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Electronic states in $Ga_{1-x}Mn_xAs$: Substitutional versus interstitial position of Mn

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By using spin-polarized full potential linearized augmented plane wave method we obtained the electronic structure of (Ga,Mn)As crystals with Mn in substitutional, interstitial, and both positions. It is shown that the interstitial Mn acts as a double donor and compensates the holes created by two Mn atoms in substitutional positions. This explains why the number of holes in $Ga_{1-x}Mn_xAs$ is usually much smaller than x. The effective Mn doping efficiency is simply related to the proportion of substitutional and interstitial Mn and does not depend on x provided that the proportion is fixed. The calculated local electronic structure of the substitutional and interstitial Mn differ appreciably, so that the x-ray L emission spectra can be used to distinguish the two positions of Mn.

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I. INTRODUCTION

The ferromagnetic behavior of III-V diluted magnetic semiconductors (DMS) containing Mn (Refs. 1–4) makes these materials very promising for applications in semiconductor structures for spin electronics. It is now generally accepted that the ferromagnetic coupling of the local magnetic moments in these DMS is connected with their p-type nature.[2] An Mn atom, substituted for a three-valent cation of the host, acts as an acceptor and creates a hole in the valence band. If the content of Mn is of order of one percent or more, the effect of all other electrically active defects and impurities is only marginal and the Fermi energy is pinned inside the valence band. The main part of the exchange interaction is then mediated by free carriers (holes). As the Fermi surface remains close to the center of the Brillouin zone, the period of the oscillatory RKKY interaction exceeds the typical Mn-Mn distance and the coupling of the local moments is ferromagnetic. The correlation between magnetic and transport measurements[3–5] supports this picture.

Recently, the electronic structure of Mn-doped III-V compounds has been investigated theoretically in order to clarify the behavior of these materials at a microscopic level. Basically, ordered superstructures were considered and their band structures were calculated from first principles.[6–11] All these calculations confirm the p-type character of III-V DMS with Mn, the presence of localized magnetic moments at Mn sites and their ferromagnetic coupling, as well as the importance of the holes for the ferromagnetism. The restriction of all of these calculations to particular Mn concentration was overcome by applying both KKR version[12] and our tight-binding version of the coherent potential method which is suitable for extrapolation to the low-concentration case.

There are, however, still some unclear points. One of the most striking features is a remarkable difference between the nominal concentration of Mn impurities and the number of free holes from the transport measurements, i.e., very low effective doping efficiency of Mn. It is of order 0.1 to 0.2 and does not depend much on the content of Mn.[13] Particularly the latter fact indicates that the strong compensation is an intrinsic property of the Mn subsystem, with only minor influence of other dopants. To explain the compensation, it is assumed that most of the holes cannot participate in the conduction because they are either tightly bound to the acceptors,[14] localized due to the disorder,[15] or compensated by the As antisite defects.[4,16] Another explanation is that only a few Mn impurities act as acceptors. In the last case, however, the explanation why most of Mn atoms should be electrically inactive Mn is lacking.

We propose an alternative explanation of the self-compensation property of the Mn impurities.[17] We assume that some of the Mn atoms do not substitute into the cation sublattice of the host, but occupy interstitial position in the zinc blende structure. An interstitial Mn is expected to act as double donor, because there is no space for its two 4s electrons in the covalent bonding. If it is so, than one interstitial Mn compensates the holes created by two substitutional atoms.

Another reason to think about other than substitutional positions of Mn in the zinc blende lattice is its low solubility in the III-V materials, reflected in a strong tendency to precipitate.[18,19] The interstitial incorporation of Mn might be also one of the reasons for the observed increase of the lattice constant with increasing concentration of Mn in $Ga_{1-x}Mn_xAs$.[20] In an ordinary mixed crystal with only substitutional Mn one would expect rather decreasing lattice constant because the Mn-As tetrahedral bonding distance, estimated from atomic radii,[21] is smaller than the estimate for Ga-As pair.

To check this idea, we consider a series of hypothetical crystals whose large unit cells consist of a few conventional cubic cells of GaAs and contain Mn in either substitutional or interstitial positions. We calculated the electronic structure for these superstructures and found the positions of the Fermi level with respects to the valence and conduction bands. The Fermi level lying in the valence band indicates that the impurity behaves as an acceptor and the number of empty states per unit cell defines its degree of ionization. Similarly, the donor case can be recognized according to partly occupied conduction band. In addition, we investigated also crystals with one interstitial and two substitutional Mn atoms where a complete compensation is expected. The real charge distribution in these crystals is assumed to approach the situation in real, largely compensated materials better that the charge distribution calculated for a metallic phase of either p or n type. The compensated model is therefore most suitable to compare the local electronic structures at substitutional and interstitial atoms.

The paper is organized as follows. In Sec. II we specify the structural models used to represent $Ga_{1-x}Mn_xAs$ in various regimes of doping. In Sec. III we extend our preliminary study[17] and present the band structures and densities of states for the various structural models and discuss their differences. The local densities of Mn d states, reflected in the L spectra, are used to show that the interstitial Mn atoms can be distinguished from the substitutional ones by using the x-ray absorption. The conclusions are summarized in Sec. IV.

II. STRUCTURAL MODELS

As a basic unit, we consider a tetragonal large unit cell (LUC) consisting of four conventional cells (cubes) of the zinc blende crystal. It is constructed by doubling both the area of the base in the xy plane, and the c axis. The LUC contains 16 molecular units of the host GaAs and its lattice parameters are $(\sqrt{2}a, \sqrt{2}a, 2a)$, a being the lattice parameter of the underlying zinc blende structure. In our convention, the corners of the LUC are occupied by cations.

When Mn atoms are introduced, the size of the LUC is changed. We assume that this change is isotropic and that the lattice constant a of the $Ga_{1-x}Mn_xAs$ varies linearly with the Mn concentration x, $a = 5.66 + 0.32x$(Å).[22] We scale the lattice constant with the entire nominal concentration of Mn, i.e., we do not distinguish the effects due to substitutional and interstitial Mn. We also do not consider any local relaxation around Mn impurities, i.e., the mixed systems are taken with a perfect tetrahedral bonding. Recently, it was shown that the relaxation is not very important for the case of substitutional doping,[11] and we expect the same for the interstitial case.

We consider first a $Ga_{14}Mn_2As_{16}$ crystal with two Mn atoms substituting for Ga in the cationic lattice. Two impurities are considered because we expect that this is the number of substitutional Mn atoms, which can be compensated by a single interstitial Mn. The Mn atoms are placed symmetrically at the most distant positions in the LUC with relative coordinates (1/2, 1/2, 1/4) and (1/2, 1/2, 3/4). This choice does not change the tetrahedral symmetry of the host LUC. Moreover, the unit cell of $Ga_{14}Mn_2As_{16}$ can be decomposed into two equal cells Ga_7MnAs_8, which were used in the actual calculations of the band structure for this model.

There are several possibilities for the interstitial incorporation of Mn. We consider the most probable case when the Mn atom occupies a tetrahedral interstitial position surrounded by anions. In this case, the geometry and chemical composition of the nearest neighbor sphere around the interstitial Mn is the same as in the substitutional case. In addition to four As atoms at the bonding distance d there are other six close Ga atoms at the distance $1.154d$. We put the interstitial Mn at the center of the vertical edge of the LUC [relative coordinates (0, 0, 1/2)]. With this choice, the unit cell of the $Ga_{16}MnAs_{16}$ crystal has again the complete tetragonal symmetry.

Finally, the systems with Mn in both substitutional and interstitial positions are represented by $Ga_{14}Mn_3As_{16}$ crystal. Two Mn occupy the regular cationic position, the third one is an interstitial. This choice is expected to yield a complete compensation. The positions of the Mn atoms are taken as before, i.e., with relative coordinates (1/2, 1/2, 1/4), (1/2, 1/2, 3/4), and (0, 0, 1/2). The smallest Mn-Mn distance in this structure equals to the conventional lattice constant a of the underlying zinc blende crystal. It corresponds to the next nearest neighbors in the cationic sublattice. The closest Mn-Mn pairs are avoided and the system can still be considered to be dilute, even though the content of Mn (≈ 18 at. %) in this model largely exceeds the upper limit (≈ 8 at.%) for the Mn concentrations in real III-V DMS.

To approach the actual situation in materials with lower content of Mn, we also considered $Ga_{30}Mn_3As_{32}$ crystal (9 at. % of Mn). The corresponding LUC is a cube formed by eight conventional cells, with Mn in (1/2, 1/2, 1/4), (1/2, 1/2, 3/4), and (0, 0, 1/2) positions.

III. ELECTRONIC STRUCTURE

To obtain the spin-polarized electronic structure of the considered systems we used the full potential linearized augmented plane wave (FPLAPW) method, as implemented in the WIEN97 program package.[23] The generalized gradient approximation[24] (GGA) was used.

As a basic reference, we calculated the band structure of the host GaAs crystal. The calculated band gap of GaAs is 0.57 eV. This value is larger than the band gap obtained by using the standard local density approximation (0.43 eV), that is why we use only the GGA in all further calculation.

Even with this choice, the width of the bandgap of GaAs remains strongly underestimated with respect to reality [1.53 eV (Ref. 21)]. A comparable relation between calculated and real values of the band gap can be expected also for the systems containing Mn.

A. Substitutional case

We start with the electronic structure of Ga_7MnAs_8 crystal in which one Ga is replaced with Mn (i.e., the halved basic LUC). The spin-polarized bands along high-symmetry lines, shown in Fig. 1, represent a semimetallic material.

There is a narrow energy gap (0.11 eV) for the majority-spin electrons, separating the bands derived from the valence and conduction bands of the host. The Fermi level (used as a reference energy) crosses the valence band 0.75 eV bellow the top, leaving just one state per unit cell empty. This is fully consistent with the previous findings that substitutional Mn in GaAs acts as an acceptor. For the minority-spin electrons, the band gap is much wider (0.82 eV) and the Fermi energy lies close to its center. Both band gaps are direct and located in the Γ point.

The main feature due to the presence of Mn is the appearance of the d states in the valence and conduction band. As shown in Fig. 2, the occupied, majority-spin d states contribute to the valence band spectrum in a much wider range of binding energies (0.5–4.0 eV) than is known in II-VI

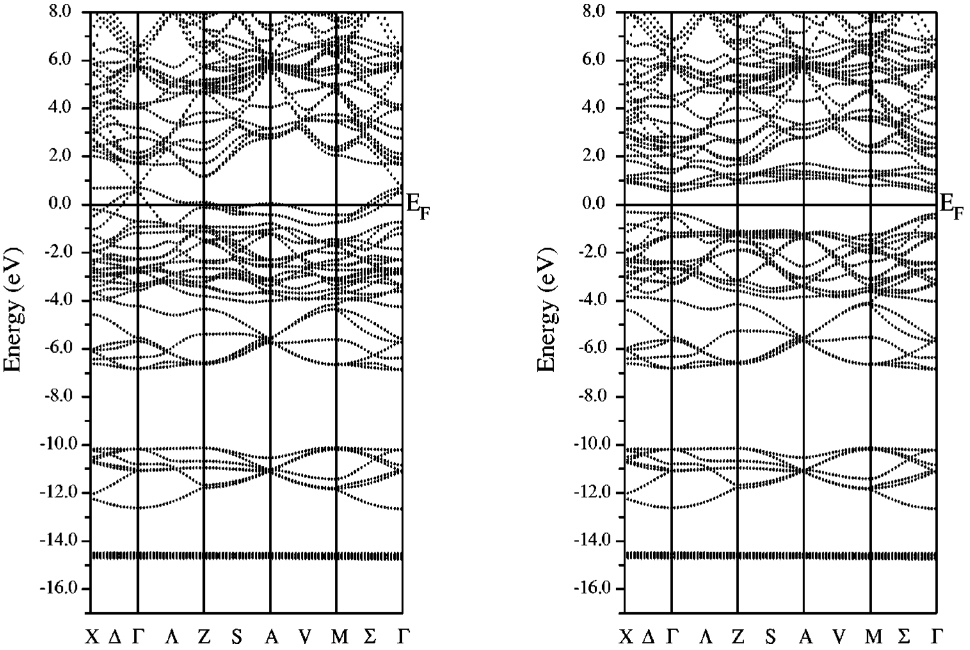

FIG. 1. Spin-polarized band structure of Ga$_7$MnAs$_8$ crystal with Mn in the substitutional position. Left panel: majority spin. Right panel: minority spin.

compounds.[25] They are spread over the whole upper part of the valence band. There is also a remarkable mixing of the minority-spin *d* states with the lowest conduction bands of the host crystal. As a result, the average exchange splitting of the *d* states is reduced from ≈6 eV typical for Mn to ≈4 eV. The underestimate of the exchange splitting of the *d* states is, however, not surprising in the density-functional calculation. In reality, we have to expect that the empty Mn *d* states will be located at a higher energy, not just at the edge of the conduction band.

Another important change of the electronic spectrum of Ga$_7$MnAs$_8$ is a redistribution of cationic *s* states, as we already observed in the tight-binding calculations. The Ga *s* states in GaAs are known to contribute mostly to the bottom of the conduction band and to the lower valence band (4–7 eV bellow the Fermi level). The Mn *s*-states appear, both in valence and conduction bands, at much higher energies. They are shifted by approximately 4 eV. This large difference of the atomic levels of the host cations and of the substituted atoms represents an important channel for the scattering of band carriers in the mixed crystal. The strong alloy scattering can be also expected to assist at nondirect optical transitions.[26]

The total spin of the unit cell (which is assigned to one Mn) is just $4\times1/2$. It results from the saturated spin polarization of five Mn 3*d* electrons, which form a local magnetic moment, and from the spin of the hole, which has a sign opposite to the local moment. The charge distribution in the unit cell of Ga$_7$MnAs$_8$ does not indicate any localization of the hole around the Mn impurity. This may be, however, specific for this mixed crystals with a high content of Mn ($x=0.125$ in the present case). We can only deduce that the localization radius of the hole cloud exceeds the dimensions of the LUC.

B. Interstitial case

The band structure of Ga$_{16}$MnAs$_{16}$ crystal with Mn in an interstitial position is metallic for both spin directions. The identity of the host valence and conduction bands can be, however, still recognized (Fig. 3). Similarly to the substitu-

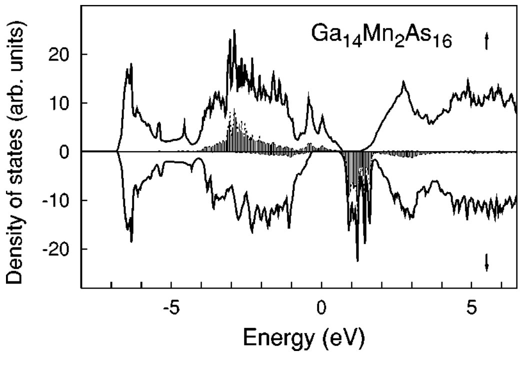

FIG. 2. Spin-polarized density of states for Ga$_7$MnAs$_8$ with Mn in the substitutional position. The hatched areas show the Mn *d* states.

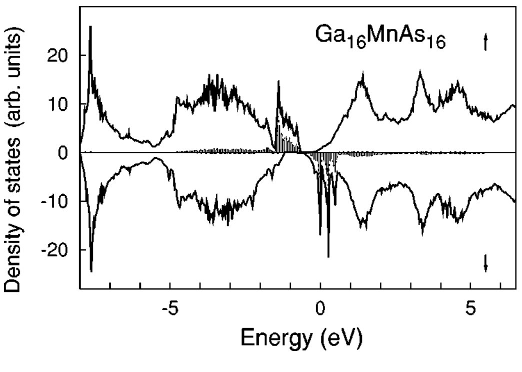

FIG. 3. The same but for Ga$_{16}$MnAs$_{16}$ with Mn in the interstitial position.

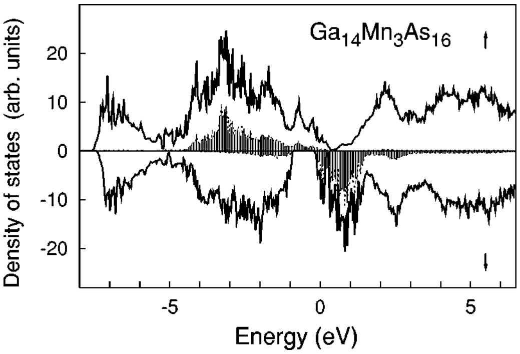

FIG. 4. The same but for $Ga_{14}Mn_3As_{16}$ with two substitutional and one interstitial Mn.

tional case, the gap for the majority-spin electrons is much narrower (0.14 eV) than the band gap for the minority-spin electrons (0.37 eV). This is a typical result of the strong hybridization of the valence-band states with the magnetically polarized *d* states.[25]

The Fermi energy lies, for both spins, in the conduction band. There are, altogether, two electrons in the conduction band, which confirms the idea that the interstitial Mn in GaAs acts as a double donor. Most of the conduction electrons have the minority spin. Although the states at the edge of the conduction band do not mix with the Mn *d* states from the symmetry reasons, the minority-spin *d* states largely participate in the lowest part of the conduction band. As a result, they are partly occupied what reduces the magnetic moment. The total spin of the unit cell is only $3.11\times 1/2$. Its main part $(2.70\times 1/2)$ is localized at the Mn site. The remaining magnetization is distributed over the neighboring As atoms and in the interstitial space around Mn. The spin of all other atomic spheres is negligible.

The reduced magnetic moment of Mn is closely related with a corresponding reduction of the average exchange splitting of the Mn *d* states to less than 2 eV. This has a pronounced effect on the distribution of the *d* states in the valence band. In contrast to the substitutional case, the *d* states do not appear at the binding energies around 3 eV, but they contribute mostly to the uppermost part of the valence band with binding energies up to 2 eV.

C. Compensated case

Finally, we present the electronic structure for a hypothetical crystal $Ga_{14}Mn_3As_{16}$. In presence of one interstitial and two substitutional Mn we assume a complete compensation. The calculated density of states (DOS) presented in Fig. 4 indicates this. The Fermi energy does not immerse deep into the valence or conduction band as in the two above examples, but it is located close to the minimum of the DOS between the valence and conduction bands.

For the majority-spin electrons we have, in fact, no gap because the valence and conduction bands touch and slightly overlap around the center of the Brillouin zone. According to the symmetry of the bands in the Γ point, the origin of the bands can be still identified. The bottom of the "conduction" band is $E_c = 0.22$ eV. The top of the "valence" band is $E_v = 0.37$ eV, measured from the Fermi level. This means that, while the majority-spin conduction band is empty, there are some holes in the valence band. Their concentration is 0.562 per unit cell, i.e., 0.187 per Mn atom, which is much less than in the case of only substitutional doping.

The minority-spin electrons have bands with a distinct band gap (0.60 eV). The band gap is, however, shifted to lower energies so that the Fermi energy crosses the conduction band $(E_c = -0.35$ eV). The number of the conduction electrons equals to the number of holes (0.562 per unit cell).

An important feature of this strongly polarized band structure is that the spins of the conduction electrons and of the holes add and the resulting magnetic moment of the free carriers is antiparallel to the local moments at Mn. The total spin of the LUC is $13.88\times 1/2$. It is important to notice that all these numbers depend very sensitively on the degree of semimetallicity, characterized by the difference $E_v(\uparrow) - E_c(\downarrow)$. This overlap, which is also a measure of magnetic polarization of the bands, is clearly affected by the local density approximation, and it depends on the concentration of Mn. With the decreasing overlap $E_v(\uparrow) - E_c(\downarrow)$ also the number of free carriers will decrease to zero.

The calculated band structure of the crystal $Ga_{30}Mn_3As_{32}$ with the doubled LUC shows that the overlap of the valence and conduction band decreases from 0.7 eV to 0.2 eV (Fig. 5). Correspondingly, also the number of conduction electrons (holes) reduces from 0.56 to 0.19 in the unit cell (i.e., to 0.06 per Mn atom).

Using a linear extrapolation we can estimate that the calculated overlap disappears completely for $Ga_{1-x}Mn_xAs$ with $x < 0.04$. This means that in mixed crystal with realistic concentration of Mn there is a common band gap for both spin up and down. Moreover, with the special proportion (2:1) of substitutional and interstitial Mn, the extrapolated position of the Fermi level is in this band gap and the material behaves as a usual compensated semiconductor.

D. X-ray spectra

Although the local geometry of both substitutional and interstitial Mn is very similar, their local electronic structures are different because of different charging (acceptor vs donor). The main difference concerns the local density of *d* states. We have already discussed the effect connected with the reduced exchange splitting in the case of interstitial doping, causing a transfer of the *d* states to the upper part of the valence band. The weak point of this comparison was, however, a completely different nature of the band structures of Ga_7MnAs_8 and $Ga_{16}MnAs_{16}$ crystals.

We now consider the corresponding local densities in $Ga_{14}Mn_3As_{16}$. Although the concentration of Mn is overestimated, the large degree of compensation makes this model most relevant for the comparison with the real materials containing Mn atoms in both substitutional and interstitial positions.

Figure 6 shows the partial DOS at the *d* states at one of the substitutional (dotted) Mn and at the interstitial Mn (full line). The spectrum from the substitutional Mn is sharply

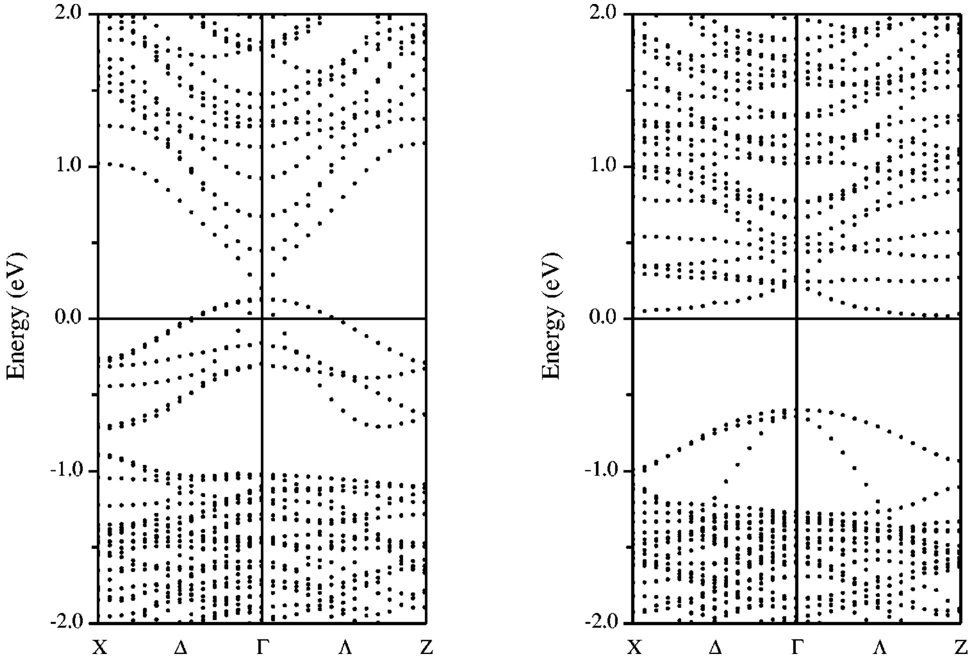

FIG. 5. Spin-polarized band structure of $Ga_{30}Mn_3As_{32}$ crystal with two Mn atoms in the substitutional and one in the interstitial position.

peaked at 3.3 eV bellow the Fermi level (reference energy). This is quite similar to the spectra from Mn in II-VI materials.[25]

On the other hand, the spectrum from the interstitial atom is rather wide. In contrast to the *n*-type $Ga_{16}MnAs_{16}$ crystal in which the distribution of the *d* states was determined by the suppressed exchange splitting, the *d*-states in the present case are distributed over the whole upper part of the valence band. Their binding energies range from 1.5 to 4.5 eV. The tendency of the *d* states to the double peak structure is an indication of their enhanced hybridization with valence band, most probably because of the close second neighbors of the substitutional Mn.

As the *L* spectra from Mn essentially follow the local densities of the *d* states, they differ appreciably for the two crystallographic positions of Mn and they could serve for identification of the interstitial Mn in the $Ga_{1-x}Mn_xAs$ mixed crystals.

IV. CONCLUSIONS

Using density-functional calculations of the electronic structure of (Ga,Mn)As supercells, we showed that the interstitial Mn in GaAs acts as a double donor. It can compensate two acceptors, in particular two Mn atoms substituted for Ga in the cationic sublattice. As a result, the effective doping efficiency of Mn can be substantially reduced if only a minor portion of Mn occupies interstitial instead of substitutional positions. In this sense, the interstitial Mn behaves similarly, e.g., to the As antisite defect.

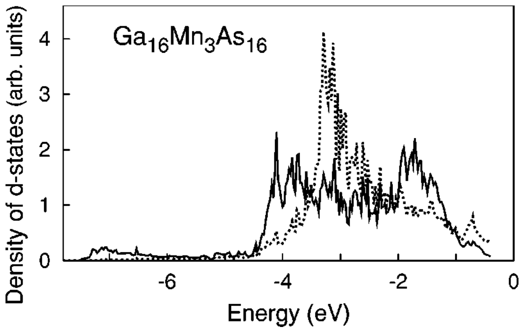

FIG. 6. Local density of Mn *d* states for substitutional (dotted line) and interstitial Mn (full line) in $Ga_{14}Mn_3As_{16}$.

In contrast to As antisite, however, the compensation due to the interstitial Mn is consistent with the fact, that the doping efficiency does not depend much on the Mn concentration *x*.[13] This observation can be explained only by assuming that the numbers of donors (whatever their nature may be) and acceptors are correlated. This means that not only the number of acceptors, but also the number of donors should be approximately proportional to the concentration *x* of Mn. This assumption is quite natural for Mn interstitials, but it can hardly be applied to any other compensating donor. If the concentration of Mn interstitials is $x_i = cx$, the number of holes $n_h = x(1-3c)$ is also proportional to the concentration of Mn and the effective doping efficiency n_h/x can be substantially reduced for *c* approaching 1/3. For $c = 1/4$, when most of Mn atoms are assumed in regular, substitutional positions, the doping efficiency reduces four times. With the observed doping efficiency of order 0.1–0.2 we can estimate the proportionality factor *c* to be roughly 0.3.

Moreever, assuming that at higher concentration the Mn atoms have a reduced disposition for the substitution, i.e., that the balance between substitutional and interstitial position turns in favor of the latter, a transition to the insulating state takes place above some critical concentration of Mn. The balance between the substitutional and interstitial impurities deserves a detailed discussion in terms of corresponding formation energies and their dependence on the chemical composition. These quantities can be, in principle, obtained from the LDA theory, but our supercell calculations are not suited for this purpose.

It is evident that the mutual compensation of the two kinds of Mn impurities in (Ga,Mn)As has a direct impact on the transport properties. It has, however, also an indirect effect on the magnetic coupling of the local moments, which is mediated by the holes. Because the average density of holes is reduced due to the compensation, the strength of the exchange coupling, and consequently also the Curie temperature decreases.

Even though our calculations for systems with very high content of Mn do not show any indication for localization of holes and electrons around the Mn impurities, we cannot exclude it for lower concentrations. Recent calculations for Mn δ layers in GaAs (Ref. 27) have indicated that the holes are localized within approximately 10 Å around Mn. In the case of holes trapped close to substitutional Mn (Ref. 14) (and similarly electrons bound to interstitial Mn), we arrive to a specific situation with low and strongly inhomogeneous carrier density, with the holes expelled from the vicinity of Mn atoms in the interstitial positions. Their magnetic moments, without contact with the hole sea, can eventually decouple from the ferromagnetically ordered moments of the Mn atoms in the substitutional sites. Observation of this special feature, i.e., the coexistence of aligned and paramagnetic moments, e.g., in the field dependence of magnetization, would be an experimental indication of both carrier localization and of the presence of Mn interstitials as donors.

Finally, the Mn interstitials should be observed directly in the local structure measurements. The x-ray emission spectra seem to be particularly well suited to distinguish substitutional and interstitial Mn because the *L* spectra from Mn reflect the local density of Mn *d* states. We have shown that the distribution of Mn *d* states in the valence band differs substantially for the two positions in question, although the geometry of the nearest-neighbor sphere is the same in both configurations.

The *d* states at the substitutional Mn contribute to the valence band for binding energies ranging from 2 to 4 eV. On the other hand, the interstitial Mn with smaller magnetic moment have also the exchange splitting of the *d* states reduced. This brings the occupied *d* states much closer to the top of the valence band and their binding energies do not exceed 2 eV.

ACKNOWLEDGMENTS

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