promising candidate for spintronics applications.

3. Amorphous (Ge,Mn) nanocolumns / Ge(001)

For Ge$_{1-x}$Mn$_x$ films grown at higher temperatures ($T > 150^\circ$C) and high Mn concentration ($\geq 10\%$), amorphous nanocolumns are observed in TEM (see Fig. 57). As for small crystalline nanocolumns grown at 100$^\circ$C (see Sec. IV.D.1), the Mn concentration in the columns is close to 50%. These amorphous nanohubes have $T_C$ close to 170 K. The contribution from isolated paramagnetic Mn atoms is still observed at low temperature, as shown in Fig. 62.

The magnetic anisotropy of these columns is studied by EPR (Jain et al., 2010). The data are shown in Fig. 63 and the angular dependence of the resonance field is fitted using the Smit-Beljers formalism (Smit and Beljers, 1955) assuming that nanocolumns are non-interacting and single domain. A single perpendicular uniaxial anisotropy is found, the corresponding anisotropy field is: $\mu_0 H_{ax,2} \simeq -0.09$ T and $\gamma/\gamma_c \simeq 1.24$. From the saturation magnetization of amorphous nanocolumns $M_S = 220 \pm 20$ kA/m, the anisotropy energy density is calculated to be $K_2 \simeq -1.1 \times 10^4$ J/m$^3$. This value corresponds to that of shape anisotropy $\mu_0 M_S^2/4 = 1.5 \times 10^4$ J/m$^3$ of nanocolumns assuming their aspect ratio is high ($\approx 24$). As expected for amorphous nanocolumns, no cubic magneto-crystalline contribution is found. In the case of uniaxial magnetic anisotropy, the blocking temperature of nanocolumns can be easily estimated using the classical Néel-Brown formula (Jamet et al., 2001): $KV = 25 k_B T_B$, where $K$ is the anisotropy constant, $V$ the column volume, $k_B$ the Boltzmann constant and $T_B$ the blocking temperature. From the average diameter and length of nanocolumns (6 nm and 80 nm respectively) given by TEM observations, one can estimate their volume and the blocking temperature: $T_B \simeq 72$ K which corresponds to the second broad peak in the ZFC curve. The first peak with a maximum close to 25 K can correspond either to shorter magnetic nanocolumns with an average length of $\simeq (25/72) \times 80$ nm = 28 nm or to the manifestation of a disordered magnetic state within the thin shell around nanocolumns and containing substitutional Mn atoms (Prestat et al., 2014). In the first assumption it means that increasing the growth temperature partly activates Mn diffusion along the growth direction which leads to the formation of elongated clusters rather than continuous nanocolumns spanning the whole film thickness.
4. Ge₃Mn₅ clusters / Ge(001)

The growth of Ge₁₋ₓMnₓ films at high temperature (>180°C) on Ge(001) or annealing Ge₁₋ₓMnₓ films grown at low temperature above 600°C leads to the formation of randomly distributed spherical Ge₃Mn₅ clusters. The RHEED pattern of annealed samples is very similar to that of Ge as in HRTEM the clusters are observed away from the surface (Fig. 57).

The structure of Ge₃Mn₅ clusters was investigated using grazing incidence SXRD. The mean cluster diameter was estimated to be 10.6 ± 1 nm in agreement with TEM observations. Moreover 97% of the clusters have their c-axis perpendicular to the film plane and 3% in-plane. Finally, by searching for all possible Ge₃Mn₅ reflections in the plane parallel to the sample surface, a slight in-plane distortion of the hexagonal lattice was found (Jain et al., 2011). Magnetic properties were studied using SQUID magnetometry and EPR. Temperature dependent magnetization measurements clearly show the presence of two magnetic phases: the Ge₃Mn₅ with TₓC of 300 ± 5 K and the paramagnetic contribution of isolated Mn atoms. Hysteresis curves at 5 K clearly show that most of Ge₃Mn₅ clusters exhibit perpendicular magnetic anisotropy. Since the clusters are spherical, perpendicular anisotropy arises from magneto-crystalline anisotropy. This result is in good agreement with XRD data. Indeed, bulk Ge₃Mn₅ crystal is hexagonal with uniaxial magnetic anisotropy along the c-axis. From hysteresis loops recorded with the field perpendicular to the film plane, the fraction of magnetic signal from Ge₃Mn₅ clusters is estimated to be 70%. The remaining signal likely comes from amorphous Mn-rich precipitates with very low coercive field. From the anisotropy field µ₀Hₐ ≈ 0.6 T and using the bulk Mₛ value (1100 kA/m) (Forsyth and Brown, 1990), the anisotropy constant can be calculated: \( K = \mu_0 H_a M_S/2 \approx 3.3 \times 10^5 \, J/m^2 \) which is less than the reported bulk value 4.2 × 10⁶ J/m² (Tawara and Sato, 1963). This feature is explained by the in-plane distortion of the Ge₃Mn₅ crystal observed by XRD which is due to the epitaxy on the germanium matrix. It introduces an additional in-plane magneto-elastic component to magnetic anisotropy. Finally the same anisotropy field and perpendicular anisotropy were obtained from EPR measurements in good agreement with SQUID data (Jain et al., 2011).

VII. SPINODAL NANODECOMPOSITION IN (Ge,Fe)

A. Introduction

Apart from Mn other TM atoms such as Cr, Co or Fe have also been incorporated into Ge films to obtain FM properties (Kim et al., 2005; Kioseoglou et al., 2004; Tsui et al., 2004). In particular, FM order was predicted in Fe-doped germanium films (Weng and Dong, 2005; Zhou et al., 2004) and experimentally demonstrated in Fe-implanted films (Venugopal et al., 2002), Fe-doped germanium nanowires (Cho et al., 2008a) or quantum dots (Xiu et al., 2010b) as well as in Fe-doped bulk Ge single crystals (Choi et al., 2003).

In order to enhance the solubility limit of Fe, LT-MBE was used to grow Ge₁₋ₓFeₓ films with x up to 17.5% (Shuto et al., 2006b). In this section, we describe the growth, characterization, and magnetic properties of such Ge₁₋ₓFeₓ thin films, in particular, the relation between growth or annealing temperatures, defect formation, Fe distribution, and resulting magnetism (Shuto et al., 2006a,b, 2007, Wakabayashi et al., 2014a,b).

B. MBE growth

Ge₁₋ₓFeₓ thin films were grown on Ge (001) substrates by LT-MBE. After a LT Ge buffer layer was grown at the substrate temperature Tₘ = 100°C, a 16-nm-thick Ge₁₋ₓFeₓ film was grown at Tₘ = 100, 200, 300, or 400°C. The Fe content (x) varied from 2.0 to 24.0%. In-situ RHEED was used to monitor the crystallinity and surface morphology of the Ge buffer layer and the Ge₁₋ₓFeₓ film during the epitaxy. Although the diffraction pattern of the LT Ge buffer layer revealed intense and sharp 2 × 2 streaks, the pattern was quickly changed at the initial stage of Ge₁₋ₓFeₓ epitaxy. The Ge₁₋ₓFeₓ films grown at Tₘ = 100 and 200°C showed 2D growth mode and exhibited diamond-type crystal structure.

When the Ge₁₋ₓFeₓ film was grown at Tₘ = 300 (or 400°C), a spotty pattern was clearly observed in the RHEED image, indicating a 3D growth mode or surface roughening. Thus, the growth mode of the Ge₁₋ₓFeₓ film was changed from the 2D mode to the 3D mode between Tₘ = 200°C and 300°C. This growth mode change at around Tₘ = 300°C would be caused by the precipitates of Fe-Ge FM compounds in the film (crystallographic phase separation), as discussed below. This growth mode change at around Tₘ = 300°C would be caused by the precipitates of Fe-Ge FM compounds in the film (crystallographic phase separation), as discussed below.

C. Structural and chemical characterization

Figure 64(a) shows a HRTEM image of a Ge₁₋ₓFeₓ film (x = 9.5%) grown at Tₘ = 200°C, projected along the exact direction of Ge[110]. The image indicates that the Ge₁₋ₓFeₓ layer was homogeneously and epitaxially grown on the Ge buffer layer without any threading dislocations, and that the surface was atomically flat with a height of roughness less than 1 nm. These features were consistent with the RHEED observations, as mentioned earlier. However, when the lattice image was projected along the angle slightly tilted from the Ge[110] direction, cluster-like dark contrast regions appeared in the epitaxially grown Ge₁₋ₓFeₓ layer, as shown in Fig. 64(b). It is well recognized in TEM observations that the con-
Contrast due to the difference in chemical compositions is enhanced when the projection direction is slightly tilted from the exact zone axis. Using spatially resolved transmission electron diffraction (TED) and EDS, the crystal structure and chemical composition of the dark region [denoted as *1 in Fig. 64(b)] and surrounding bright region [denoted as *2 in Fig. 64(b)] were investigated. The TED image of point *1 (the right inset) showed the diffraction pattern of the diamond structure projected from its [110] direction with weak extra spots caused by stacking fault defects. On the contrary, point *2 (the left inset) in the bright region exhibited the diffraction pattern of the diamond structure without any extra spots. This means that no other crystal structures except the diamond crystal structure were formed both in the dark and in the bright regions, although the dark region included tiny stacking fault defects.

The local Fe composition at point *1 measured by EDS was $\sim 12\%$, which is higher than that ($\sim 4\%$) at point *2. Therefore, the contrast in the HRTEM image shown in Fig. 64(b) was due to the nonuniform distribution of the Fe composition. Similar structural features were also observed for a Ge$_{1-x}$Fe$_x$ film with $x = 6.0\%$, in which dark and bright contrast regions appeared in the TEM image caused by nonuniform Fe distribution. Tiny stacking fault defects were also detected in the dark contrast regions. The local Fe composition in the dark and bright contrast regions of this film was about 8.0% and 1.5%, respectively. Thus, both the Fe compositions in dark and bright contrast regions increased with increasing $x$.

Thus, RHEED, HRTEM, TED, and EDS studies lead to the conclusion that Ge$_{1-x}$Fe$_x$ films grown at 200°C on Ge(001) maintain the diamond crystal structure without any intermetallic Fe-Ge compounds or Fe inclusions. Similarly, the diamond structure is preserved under annealing (Ge,Fe) below 600°C [Wakabayashi et al., 2014a]. However, the films grown at 200°C or annealed exhibit a nonuniform distribution of Fe composition $x$, i.e., they undergo spinodal nanodecomposition in the form of chemical phase separation.

In worth noting that since EDS provides chemical information averaged over the specimen width, the amplitude of actual $x$ fluctuations can be even larger than implied by the values of $x$ determined for points *1 and *2.

D. Magneto-optical characterization

Figure 65(a) shows MCD spectra taken at 10 K in reflection configuration for Ge$_{1-x}$Fe$_x$ ($x = 9.5\%$) films grown at $T_g = 100, 200, 300$, and 400°C, with magnetic field perpendicular to the sample plane. As seen, when the Ge$_{1-x}$Fe$_x$ film was grown at $T_g = 100$ (or 200°C), its MCD spectrum showed a clear $E_1$ peak whose intensity was significantly enhanced compared with that of bulk Ge [uppermost curve in Fig. 65(a)], implying the presence of $s,p,d$ exchange splitting of bands. An offset-like broad signal was also observed in the whole energy range examined here. The magnetic-field dependence of the MCD intensity at the critical point $E_1$ exhibited a FM hysteresis loop, and the hysteresis shape at any other photon energies in the offset-like signal was identical with that at $E_1$, indicating the Ge$_{1-x}$Fe$_x$ film grown at $T_g = 100–200°C$ was magnetically homogeneous without Fe-Ge FM precipitates. Note that the $E_0$ of the sample was not clearly distinguished due to measurement-light interference caused by adsorbed moisture on the sample surface [Shuto et al. 2006b].

When the Ge$_{1-x}$Fe$_x$ film was grown at $T_g = 300$ (or 400°C), the MCD intensity at the critical point $E_1$ was not enhanced at all, but the MCD spectrum of bulk Ge was overlapped with an offset-like MCD signal: The magnitude of the $E_1$ peak [denoted as $\delta$ shown in Fig. 65(a)] that was measured from the bottom of the offset-like signal level was equal to that of bulk Ge. The MCD hysteresis loop measured at $E_1$ (2.30 eV) was not identical with that measured at other energy points (for example, 2.95 eV) as shown in Fig. 65(b), indicating crystallographic phase separation. The MCD hysteresis loop at $E_1$ can be divided into two components, i.e., the paramagnetic component of the host Ge matrix and the FM
FIG. 65 (a) Growth temperature dependence of the MCD spectra of Ge$_{1-x}$Fe$_x$ films grown at $T_g = 100 - 400^\circ$C, measured at 10 K with magnetic field of 1 T perpendicular to the sample plane with reflection configuration. (b) Magnetic-field dependence of MCD intensities at 2.30 eV ($E_1$) and at other energy point (2.95 eV) for the Ge$_{1-x}$Fe$_x$ ($x = 9.5\%$) films grown at $T_g = 300^\circ$C, where the data were normalized by their MCD intensities at the magnetic field of 0 T. Adapted from Shuto et al., 2006a.

Component of FM precipitates.

Figure 66 shows $T_C$ values of Ge$_{1-x}$Fe$_x$ films as a function of Fe content $x$, where $T_C$ was evaluated from the Arrott-plots using temperature-dependent MCD hysteresis loops at the $E_1$ critical point.

For the Ge$_{1-x}$Fe$_x$ films grown at $T_g = 200^\circ$C, $T_C$ linearly increased with increasing $x$ in the range between $x = 0$ and 17.5%. Above $x = 17.5\%$, $T_C$ was saturated at around 170 - 180 K [Shuto et al., 2007]. $T_C$ of Ge$_{1-x}$Fe$_x$ films grown at $T_g = 100^\circ$C also linearly increased with increasing $x$, but $T_C$ was significantly reduced in comparison with that of the samples grown at $T_g = 200^\circ$C.

When Ge$_{1-x}$Fe$_x$ films were grown at $T_g = 300$ and 400$^\circ$C, their $T_C$ values were quite higher than those of the samples grown at $T_g = 100$ and 200$^\circ$C. For example, $T_C$ values were 120 K and 200 K in the cases of $T_g = 300$ and 400$^\circ$C, respectively, even when $x$ was only 2.0%. On the contrary, $T_C$ values were below 10 K in the cases of $T_g = 100$ and 200$^\circ$C with $x = 2.0\%$. This behavior of $T_C$ at $T_g = 300$ and 400$^\circ$C can be attributed to the precipitates of FM compounds described above.

The apparent values of $T_C^{(app)}$ not only increases with the growth temperature but can be enhanced by annealing [Wakabayashi et al., 2014a]. In either case, the magnitude of $T_C^{(app)}$ correlates with the non-uniformity of the Fe distribution and the stacking fault density [Wakabayashi et al., 2014a]. Meanwhile, channeling Rutherford backscattering and particle-induced x-ray emission measurements revealed that about 15% of the Fe atoms reside in the tetrahedral interstitial sites and that the substitutional Fe concentration, in agreement with the decomposition scenario, is barely correlated with the magnitude of $T_C^{(app)}$ [Wakabayashi et al., 2014b]. At the same time, all the (Ge,Fe) films show a weak spin-glass-like behavior in a low-temperature region (below ~ 26 K), which is insensitive to the annealing temperature. However, the ferromagnetism associated with the non-uniform Fe distribution dominates magnetic properties of the system.

In summary, studies of Ge$_{1-x}$Fe$_x$ as a function of epitaxy temperature and TM content clearly show an evolution of the alloy character from a dilute magnetic semiconductor to a decomposed system, first involving chemical and then crystallographic phase separation. This evolution is accompanied by changes in spectral depen-
dencies of MCD that is initially enhanced in the region of optical transitions specific to the host semiconductor but as nanodecomposition progresses this magnetization dependent enhancement starts to extend over a wide spectral region indirectly pointing to a metallic character of Fe-rich regions. The apparent $T_C$ values determined from the MCD hysteresis loops show a clear correlation with the degree of nanocomposition, i.e., with the upper limit of local TM concentrations as well as with the appearance of structural defects.

VIII. SPINODAL NANODECOMPOSITION IN (Zn,Cr)Te

A. Introduction

Among various DMSs, Cr-doped II-VI compounds have been studied for a long time, attracting attention due to their peculiar magnetic and magneto-optical properties. Excitonic magnetospectroscopy indicated that the $p-d$ exchange interaction is FM (Mac et al., 1996), in contrast to the AF interaction in Mn-doped II-VI compounds. According to the Schrieffer–Wolff transformation, the FM $p-d$ interaction results from the position of the Cr 3d donor level above the top of the valence band (Kacman et al., 2001, Mizokawa and Fujimori, 1997).

Concerning the spin dependent coupling between Cr spins in (II,Cr)VI, it was theoretically predicted that the superexchange interaction becomes FM for $d^4$ ions in the tetrahedral crystal field (Blinowski et al., 1996). Later, a FM ordering of Cr spins in II-VI compounds was found by DFT first-principle calculations (Sato and Katayama-Yoshida, 2002). Hence, the theoretically expected ferromagnetism can be understood in the picture of double-exchange interaction between the Cr 3d electrons in the localized level within the band-gap (Fukushima et al., 2004). Sato and Katayama-Yoshida (2002) or as FM superexchange interaction of highly localized Cr spins (Blinowski et al., 1996). In either case, the FM interaction between Cr spins is short-range, extending over few nearest neighbors.

Experimentally, the FM behavior was observed in (Zn,Co)Te (Saito et al., 2002) and (Zn,Co)Se (Karczewski et al., 2003) with Cr contents reaching a few percent, and later ferromagnetism at RT was achieved in Zn$_{1-x}$Cr$_x$Te with a high Cr content $x = 0.2$ (Saito et al., 2003). The FM transition temperature $T_C$ was reported to increase almost linearly with Cr content $x$, reaching 300 K at $x = 0.2$, in agreement with the ab initio prediction (Fukushima et al., 2004). In addition, the intrinsic nature of ferromagnetism appeared to be confirmed by the similar magnetic-field dependencies of magnetization and MCD (Saito et al., 2003). However, according to Karczewski et al. (2003), the ferromagnetism in Zn$_{1-x}$Cr$_x$Se resulted from the precipitation of a FM compound, as $T_C$ was independent of $x$.

It was also found that the FM properties of (Zn,Cr)Te were significantly affected by the co-doping of donor or acceptor impurities; the ferromagnetism was suppressed by co-doping with acceptor impurity nitrogen (N) (Ozaki et al., 2005) while it was enhanced due to co-doping with iodine (I) donor impurities (Ozaki et al., 2006). In particular, for a fixed Cr content $x = 0.05$, the FM transition temperature $T_C$ increased up to 300 K with the co-doping of iodine at a concentration of the order of 10$^{18}$ cm$^{-3}$, from $T_C \sim 30$ K in a layer without co-doping (referred to as undoped sample). However, it was difficult to understand the realization of high-temperature ferromagnetism at a low Cr content, $x \approx 0.05$, which is below the percolation limit of the $z$ structure, if we assume a short-range interaction between Cr spins. Moreover, the combined analysis of the nano-scale chemical probing using TEM and the magnetization measurements with SQUID revealed that there is a systematic correlation between FM properties and the heterogeneity of the Cr distribution (Kuroda et al., 2007). In I-doped (Zn,Cr)Te crystals exhibiting ferromagnetism at RT, it was found that the Cr distribution is strongly inhomogeneous, i.e., nanoscale regions are formed, in which the concentration of Cr cations is high. According to the current understanding, in these Cr-rich volumes, Cr spins are ordered ferromagnetically due to the short distance between them. These FM clusters give rise to super-paramagnetism controlled by the magnetic anisotropy of individual Cr-rich NCs and interactions among them.

The electronic structure of the Cr ions and host bands were investigated in Zn$_{1-x}$Cr$_x$Te ($x = 0.03$ and 0.15) using XMCD and photoemission spectroscopy (Kobayashi et al., 2008). It was concluded that neither double exchange mechanism nor carrier-induced ferromagnetism are important, and the inhomogeneous distribution of Cr atoms dominantly influences the FM properties of Zn$_{1-x}$Cr$_x$Te.

In the case of (Zn,Cr)Te, similarly to other DMSs discussed in this survey, both chemical and crystallographic phase separations can be induced depending on Cr content and growth conditions (Kobayashi et al., 2012). The pairing energy of Cr ions, which is the driving force of the phase separation (see, Sec. II.B), is expected to vary with the Cr charge state (Dietl, 2006). Since the Cr 3d electrons form deep donor and acceptor levels in the band-gap of ZnTe (Godlewski and Kamińska, 1980), the studies of (Zn,Co)Te demonstrated that the shift of the Fermi level produced by a change in the concentration of electrically active defects or shallow impurities alters the Cr charge state, which affects the Coulomb interaction between Cr ions and hence their aggregation (Kuroda et al., 2007).

In this section, we review recent experimental studies on spinodal nano-decomposition in (Zn,Cr)Te grown by MBE (Ishikawa et al., 2009, Kobayashi et al., 2012, Kuroda et al., 2007, Nishio et al., 2009) as well as associated magneto-optical (Kuroda et al., 2007) and magnetotransport properties (Kuroda et al., 2007). In the first part (Sec. VIII.B) we describe the properties of (Zn,Cr)Te films grown in the [001] crystal-
lographic direction under the standard condition of MBE growth for the host binary compound ZnTe – at a substrate temperature of $T_s = 300^\circ$C and at a fixed growth rate of $\sim 1 \text{ Å/sec}$. We discuss also the effect of co-doping by I donors and N acceptors as well of varying the stoichiometry by changing the ratio of Zn and Te fluxes. The influence of the growth rate and temperature on the structural and magnetic properties of (Zn,Cr)Te:I is presented in Sec. VII.C. The accumulated data demonstrate the possibility of controlling the Cr aggregation by growth conditions and co-doping with shallow impurities, corroborating the theoretical considerations on the pairing energy presented in Sec. II.B as well as provide experimental illustration of the dairiseki and konbu phases discussed theoretically in Secs. II.C.1 and II.C.2. This control over the size and shape of Cr-rich regions substantiates the prospects of spinodal nanotechnology discussed in Sec. IX.

B. Chemical phase separation and its control by the Fermi level position

1. Visualization of Cr distribution

Figure 67 shows the EDS mapping images of the local Cr composition in I-doped, undoped, and N-doped Zn$_{1-x}$Cr$_x$Te films with relatively low and high values of the average Cr content $x \approx 0.05$ and 0.2. In the case of the low Cr composition $x \approx 0.05$, the Cr mapping images exhibit clear differences in the uniformity of Cr distribution between particular samples (Kuroda et al. 2007): uniform distributions in the undoped films grown under Te-rich flux (Fig. 67A) and in the N-doped film (D) versus non-uniform distributions in the undoped film grown under Zn-rich flux (B) and in the I-doped film (C). In the case of non-uniform distributions, the typical length scale of the compositional fluctuation is estimated to be 20-50 nm. According to the spot analysis of the EDS spectra, a typical value of the local Cr composition inside the Cr-rich regions is $x \approx 0.1$.

The TEM observation of the series of the films with the Cr composition $x \approx 0.05$ revealed that the structural properties are not much affected by the co-doping of iodine or nitrogen, or the growth under different Zn/Te flux ratios. As a typical example of the series of the films, the result of the I-doped film is shown in Fig. 68. The TEM image in Fig. 68(a) exhibits mostly zb crystalline structure, but there appear many stacking faults along the \{111\} planes. It was suggested that strain associated with a preferential formation of TM cation dimers with different crystallographic orientations at the end of the growth process. However, any apparent precipitates of other crystal structures were detected neither in the lattice image nor in the diffraction pattern.

FIG. 67 (Color online) Mapping images of the emission intensity of the EDS Cr K$_\alpha$ line for cross-sectional pieces of Zn$_{1-x}$Cr$_x$Te films with average Cr contents $x \approx 0.05$ (A-D) and $x \approx 0.2$ (E-H). A, E: undoped films grown under Te-rich flux; B, F: undoped films grown under Zn-rich flux; C, G, H: I-doped films with iodine concentrations of $\sim 2 \times 10^{18}$ cm$^{-3}$ (C, G) and $\sim 1 \times 10^{19}$ cm$^{-3}$ (H); D: N-doped film with a nitrogen concentration of $\sim 2 \times 10^{20}$ cm$^{-3}$. All these films were grown in the [001] crystallographic direction using GaAs (001) substrates under the standard condition of the MBE growth for ZnTe (the substrate temperature $T_s = 300^\circ$C and the growth rate around 1Å/sec). Adapted from Kuroda et al. 2007 and Ishikawa et al. 2009.

FIG. 68 TEM and electron diffraction images of the I-doped Zn$_{0.95}$Cr$_{0.05}$Te film (sample C in Fig. 67). Cross-sectional lattice image (a). Electron diffraction image from a region close to the interface with the ZnTe buffer layer (b) and from a region close to the surface (c). From Kuroda et al. 2007.
For the high Cr composition of $x \sim 0.2$, the Cr distribution is always non-uniform, irrelevant of the co-doping or the Zn/Te flux ratio, but the degree of inhomogeneity changes depending on the co-doping or the Zn/Te flux ratio [Ishikawa et al., 2009]. As shown in Fig. 67–H, the inhomogeneity of Cr distribution in the undoped film grown under Te-rich flux is not significant, whereas the Cr distribution in the I-doped films and the undoped film grown under Zn-rich flux is strongly inhomogeneous. In particular, the size of Cr-rich regions becomes larger in the I-doped film with a higher iodine concentration of $\sim 1 \times 10^{19} \text{cm}^{-3}$ (H). A typical length scale of the Cr-rich regions is estimated to be 30–70 nm. According to the EDS spot analysis, a maximum value of the local Cr composition in the Cr-rich regions is $x = 0.4–0.5$. It is concluded from these results that the inhomogeneity of Cr distribution is enhanced either by co-doping with iodine or by the growth under the Zn-rich condition for both low and high Cr contents.

2. Superparamagnetic behavior due to the Cr aggregation

The measurements of the temperature and magnetic-field dependencies of magnetization $M(T, H)$ using SQUID revealed that the magnetic properties also depend significantly on the Zn/Te flux ratio or co-doping with donor or acceptor impurities [Ishikawa et al., 2009; Kuroda et al., 2007]. In Fig. 69, the temperature dependence of magnetization is compared for undoped films grown under Te-rich flux and I-doped films. As seen, superparamagnetic features, such as the irreversibility between magnetizations determined under FC and ZFC conditions, and a cusp in the $M(T)$ dependence taken in the ZFC process, are more pronounced in the case of the I-doped films than for the undoped films grown under Te-rich flux. The magnitude of blocking temperature $T_b$, i.e., a temperature value corresponding to the maximum in the $M(T)$ dependence taken in the ZFC process, is much higher for the I-doped films than in the case of undoped films grown in the Te-rich flux. The paramagnetic Curie-Weiss temperature $\theta_p$ obtained from the linear fitting of the temperature dependence of the inverse magnetic susceptibility $\chi(T)$ is also higher in case of the I-doped films comparing to the undoped films grown under Te-rich flux.

The magnitudes of three characteristic temperatures, $T_b$, $\theta_p$, and the apparent Curie temperature $T_C^{(app)}$ deduced from the Arrott plot analysis of the $M(H)$ dependence, are plotted in Fig. 70 for samples with the average Cr contents $x \simeq 0.05$ and 0.2 as a function the iodine concentration and Te/Zn flux ratio. In the case of $x \simeq 0.05$, these temperatures are closely correlated with the uniformity of the Cr distribution: $T_C^{(app)}$, $T_b$, and $\theta_p$ assume maximum values at the iodine concentration $\sim 2 \times 10^{18} \text{cm}^{-3}$ for the I-doped films and Te/Zn flux ratio 0.7 (Zn-rich flux) for the undoped films, which correspond to the most pronounced inhomogeneity of the Cr distribution. On the other hand, in the case of $x \sim 0.2$, $T_C^{(app)}$ and $\theta_p$ are already high even in the undoped film grown under Te-rich flux and do not increase much for the growth under Zn-rich flux or the co-doping of iodine. In contrast, $T_b$ shows a sizable change depending on the flux ratio or the I-doping; in the undoped films, $T_b$ increases with the decrease of the Te/Zn flux ratio, and in the I-doped films, $T_b$ increases with the increase of iodine concentration at first and reaches a maximum at $\sim 5 \times 10^{18} \text{cm}^{-3}$, and then decreases gradually with a further increase of iodine content. These findings indicate that the magnitude of $T_b$ shows a close correlation with the degree of inhomogeneity in the Cr distribution at high Cr compositions.

![Fig. 69](image-url) Temperature dependence of magnetization and the inverse magnetic susceptibility of Zn$_{1-x}$Cr$_x$Te films: (a) undoped Zn$_{0.95}$Cr$_{0.05}$Te film grown under Te-rich flux (sample A in Fig. 67); (b) I-doped Zn$_{0.95}$Cr$_{0.05}$Te film (sample C); (c) undoped Zn$_{0.81}$Cr$_{0.19}$Te film grown under Te-rich flux (sample E); (d) I-doped Zn$_{0.81}$Cr$_{0.19}$Te film (sample H). Adapted from Kuroda et al., 2007.

These experimental observations demonstrate that the magnetic properties of (Zn,Cr)Te films are closely correlated with the uniformity of Cr distribution. In particular, non-uniform Cr distributions give rise to higher values of characteristic temperatures introduced above. Since the FM exchange interaction between Cr spins is considered to be of short-range [Bergqvist et al., 2004], the long-range FM order cannot be expected for average Cr compositions below the percolation limit for the nearest neighbor coupling in the fcc lattice, $x < 0.20$, if we assume a random distribution of Cr ions. On the other hand, if the alloy is phase-separated into regions with low and high Cr contents, Cr spins inside the Cr-rich regions can order ferromagnetically, so that the crystal containing these FM nanoclusters is expected to exhibit superparamagnetic features. Below the blocking temperature $T_b$, whose magnitude is given by the product of the mean cluster volume $V$ and the density of the magnetic anisotropy energy $K$, FM-like properties are observed in superparamagnetic systems, including magnetization hysteresis and remanence. A clear correlation...
between the values of $T_b$ and the inhomogeneity of Cr distribution confirms this interpretation. In addition, rather broad peaks in the $M(T)$ curves obtained under the ZFC condition reflect a dispersion in values of blocking temperatures. The apparent Curie temperature $T_C^{(app)}$, corresponding to temperature at which hysteretic behaviors due to the magnetic anisotropy of the clusters disappear entirely, is determined by an upper bound of the $T_b$ distribution. On the other hand, the paramagnetic Curie-Weiss temperature $\theta_P$, deduced from the fitting of the linear dependence in the $\chi^{-1}(T)$ curves in the high-temperature range, is determined by interactions between Cr spins inside the Cr-rich NCs and, therefore, is virtually independent of their volume $V$. This is consistent with the observation that $\theta_P$ is less dependent on the uniformity of the Cr distribution than $T_C^{(app)}$ and $T_b$.

Altogether, the data imply that zb Cr-rich (Cr,Zn)Te with the ZnTe lattice parameter is characterized by $T_C \approx 300$ K. A ferromagnetic ground state was theoretically predicted for such zb-CrTe (Zhao and Zunger 2005).

3. Mechanism of Cr aggregation

Similarly to the most combinations of magnetic elements and host semiconductors, the solubility of Cr in ZnTe is low and the incorporation of Cr beyond a certain limit results in the crystallographic or chemical phase separation. The driving force of the phase separation is an attractive interaction between magnetic cations. The key to understanding the observation that the uniformity of Cr distribution varies with the Zn/Te flux ratio or the co-doping of donor or acceptor impurities is the dependence of the attractive interaction on the Fermi level position within the band-gap. In the case of intrinsic ZnTe, Cr assumes the $2^+$ charge state. However, this charge state can be changed by trapping a hole or an electron since the substitutional Cr forms the deep donor Cr$^{2+/3+}$ and acceptor Cr$^{1+/2+}$ levels within the band-gap of the host ZnTe (Godlewski and Kamińska 1980). Therefore, the co-doping with shallow impurities changes the Cr valence and, thus, the Cr-Cr interaction. In particular, an additional Coulomb repulsion between those Cr ions that have trapped a carrier hinders the Cr aggregation, leading to a uniform distribution of Cr cations. This is in contrast to a non-uniform distribution driven by the attractive interaction between isoelectronic Cr$^{2+}$ ions, associated with the contribution of TM 3d states to bonding, as discussed in Sec. 3.13.

In order to understand the observed phenomena based on the above model, it should be taken into account that ZnTe crystals, due to the native formation of Zn vacancies, have a tendency to become p-type even without intentional doping (Baron et al. 1998). In (Zn,Cr)Te films grown under the Te-rich condition, the Zn vacancies are formed, so that a part of the Cr ions assumes the Cr$^{3+}$ charge state. The growth under the Zn-rich condition or co-doping with iodine donors restore the isoelectronic Cr$^{2+}$ configuration, as the Zn vacancies are suppressed by a surplus supply of Zn or compensated by the I donors. In the I-doped films, the degree of inhomogeneity and the value of the blocking temperature $T_b$ (and also $T_C^{(app)}$ for $x \approx 0.05$) attain a maximum when the iodine and Zn vacancy concentrations become equal, so that the charge state of all Cr ions is $2^+$. In contrast, co-doping with N increases the concentration of Cr$^{3+}$ ions (as observed by XMCD (Yamazaki et al. 2011)), which diminishes attractive forces between Cr cations and results in their uncorrelated distribution.

4. Magnetooptical and magnetotransport properties

Magnetooptical properties were investigated for crystals exhibiting a high temperature ferromagnetism assigned, as explained above, to a non-uniform Cr distribution. Figure 71 shows the result of the MCD measurement on an I-doped Zn$_{1-x}$Cr$_x$Te film with a relatively low Cr content of $x = 0.07$ and $T_C^{(app)} \approx 300$ K (Ozaki et al. 2006). As shown in Fig. 71(a), the MCD spectrum exhibits a broad band below the band-gap energy 2.38 eV of ZnTe, in contrast to a sharp peak in the spectrum of ZnTe. According to Fig. 71(b), the MCD intensity at a fixed photon energy shows virtually identical magnetic-field dependence as magnetization measured by SQUID. These features of MCD were also observed in undoped...
C. Crystallographic phase separation and konbu phase

1. Structural nanocharacterization

Structural, compositional, and magnetic properties were investigated for a series of I-doped Zn$_{1-x}$Cr$_x$Te films varying substrate temperature during the growth, growth rate, and crystallographic orientation of the substrate (Nishio et al. 2009). It was found that the substrate temperature is a critical factor controlling the phase separation. For the lower average Cr content $x \approx 0.05$, the structural properties of I-doped Zn$_{1-x}$Cr$_x$Te films change with the substrate temperature $T_\text{g}$, while the uniformity of Cr distribution is not much different. Figure 72 shows the results of TEM and EDS studies of I-doped Zn$_{1-x}$Cr$_x$Te ($x \approx 0.05$) films grown in the [001] direction at various values of $T_\text{g}$. As shown in the TEM and diffraction images (left column), the crystallinity exhibits a marked variation with $T_\text{g}$: at an intermediate temperature of $T_\text{g} = 270^\circ\text{C}$, the crystal consists dominantly of the zb structure, but the stacking faults along the [111] planes are observed in the lattice image and additional spots corresponding the triplet periodicity of the stacking faults appear in the diffraction image. The crystallinity is deteriorated by decreasing $T_\text{g}$ down to $240^\circ\text{C}$, exhibiting polycrystalline features in addition to the stacking faults, while it looks much improved by increasing $T_\text{g}$ up to $360^\circ\text{C}$, the TEM and diffraction images exhibiting almost perfect zb structure without the stacking faults. On the other hand, as shown in the Cr mapping images (right column), the Cr distribution is inhomogeneous in all the films, but the degree of inhomogeneity seems to be slightly reduced with the increase of $T_\text{g}$. The results of XAS measurements at Cr K-edge for the same series of I-doped Zn$_{1-x}$Cr$_x$Te ($x \approx 0.05$) films suggested a change in the local crystallographic structure depending on the substrate temperature (Ouchi et al. 2006), which is correlated with the results of the TEM observation.

A natural explanation of the above results would be that lattice defects appearing at low $T_\text{g}$ lower kinetic barriers for Cr diffusion, so that the Cr aggregation is efficient even at low $T_\text{g}$.

In contrast, for the higher average Cr content $x \sim 0.2$, the substrate temperature affects significantly the form of the phase separation (Nishio et al. 2009). Figure 73 presents Cr mapping images of the films grown onto either (001) or (111) substrates at intermediate and high substrate temperatures, $T_\text{g} = 300^\circ\text{C}$ and $360^\circ\text{C}$. As shown in Fig. 73(a), the Cr-rich regions form isolated NCs at $T_\text{g} = 300^\circ\text{C}$, whereas according to Figs. 73(b,c), in
the case of films grown at $T_g = 360^\circ$C, Cr-rich regions look like continuous nanocolumns aligned approximately along the (111) direction of the host crystal. As estimated by the EDS spot analysis, a maximum value of the local Cr composition is $x = 0.4$–0.5, both in the case of Cr-rich NCs and nanocolumns.

Figure 74 shows TEM and EELS images allowing to shed some light on the crystal structure of Cr-rich regions in an I-doped Zn$_{1-x}$Cr$_x$Te films ($x \approx 0.25$) grown at $T_g = 360^\circ$C (Kobayashi et al. 2012). In the TEM image in Fig. 74(a), Moiré fringes appear in many regions, which suggests that these regions are composed of a mixed phase with different crystal structures, pointing to the presence of crystallographic phase separation. By comparing the TEM image [Fig. 74(a)] with the EELS image [Fig. 74(b)] of the same area, it is confirmed that the Moiré regions in the TEM image correspond to the regions with a high value of Cr content. In a magnified lattice image in Fig. 74(c), the Moiré region is boarded by the two \{111\}$_{\text{zb}}$ planes, and there appears another region exhibiting a different structure, identified as a hexagonal structure from the arrangement of diffraction spots in the FFT image shown in Fig. 74(d). The lattice parameters deduced from the spacing between the spots are $c = 6.32$ Å and $a = 4.18$ Å, close to the values reported for bulk CrTe in the NiAs structure (Dijkstra et al. 1989; Ohta et al. 1993). This suggests that the precipitates consist of NiAs-type CrTe or of non-stoichiometric Cr$_{1-\delta}$Te in a hexagonal structure. According to the TEM and diffraction images in Fig. 74, the $c$-axis of elongated hexagonal NCs is nearly parallel to the \{111\}$_{\text{zb}}$ planes of the host. In the case of $T_g = 360^\circ$C, a 3D analysis using atom probe tomography revealed that the Cr-aggregated regions were formed as thin plates with the base plane nearly parallel to the \{111\}$_{\text{zb}}$ planes (Kodzuka 2012).

The above observations of the crystallographic phase separation support theoretical computations indicating that zb-CrTe with the lattice parameter of ZnTe is unstable against the formation of CrTe in the NiAs crystal structure (Zhao and Zunger 2005).

In the conventional $\omega$–2$\theta$ XRD scan, which probes XRD from the film plane, only maxima corresponding to the zb host crystal were detected for the (001) Zn$_{1-x}$Cr$_x$Te:I films with $x \approx 0.2$. However, hexagonal Cr$_{1-\delta}$Te precipitates that have principal diffraction planes inclined against the film plane, can be detected in the $\omega$-scan, as shown in Fig. 75. This measurement was performed with the incident and reflected x-ray in the (110) plane of the host zb structure. By locking 2$\theta$ to the values corresponding to the (1101) and (1102) planes of the hexagonal Cr$_{1-\delta}$Te, the diffractions from these planes were detected in an almost symmetric way in respect to $\omega$. The values of $\omega$ of the diffraction peaks are close to the ones expected from the crystallographic relation of
these NCs to the host crystal revealed by the TEM observation. On the other hand, in the same ω-scan measurement in another configuration with the incident and reflected x-ray in the (110)zb plane, the intensity of the diffraction from the hexagonal nanocrystals was much reduced (Kobayashi et al., 2013). This result suggests that the hexagonal Cr$_{1-\delta}$Te tends to stack preferentially on the (111)$_{zb}$ plane [or Zn-terminated (111)A plane] rather than (\bar{1}11)$_{zb}$ plane [or Te-terminated (111)B plane]. This preference could be understood from the arrangement of atoms on the interface between the hexagonal Cr$_{1-\delta}$Te and the host zb crystals.

The intensity of the above diffraction from the hexagonal Cr$_{1-\delta}$Te gives us an estimate of the amount of the precipitates formed in the crystal. The ω-scan measurement on the series of Zn$_{1-x}$Cr$_x$Te:I films grown at different substrate temperatures revealed how the amount of the precipitates depends on the growth temperature. As clearly seen in Fig. 76, in which the diffraction intensity from the (1101) plane of the hexagonal Cr$_{1-\delta}$Te is plotted as a function of the substrate temperature $T_g$, the hexagonal precipitates are formed in a larger quantity at a higher $T_g$.

As described above, it was revealed that the substrate...
temperature during the growth affects the Cr aggregation significantly; the Cr-aggregated regions are formed in almost spherical NCs at a low $T_g$ while they are formed in thin plates at higher $T_g$. In addition, the amount of the hexagonal precipitates increases with the increase of $T_g$. The observed variation in the shape of Cr-aggregated regions with the substrate temperature reflects a difference in the dimensionality of the spinodal decomposition, which results in the formation of the daireishi or konbu phase, as discussed in Secs. II.C.1 and II.C.2. According to a theoretical consideration (Fukushima et al. 2006b), the spinodal decomposition in the layer-by-layer growth mode results in the formation of one-dimensional columnar regions with high content of the magnetic element. With an enhanced migration of impinging atoms on the growing surface at a higher substrate temperature, Cr atoms tend to aggregate in such places on the surface where Cr-aggregated areas are already formed in the layer just below the growing surface. As a result, the Cr-rich regions form continuous nanocolumns, instead of isolated clusters appearing in the case of slow surface migration. Once Cr-aggregated regions are formed inside the crystal, they can transform at sufficiently high $T_g$ into a stable Cr$_{1-x}$Te hexagonal compound that assumes crystal orientation insuring the best much of atom positions with the host, i.e., minimizing the interfacial energy.

2. Magnetic properties

Three characteristic temperatures $T_C^{(app)}$, $\theta_P$, and $T_b$ are presented in Fig. 77 as a function of $T_g$ for the two series of I-doped Zn$_{1-x}$Cr$_x$Te films with the low and high average Cr contents of $x \simeq 0.05$ (full symbols) and 0.25 (empty symbols). In the case of $x \simeq 0.05$, the film grown at the lowest $T_g$ of 240°C did not exhibit ferromagnetism even at 2 K, presumably due to the deterioration of crystallinity. In contrast, the films obtained at $T_g$ from 270°C to 390°C show high temperature ferromagnetism, consistent with the presence of Cr-rich regions. The observed values $T_C^{(app)} \simeq 300$ K and $\theta_P \simeq 330$ K for films with $x \simeq 0.25$ are consistent with the fact that Cr$_{1-x}$Te in bulk form exhibits ferromagnetism with $T_C = 325$–360 K for a relatively a small amount of Cr deficiency (Shimada et al. 1996), though $T_C$ decreases when the amount of Cr deficiency increases further on (Ohta et al. 1993). Furthermore, in agreement with TEM data pointing to smaller volumes of Cr-rich regions in the case of samples with lower $x$, the magnitudes of $T_b$ are significantly lower for $x \simeq 0.05$ comparing to the values found for $x \simeq 0.25$. However, rather surprisingly, $T_C^{(app)}$ and $\theta_P$ tend to decrease from 300 K down to 250 K with $T_g$ for samples with $x \simeq 0.05$. This result points to a complex interplay between the degree of host crystallinity, TM aggregation, and resulting $T_C$ of embedded NCs.

It can be expected that strain and shape of NCs affect their magnetic anisotropy. Figure 78 presents magnetization loops $M(H)$ for magnetic fields perpendicular and parallel to the film plane for the I-doped (111) Zn$_{1-x}$Cr$_x$Te film ($x = 0.22$), in which Cr-rich NCs show the elongated shape with long axes almost perpendicular to the film plane (Nishio et al. 2009). As seen, hysteretic behaviors are more pronounced (i.e., the coercive force is larger) for the perpendicular magnetic field. This suggests that the easy direction is parallel to the long axis of the NCs, the expected result for the shape-dependent direction of the demagnetization field and weak in-plane crystalline magnetic anisotropy.

D. Summary

The comprehensive studies of (Zn,Cr)Te described in this section show that the Cr distribution is affected significantly by co-doping with donor or acceptor impurities or by the growth under different Zn/Te flux ratios. This behavior originates from the influence of co-doping and growth conditions upon the position of the Fermi level in the band gap, which controls the Cr charge state: from Cr$^{+1}$ for high I donor concentrations to Cr$^{3+}$ at high density of N acceptor impurities or Zn vacancies. These findings corroborate the influence of Coulomb interactions upon the chemical forces between TM ions. The magnetic properties are closely correlated with the heterogeneity of the Cr distribution. In particular, the Cr-rich regions give rise to the appearance of high-temperature ferromagnetism. The systematic investigations on (Zn,Cr)Te films grown under various MBE conditions revealed that the growth temperature plays a crucial role in the phase separation: the crystallographic structure and the shape of the Cr-rich regions change with the substrate temperature during the growth. The ability to fabricate in a self-organized fashion hybrid sys-
IX. PROSPECTS OF SPINODAL NANOTECHNOLOGY

It is believed that the application of embedded metallic NCs will revolutionize the performance of various commercial devices, such as flash memories. Similarly colloidal or embedded semiconducting NCs, i.e., semiconductor quantum dots and nanowires, are extensively studied as perspective media for lighting, low current semiconductor lasers, solar cells, single-photon emitters and detectors, quantum processors and memories.

In view of the results presented in the previous sections, the incorporation of TM impurities into semiconductors opens the door to fabrication of dense arrays of TM-rich NCs coherently embedded into a semiconductor matrix. Depending on growth and processing conditions as well as on the combination of host semiconductor, TM impurity, and co-doping the self-assembled NCs can be metallic or semiconducting, form nanodots or nanocolumns, exhibit FM, ferrimagnetic, or AF spin ordering persisting usually to above RT. Thus, spinodal nanotechnology not only allows one to explore the feasibility of device fabrication with a new and versatile bottom-up method but also enlarges considerably the spectrum of possible functionalities offered by nanoscale heterogeneous systems (Dietl, 2008c; Katayama-Yoshida et al., 2007).

As an example, Fig. 79 presents results of Monte Carlo simulations in which the Cr flux was altered during the 2D growth of CrTe nanocolumns (the konbu phase) embedded in ZnTe (Fukushima et al., 2007). This example suggests that dense arrays of various nanodevices can be fabricated by selecting appropriate growth protocols. For instance, by reducing the flux for time corresponding to the growth of a few monolayers, the formation of magnetic tunnel junctions is predicted for nanocolumns of a FM metal (Fukushima et al., 2007). Such junctions can serve for low-power high-density magnetic storage, including spin-torque magnetic random access memories and, if sufficiently high TMR will be found, for the field programmable logic, i.e., TMR-based connecting/disconnecting switches (Reiss and Meyners, 2006), and even all-magnetic logic, characterized by low power consumption and radiation hardness. Furthermore, nanocolumns might form racetracks for domain-wall based 3D memories (Thomas et al., 2007).

Another kind of possible spintronic applications makes use of the coupling between FM leads and carriers in a semiconductor matrix. In particular, in the proposal of a scalable processor (Dery et al., 2007), the magnetization-dependent interaction between neighbor FM contacts is mediated by spin currents injected from the FM contact.

FIG. 78 (Color online) Magnetization loops in Zn$_{0.78}$Cr$_{0.22}$Te:I film grown in the [111] direction at $T_g = 360\, ^\circ\, C$ (the same film as shown in Fig. 73(c)). The upper (bottom) panel shows the results obtained for magnetic fields parallel (perpendicular) to the growth direction. The coercive field $H_c$ for the parallel configuration ($\mu_0 H_c = 0.33\, T$ at 2 K) is much larger than for the perpendicular configuration ($\mu_0 H_c = 0.14\, T$ at 2 K). From Nishio et al., 2009.

FIG. 79 (Color online) Demonstration of the nanocolumn shape control by Monte Carlo simulations of (Zn,Cr)Te epitaxy (the konbu phase). Positions of Cr cations are shown. Nano-scale seeding by zinc-blende CrTe (a). During the deposition (between two arrows), the Cr concentration is reduced to control the shape of the metallic and FM CrTe nanocolumns embedded in ZnTe (b). Adapted from Fukushima et al., 2007.
to the semiconductor. Furthermore, in the pioneering design of quantum processors involving the couplings between single spins on quantum dots, nanomagnets serve to introduce differences in spin resonance frequencies of particular dots, which makes it possible to address individual spins (Loss and DiVincenzo 1998). Actually, top-down methods were already employed to pattern nanostructures with tiny magnets whose stray fields controlled spin currents (Wrobel et al. 2004) and spin resonance frequencies (Pioro-Ladriere et al. 2008) at the nanoscale.

As already discussed in Secs. III, VI, VII and VIII, a number of decomposed alloys exhibits spin-related magnetotransport and magneto-optical phenomena typically persisting up to \( T_C \) of the relevant NCs. In particular, AHE was observed in (Ge,Mn) (Jamet et al. 2006) and (Zn,Cr)Te (Kuroda et al. 2007). A sizable magnitude of AHE together with heterogeneity-induced mixing between diagonal and off-diagonal conductivity components, resulted in a large positive MR of (Ge,Mn) (Jamet et al. 2006). A related effect was also observed in granular films with MnSb (Akinaga et al. 2000b) and MnAs (Yokoyama et al. 2000) NCs. Furthermore, TMR was found in a device containing MnAs and GaAs:MnAs electrodes (Hai et al. 2006). All these findings could possibly be exploited in magnetic field sensors with characteristics (e.g. impedance) that could be tailored over a wide range.

At the same time, as elaborated in Secs. III, VI, VII and VIII, magnetic circular dichroism (MCD) was reported for decomposed (Ga,Mn)As, (Ge,Mn), (Ge,Fe), and (Zn,Cr)Te as well as for other systems such as (Ga,Mn)P (Monette et al. 2010). A combination of strong and spectrally broad MCD specific to FM metals and weak losses characterizing the semiconductor hosts suggests possible applications of decomposed semiconductor alloys as optical isolators (Amemiya et al. 2006) as well as 3D tunable photonic crystals and spatial light modulators for advanced photonic applications (Park et al. 2002a).

Metallic nanocolumns and nanodots could also serve as high quality nanocontacts in nanoelectronics and optoelectronics as well as metallic elements in nanoplasmatics. Dense arrays of nanocolumns are also attractive for thermoelectric applications (power generators and coolers) as a specific form of density of states in 1D systems is expected to result in a significant enhancement of the Seebeck and Peltier effects (Shinya et al. 2014; Vu et al. 2011). Furthermore, the growth process presented in Fig. 29 can be adapted to fabricate devices for all-metal nanoelectronics based, for instance, on single-electron transistors. Actually, the Coulomb blockade was demonstrated for a single MnAs NC, tunnel-coupled to MnAs electrodes patterned lithographically (Hai et al. 2010). A long spin relaxation time, of the order of 10 \( \mu s \), was evaluated from these data.

If, in contrast, nanocolumns were semiconducting, appropriate band gap engineering could improve efficiency of photovoltaic solar cells by leading to spatial separation of photoelectrons and photoholes in such all-semiconductor superstructures (Oshitanı et al. 2011). As a one more example of possible functionalities worth mentioning is the case of catalysts for automotive-emissions control. Here, by using decomposed alloy with spatially separated NCs containing the relevant metal, e.g., Pt, the destructive process of metal agglomeration could be much reduced (Hamada et al. 2011; Kizaki and Katayama-Yoshida 2013; Kizaki et al. 2008).

### X. SUMMARY AND OUTLOOK

We have reviewed the recent progress in the understanding of high-temperature ferromagnetism in a range of magnetically doped semiconductors, including primarily (Ga,Mn)As, (Ga,Mn)N, (Ga,Fe)N, (Ge,Mn), (Ge,Fe), and (Zn,Cr)Te. As we have emphasized, the abundance of contradicting views on the mechanisms accounting for surprisingly large magnitudes of Curie temperature \( T_C \) resulted from intertwined theoretical and experimental challenges requiring the application of cutting-edge computational and materials nano-characterization methods that have mostly become available only recently. In this way, semiconductors doped by transition metals (TMs) have emerged as outstanding systems to test our understanding of unanticipated relationships between (i) growth conditions, co-doping, and processing; (ii) alloy nanostructure, and (iii) pertinent macroscopic properties.

The key ingredient of the materials families that have been described in this review is spinodal nanodecomposition leading to the formation of TM-rich nanocrystals (NCs) either commensurate with the TM-depleted host (chemical phase separation) or precipitating in another crystallographic and/or chemical form (crystallographic phase separation). Whether magnetic ions are distributed randomly or form aggregates is determined by the competition between attractive forces among TM ions (revealed by \( ab \) initio computations) and kinetic barriers for TM diffusion at the growth surface or in the bulk. Accordingly, the alloy decomposition is more efficient at high growth temperatures and slow growth rates, and depends also on the Fermi level position (co-doping) that changes TMs valence and their diffusion coefficients. Remarkably, according to both theoretical simulations and experimental results the TM-rich regions (condensed magnetic semiconductors - CMSs) assume the form of either nanodots (the \( dairei\)seki phase) or nanocolumns (the \( konbu \) phase). Furthermore, the nanodots can be distributed randomly or accumulate in a plane adjacent to the interface or surface. Similarly, nanocolumns can extend along the growth direction or assume another spatial orientation.

A rich spectrum of forms assumed by spinodal nanodecomposition, such as chemical phase separation or aggregation of precipitates in one plane, have elucidated
the reason why uncovering the presence of a non-random distribution of magnetic ions was so challenging in DMS research and, in particular, why the application of standard in-house structure characterization techniques (e.g., x-ray diffraction) was often misleading. The comprehensive element-specific nano-characterization investigations described in this review have demonstrated the existence of a tight correlation between the presence of TM-rich NCs and high-$T_C$ ferromagnetism. Within this scenario the puzzling $T_C$ independence of the average TM concentration $x$ has been explained. However, it has been found that the reverse is not true, i.e., variations of $T_C$ with $x$ do not prove a uniform distribution of TM ions. Furthermore, according to the evidence, spontaneous magnetization of decomposed systems is usually smaller than expected from the TM concentration, as typically a part of TM ions is distributed randomly giving rise to a paramagnetic, and not FM or superparamagnetic response. It also happens that NCs formed by spinodal decomposition are weak ferromagnets or even antiferromagnets [see, e.g., the data for (Ga,Fe)N in Sec. V] or that coupling between them results rather in a superferromagnetic behavior than in a superparamagnetic phase [Sawicki et al. 2013].

It was often argued that the presence of the magnetic circular dichroism (MCD) points to a random distribution of TM ions over cation sites (Ando 2006). Actually, because of boundary conditions for electromagnetic waves, the dielectric function of heterogeneous media contains contributions from all constituents. Hence, TM-rich NCs not only give a specific contribution to the magnetic response but, in general, can also affect, in a magnetization-dependent fashion, magneto-optical properties, as observed for (Ga,Mn)As, (Ge,Mn), (Ge,Fe), and (Zn,Cr)Te (Secs. III, VI, VII, and VIII, respectively). In particular, metallic NCs rather than enhancing MCD only at host critical points of the Brillouin zone, produce a large MCD signal over a wide spectral range. However, no enhancement of MCD has been reported for (Ga,Mn)N and (Ga,Fe)N (Secs. IV and V, respectively). Presumably, in the case of (Ga,Mn)N, Mn-rich NCs are wide band-gap insulators, whereas in (Ga,Fe)N the NCs aggregate in a narrow plane parallel to the film surface, which reduces their coupling to light.

A similar question arises to what extent magnetotransport studies could tell whether the TM distribution is uniform or one deals rather with spinodal nanodecomposition. A weak negative contribution to the Hall signal, resembling the anomalous Hall effect (AHE), can originate from stray fields generated by magnetic NCs. More often, spin-depending coupling between host charge current and magnetic NCs results in a sizable AHE, as observed in (Ge,Mn) and (Zn,Cr)Te, and mentioned in Secs. VI and VII. Particularly challenging is the question of magnetoresistance (MR). Here positive MR, specific to semiconductor-metallic nanocomposite (Solin et al. 2000), may appear, particularly if the magnitude of AHE is significant, the effect being discussed for (Ge,Mn) in Sec. VI. Moreover, as in other non-magnetic and magnetic semiconductors, one expects a range of MRs associated with quantum localization phenomena (Dietl 2008b). In particular, strong spin disorder scattering near $T_C$ accounts for colossal negative MR. However, a weak negative MR away from $T_C$, according to straightforward and parameter-free theoretical modeling, originates rather from the influence of magnetic flux upon interference of scattered carrier de Broglie waves (weak localization MR) than from spin disorder scattering. This is in contrast with magnetically doped metals in which effects of spin disorder scattering dominate, as competing scattering mechanisms and associated localization effects are typically weak.

Despite the recent progress, there is a number of challenging and open questions ahead. As an example we note that an important theoretical issue is the determination of kinetic barriers for TM diffusion at the growth surface and in the bulk, crucial parameters to simulate quantitatively the NC assembly during epitaxy, co-doping, or post-growth annealing. Furthermore, since CMSs assume a form imposed by the matrix, their chemical composition and associated properties are by no means obvious. In particular, it is hardly known whether open $d$ shells remain localized in CMSs (as in the parent DMS) or rather a Mott-Hubbard transition occurs, leading to itinerant magnetism specific to certain end compounds such as MnAs and CrTe. It was actually suggested that Mn-rich zinc-blende (zb) NCs in decomposed (Ga,Mn)As contain only about 20% of Mn and retain the properties of (Ga,Mn)As in which spins are localized (Lawniczak-Jablonska et al. 2011). A related question concerns the crystalline magnetic anisotropy of particular combinations of CMSs and hosts. This anisotropy, together with shape anisotropy and dipolar or exchange coupling between NCs, accounts for macroscopic magnetic properties, including the apparent magnitude of $T_C$ and the character of magnetic hysterescys. A theoretical and experimental evaluation of this anisotropy awaits for future studies.

Furthermore, FM-like features brought about by uncompensated spins at the surface of antiferromagnetic (AF) NCs, as discussed theoretically (Dietl et al. 2007), have not yet been put into evidence experimentally in the materials considered here. We also note that the FM proximity effect or the exchange bias in the case of AF CMSs can lead to spin polarization of a semiconductor surrounding a given NC. Such induced polarization will persist up to the spin ordering temperature of the CMS and, according to the RKKY theory, will extend over a distance of the order of the inverse Fermi vector in the presence of band carriers and perhaps over two or three bond lengths in their absence. This effect was examined in Fe/(Ga,Mn)As heterostructures (Macherozzi et al. 2008) but not yet in decomposed alloys, in which it can lead to an erroneous conclusion that the host is intrinsically FM up to high temperatures.

Whilst theoretical and experimental results described
in this review have concerned with a limited set of compounds, there is a ground to expect that the developed methodology, the observed phenomena, and the conclusions drawn from theoretical and experimental results apply to a much broader class of magnetically doped materials and also to many other alloys. We are quite certain that with a further development and with a wide-spread use of powerful nanocharacterization tools, the family of decomposed alloys will steadily grow. Future work will also show the role of structural defects, residual impurities (e.g. H) or contaminants (e.g. Fe-rich nanoparticles) in the appearance of high-$T_C$ ferromagnetism in semiconductors and oxides.

It is clear that the understanding of the origin of high-$T_C$ ferromagnetism and detailed knowledge on the TM distribution are preconditions for a meaningful design of devices that could exploit the outstanding properties of magnetically doped semiconductors and insulators. As discussed in Sec. [X] the demonstrated and predicted functionalities of decomposed magnetic alloys might be of interest not only for spintronics but also for electronics, photonics, plasmonics, photovoltaics, thermoelectrics, and catalysis. In general terms, the future studies of these systems will contribute to address the timely question on to what extent and when bottom-up technologies will start to be competitive with the top-down approaches dominating today.

List of abbreviations

1D, 2D, 3D one-, two-, three-dimensional
AF antiferromagnetic
AP atom probe
AFM atomic force microscopy
AHE anomalous Hall effect
CEMS Conversion electron Mössbauer spectroscopy
CMS condensed magnetic semiconductor
CPA coherent potential approximation
DFT density functional theory
DMS dilute magnetic semiconductors
DFS dilute ferromagnetic semiconductor
EDS energy dispersive x-ray spectroscopy
EELS electron energy loss spectroscopy
EPR electron paramagnetic resonance
EF energy-filtered
EXAFS extended x-ray Absorption Fine Structure
FC field cool
fcc face-centered cubic
FM ferromagnetic
FMR ferromagnetic resonance
GGA generalized gradient approximations
GISAXS grazing incidence small angle x-ray scattering
GMR giant magnetoresistance
HR high resolution
LDA local density approximation
LSDA local spin density approximation
LT low-temperature
MBE molecular beam epitaxy
MOVPE metal organic vapor phase deposition
MCD magnetic circular dichroism
MR magnetoresistance
NC nanocrystal
RHEED reflection high-energy electron diffraction
RPA random phase approximation
RKKY Ruderman-Kittel-Kasuya-Yosida
SEM scanning electron microscopy
SIMS secondary ions mass spectroscopy
SQUID superconducting quantum interference device
STM scanning tunneling microscopy
SRXD synchrotron x-ray diffraction
TEM transmission electron microscopy
TM transition metal
TMR tunneling magnetoresistance
wz wurtzite
XANES x-ray absorption near edge structure
XAS x-ray absorption spectroscopy
XES x-ray emission spectroscopy
XMCD x-ray magnetic circular dichroism
XPEEM x-ray photoemission electron microscopy
XRD x-ray diffraction
ZFC zero-field cooled
zb zinc-blende

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