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Self-Compensating Incorporation of Mn in $Ga_{1-x}Mn_xAs$

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We consider hypothetical Ga_7MnAs_8, $Ga_{16}MnAs_{16}$, and $Ga_{14}Mn_3As_{16}$ crystals with Mn in a substitutional, interstitial, and both positions. Spin-polarized full-potential linearized augmented plane wave calculations were used to obtain their electronic structure. We show 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 much smaller than x. The presence of interstitial atoms may also be the reason for the lattice expansion with increasing content of Mn. The differences in electronic behavior of substitutional and interstitial Mn are discussed.

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1. Introduction

The III–V diluted magnetic semiconductors containing Mn attracted much attention in last years [1, 2] because their ferromagnetic nature is promising for applications in semiconductor structures. The ferromagnetic behavior of III–V diluted magnetic semiconductors (DMS) is connected with their p-type nature [1]. Mn substituted for a trivalent cation acts as an acceptor and creates a hole in the valence band. If the content of Mn is of order of one percent, the Fermi energy is fixed in the valence band and all other defects and impurities are less important. The main contribution to the exchange interaction between Mn local moments is then mediated by the holes with wave vectors close to the center of the Brillouin zone. The typical period of the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction exceeds the average Mn–Mn distance and the coupling is ferromagnetic. The correlation between magnetic and transport measurements [2] supports this picture.

Recently, also the electronic structure of Mn-doped III–V compounds has been investigated. Both supercell band structure calculations [3, 4] and Korringa–Kohn–Rostoker coherent potential approximation (KKR-CPA) studies [5] confirmed the p-type character of these materials, as well as the presence of localized magnetic moments at Mn sites, and their ferromagnetic coupling.

However, there are still some unclear points. One of them is a remarkable difference between the number of Mn acceptors and the number of free holes obtained from the transport measurements. The latter quantity is usually much smaller than the former. To explain this almost complete compensation, it is assumed that most of the holes do not participate in the conduction because they are either tightly bound to the acceptors [6], localized due to the disorder, or compensated by As antisite defects [7].

We propose an alternative explanation of the self-compensation property of the Mn impurities. We assume that some of Mn atoms do not substitute into the cation sublattice, but occupy interstitial position in the zinc-blende structure. One can expect that the interstitial Mn acts as a double donor, because there is no space for its two $4s$ electrons in the bonding. If it is so, then one interstitial Mn should compensate the holes created by two substitutional atoms.

To check this idea, we constructed 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 respect 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 a $Ga_{14}Mn_3As_{16}$ crystal with one interstitial and two substitutional Mn atoms to approach the real charge distribution in a compensated case. Although the content of Mn is strongly overestimated in this case, we use it to show the differences in the local electronic structure at substitutional and interstitial atoms.

2. Details of calculation

The self-consistent, spin-polarized electronic structure of all considered systems was calculated by means of the full-potential linearized augmented plane wave (FPLAPW) method [8]. Instead of the standard form of the density functional we used the generalized gradient correction (GGA) version, giving a wider band gap and a better description of the conduction band. All calculations were done for a ferromagnetic phase.

We started with the band structure of the host GaAs crystal. The calculated band gap is 0.57 eV. Although this value is better than the gap obtained by using the local-density approximation (0.43 eV), it is still underestimated with respect

to observed value 1.56 eV. A comparable relation between calculated and observed values of the gap can be expected also for the systems containing Mn.

In our calculations we use a large unit cell (LUC) consisting of four cubic cells of the zinc-blende structure and containing 16 molecular units of the host GaAs. It is constructed by doubling the c-axis and by assuming a $\sqrt{2} \times \sqrt{2}$ superstructure in the basal plane. This LUC has a tetragonal symmetry and its lattice parameters are $A = B = a\sqrt{2}$, $C = 2a$, with $a = 0.566 + 0.032x$ nm [9] being the lattice constant of the $Ga_{1-x}Mn_xAs$. We do not take into account any local relaxation around Mn impurities, i.e. the mixed systems are considered with a perfect tetrahedral bonding. In this way, both interstitial and substitutional Mn have the same geometry of the nearest neighbor sphere. We use the convention with the basal plane coinciding with the cation layer.

3. Results

3.1. Mn in a substitutional position

We replace two Ga atoms of the GaAs LUC by Mn. Two impurities are considered because we presume that this is the number of substitutional Mn atoms, which can be compensated by a single interstitial Mn. The two Mn atoms are placed at the most distant positions in the LUC. The choice of relative coordinates (1/2, 1/2, 1/4) and (1/2, 1/2, 3/4) does not change the tetrahedral symmetry of the LUC. Moreover, this 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 for this model.

The resulting spin-polarized density of states (DOS) is shown in Fig. 1. We see that the $Ga_{14}Mn_2As_{16}$ crystal is a semimetal with the Fermi energy close to the center of a wide band gap (0.82 eV) for the minority-spin electrons. For the majority-spin electrons, however, the bands derived from the host valence and conduction bands are separated by a narrow gap (0.11 eV). The Fermi energy crosses the valence band 0.75 eV below the top, leaving just one state per unit cell empty. This agrees with the previous findings [6–8] that substitutional Mn in GaAs acts as an acceptor. The spin of the hole has a sign opposite to the local moment arising from the saturated spin polarization of the Mn $3d$-states. As a result, the total spin of the formula unit (which is assigned to two Mn) is just 4. The integer value of the spin is related to the absence of a free Fermi surface for the minority spin.

The main spectral feature due to the presence of Mn is the appearance of the d-states in the valence and conduction band. The occupied majority-spin d-states contribute to the valence band spectrum in a much wider range of binding energies (1–4 eV) than in II–VI's. There is also a remarkable mixing of the minority-spin d-states with the lowest conduction bands of the host crystal. The bottom of the conduction band is formed of d-states instead of cation s-states, as it is usual in the zinc-blende materials. The average exchange splitting of the d-states

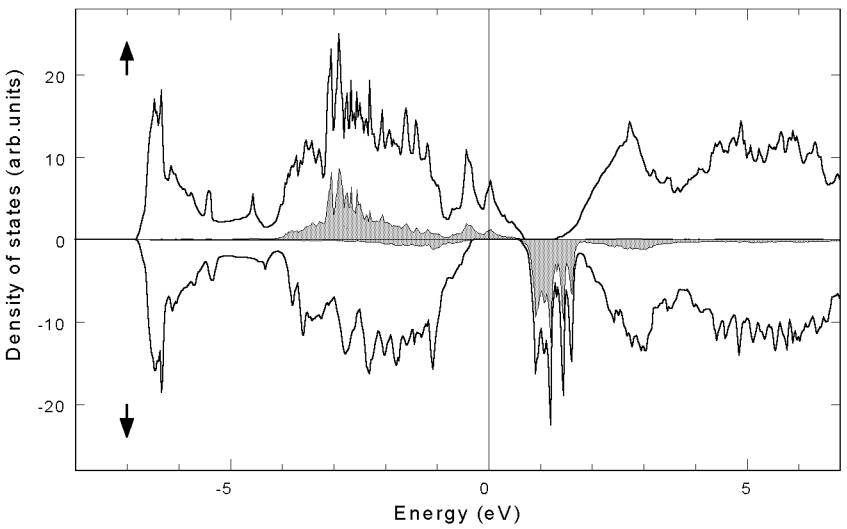

Fig. 1. Spin-polarized density of states for $Ga_{14}Mn_2As_{16}$ crystal with Mn atoms in substitutional positions. The shaded areas show the contribution of Mn $3d$-states. Vertical line indicates the position of the Fermi level.

is reduced from approximately 6 eV typical of Mn to approximately 4 eV. This underestimation of the exchange splitting is the result of the density-functional approach and, in fact, we should expect the empty Mn d-states located at a higher energy.

Another important change of the electronic spectrum of $Ga_{1-x}Mn_xAs$ concerns the cationic s-states. While the Ga s-states are known to contribute mostly to the bottom of the conduction band and to the lower valence band (4–7 eV below the Fermi level), the Mn s-states appear, both in valence and conduction bands, at much higher energies. The shift is approximately 4 eV. This large difference in the atomic level positions of the host and substituted atoms represents, besides the presence of the d-states, another important channel for the scattering of band carriers in the mixed crystal. The strong alloy scattering can be also expected to affect the near-edge optical transitions.

3.2. Mn in the interstitial position

The most probable position for a metallic interstitial in the zinc-blende structure is a tetrahedral hollow site surrounded by four anions. If we place the Mn atom to the (0, 0, 1/2) position in the LUC, the resulting structure of $Ga_{16}MnAs_{16}$ has again the complete tetragonal symmetry. The interstitial Mn has, in addition to four As nearest neighbors at bonding distances $d_1 = a\sqrt{3}/4$, six close Ga neighbors at a distance $d_2 = 1.154d_1$.

We find that $Ga_{16}MnAs_{16}$ is metallic, with the Fermi energy in the conduction band for both spin directions. The identity of the host valence and con-

duction bands can be still recognized. As in the substitutional 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). There are, altogether, two electrons in the conduction band, which confirms the idea that the interstitial Mn in GaAs acts as a double donor.

The total spin of the unit cell is 1.56. Its main part (1.35) is localized in the muffin-tin sphere at the Mn site. This local moment is so small because also minority-spin d-states, participating in the lowest conduction band, are partly occupied. The remaining magnetization is distributed over the neighboring As atoms and in the interstitial space around Mn.

The reduced magnetic moment of Mn is closely related with a corresponding reduction of the average exchange splitting of the Mn d-states (approximately 2.5 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 shrink to a narrow peak in the uppermost part of the valence band.

3.3. Compensated case

Finally, we consider a $Ga_{14}Mn_3As_{16}$ crystal containing Mn in both substitutional and interstitial positions. We assume that the two substitutional impurities and one interstitial Mn have the same, high symmetry positions as in the structures discussed in Secs. 3.1 and 3.2. In this way, the smallest Mn–Mn distance equals to the lattice constant a, i.e. it corresponds to the next nearest neighbors in the cationic sublattice. Although the concentration of Mn in this model is largely overestimated (19%), the closest Mn–Mn pairs are avoided and the system can still be considered to be dilute.

The density of states presented in Fig. 2 indicates the compensation. The position of the Fermi energy is fixed in the minimum of the total DOS. Analyzing the band structure, we found an overlap of the majority-spin valence band ($E_v(\uparrow) = 0.37$ eV) with the minority-spin conduction band ($E_c(\downarrow) = -0.35$ eV). This means that there are some holes in majority-spin valence band and the same amount of minority-spin conduction electrons. Their concentration is 0.562 per unit cell, i.e. 0.187 per Mn atom, much less than in the case of either substitutional or interstitial doping.

It is important to notice that all these numbers depend very sensitively on the relative position of $E_v(\uparrow)$ for the majority- and $E_c(\downarrow)$ for the minority-spin electrons. The number of free carriers decreases to zero with decreasing $E_v(\uparrow) - E_c(\downarrow)$. This overlap, characterizing the semimetallic state of $Ga_{14}Mn_3As_{16}$, is due to the strong magnetic polarization of the bands, which is clearly overestimated in our example with so high content of Mn. In real mixed crystals with low concentration of Mn, the overlap of the valence and conduction band will be much smaller and the compensation better. A linear interpolation indicates that the overlap disappears

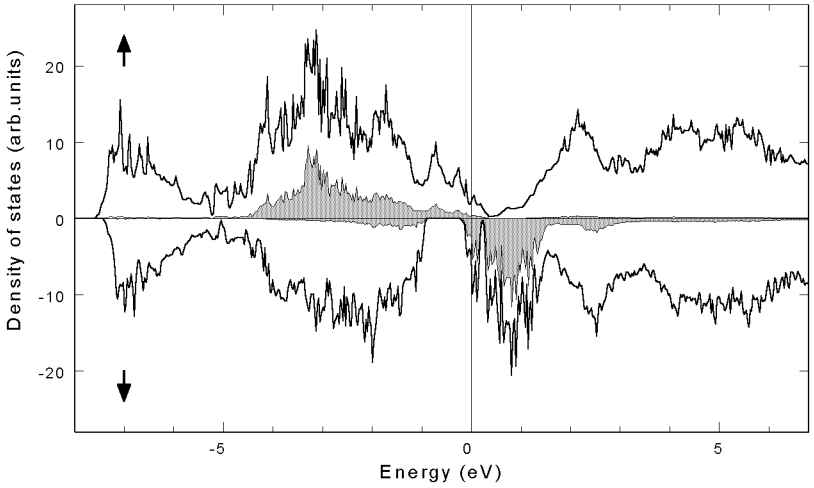

Fig. 2. Same as Fig. 1 but for $Ga_{14}Mn_3As_{16}$ crystal with one interstitial and two substitutional Mn atoms.

for $Ga_{1-x}Mn_xAs$ with $x < 0.04$ and with this proportion (2:1) of substitutional and interstitial Mn. The material then behaves as a compensated semiconductor.

Although the geometry of both substitutional and interstitial Mn is the same within the nearest-neighbor sphere, the bonding and the local electronic structures are quite different. The main difference concerns the local density of d-states. We find that the occupied d-states at the interstitial Mn approach the top of the valence band. Even though the effect is not so strong as in Sec. 3.2, the change of the d-states DOS should be visible e.g. in the X-ray emission.

4. Conclusions

Using *ab initio* FPLAPW calculations, we showed that the interstitial Mn in GaAs acts as a double donor. Such impurity compensates the effect of two Mn atoms substituted into the cation sublattice, which are known to be single acceptors. The number of holes in the valence band becomes much smaller than the total number of magnetic impurities, if only a minor portion of them occupies interstitial instead of substitutional positions. This can explain the large difference between the level of Mn doping and the resulting hole concentration observed in experiment [7].

The presence of interstitial Mn in $Ga_{1-x}Mn_xAs$ might be verified by using the X-ray emission spectra from Mn. The L spectra, corresponding to the local density of Mn d-states, should show a remarkable difference for the two bonding geometries in question. The main reason for this difference is the reduced exchange splitting of the d-states at the interstitial Mn, which brings the occupied d-states into the uppermost part of the valence band.

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