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Compositional Dependence of the Formation Energies of Substitutional and Interstitial Mn in Partially Compensated (Ga,Mn)As

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We use the density-functional theory to calculate the total energy of mixed crystals (Ga,Mn)As with a small concentration of various donors. We find that the formation energy of Mn depends strongly on the partial concentrations of Mn in the substitutional and interstitial positions, and on the concentration of other dopants. The composition dependence of the formation energies represents an effective feedback mechanism, resulting in the self-compensation property of (Ga,Mn)As. We show that the partial concentrations of both substitutional and interstitial Mn increase proportionally to the total concentration of Mn.

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1. Introduction

The dilute magnetic semiconductors (DMS), such as GaAs doped with a large amount of Mn, represent an important class of mixed crystals with promising applications in spin electronics [1]. The ferromagnetic behavior of these materials is mediated by the holes in the valence band [2, 3]. It is sensitive to the number of free carriers and to the level of charge compensation. Mn atoms substituted in the cation sublattice of a III–V semiconductor are acceptors and produce one hole

each. It is known, however, that some Mn atoms occupy the interstitial positions and act as double donors [4–8].

The interplay between the substitutional and interstitial incorporation of Mn into the GaAs lattice has, together with co-doping (cf. Ref. [9]), a crucial effect on the physical properties of the mixed crystal (Ga,Mn)As. A systematic study of formation energies of the substitutional (Mn_{Ga}) and interstitial (Mn_{int}) manganese can help to understand it on a microscopic level.

In the case of weak doping small changes in the impurity concentration can easily move the Fermi energy E_F across the band gap with a negligible influence on the density of states. That is why the dependence of the formation energies on the number of electrically active impurities is usually represented by their dependence on E_F. The Fermi-level dependent formation energy is obtained by adding (or subtracting) ΔE_F to the formation energy calculated for a particular electronic configuration [10]. In the case of a strongly doped and mixed crystals, however, the redistribution of the electron states in the valence band due to the impurities cannot be neglected and the density-of-states effect modifies the simple Fermi-level rule for the formation energies.

That is why the knowledge of the formation energy as a function of the impurity concentrations is necessary in the DMS. To calculate the energy needed to incorporate Mn and other impurities in a mixed crystal, we use the trick relating them to the composition-dependent total energy of the mixed crystal [11]. This quantity is obtained within the density-functional theory for a series of (Ga,Mn)As mixed crystals with various content of Mn in substitutional and interstitial positions, and with a variable concentration of the compensating donors. The use of the coherent potential approximation (CPA) combined with the tight–binding linearized-muffin-tin-orbital method (TB-LMTO) [12] makes possible to change the chemical composition continuously. The lattice relaxation around the impurities and the clustering of the Mn atoms are omitted within the CPA. For simplicity, we consider only the interstitial Mn atoms in the $T(As_4)$ position; the energy of the other $T(Ga_4)$ position is almost the same [13]. The formation energies are obtained as the first derivatives of the total energy with respect to the corresponding partial concentration [11].

Assuming a quasi-equilibrium deposition conditions, characterized by an effective growth temperature, we use the calculated formation energies to estimate the numbers of Mn_{Ga} and Mn_{int} in (Ga,Mn)As mixed crystal. We also present a simple way to determine the partial concentrations directly from the composition dependence of the formation energies, without solving thermodynamical balance equations.

2. Composition dependence of the formation energies

We consider an impure or mixed crystal with several kinds of impurities I_1, I_2, etc. The total energy of the mixed crystal $W(x_1, x_2, ..)$, normalized to a unit

cell, depends on their molar concentration x_i. As we showed recently [11], the formation energy E_i of an impurity I_i can be obtained by differentiating $W(x_1, x_2, ..)$ with respect to x_i, namely

$$E_i(x_1, x_2, ..) = \frac{\partial W(x_1, x_2, ..)}{\partial x_i} - E^{\text{atom}}(I_i) + E^{\text{atom}}(\text{host}). \tag{1}$$

The last two terms in Eq. (1) are the total energies of a free-standing atom I_i and of the corresponding atom of the host, which has been replaced by I_i.

Generally, the definition of the formation energy is not unique and depends on the way in which the atomic energies $E^{\text{atom}}(\text{host})$ and $E^{\text{atom}}(I_i)$ in Eq. (1) are obtained. We use the energies of neutral atoms in their ground state. It is important to notice, however, that the additional constant in Eq. (1) does not depend on the actual chemical composition of the material. It is not important for the concentration-dependent trends we have in mind.

That is why we consider now only the relative formation energies ΔE_i, obtained from their actual values E_i by subtracting the corresponding formation energy calculated for the reference material. As a reference, we take $Ga_{0.96}Mn_{0.04}As$ with all Mn atoms in regular Mn_{Ga} positions.

The composition dependence of the formation energies E_i is characterized by the coefficients of the linear expansion around the reference point,

$$K_{ij} \equiv \frac{\partial E_i}{\partial x_j} = \frac{\partial^2 W(x_1, x_2, ..)}{\partial x_i \partial x_j}. \tag{2}$$

The correlation energies K_{ij} [11] form a symmetric matrix. $K_{ij} < 0$ means that the presence of the defects I_i supports formation of I_j and *vice versa*; $K_{ij} > 0$ indicates the opposite tendency.

The dependence of the relative formation energy ΔE of Mn_{Ga} on the concentration of various donors is summarized in Fig. 1. We considered four representative examples. Se_{As} and Si_{Ga} are typical donors with one extra electron, situated at anion and cation sublattice, respectively. The other two cases, i.e., As antisite defect As_{Ga} and Mn_{int} are the most important native defects in (Ga,Mn)As, both acting as double donors. Figure 1 shows that the formation energy of Mn_{Ga} decreases in the presence of an increasing number of donors. The curves are grouped into pairs according to the charge state of the donors, with only a minor influence of the particular chemical origin of the defect. The dependence is almost linear for low concentrations and the slope of the function is roughly proportional to the charge state of the donor. This all indicates that the variations of the formation energy of Mn_{Ga} are mostly determined by the Fermi-level effect, not by the redistribution of the density of states induced by the other defects.

Analogous results are obtained for the formation energy of the interstitial Mn in the $T(As_4)$ position, as shown in Fig. 2. In this case, however, the formation energy of Mn_{int} increases with increasing number of the donors. It is important to notice that the steep increase in the formation energy represents a feedback

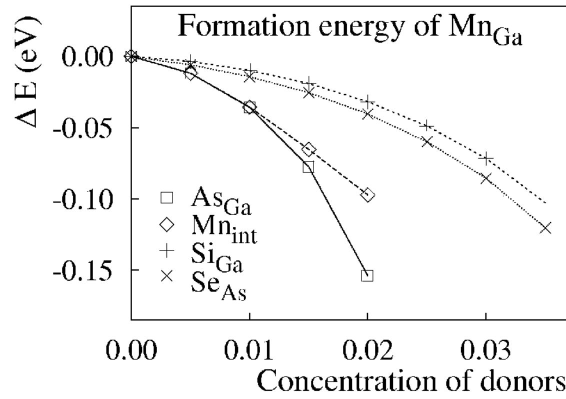

Fig. 1. Relative formation energy ΔE of the substitutional Mn_{Ga} in $Ga_{0.96}Mn_{0.04}As$ as a function of the concentration of various donors.

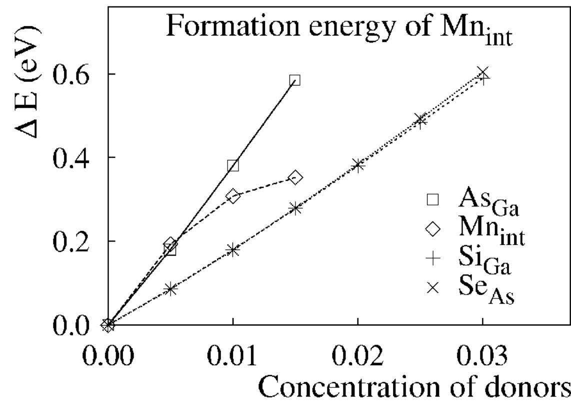

Fig. 2. Relative formation energy ΔE of the interstitial Mn in $Ga_{0.96}Mn_{0.04}As$ as a function of the concentration of various donors.

mechanism limiting efficiently the number of Mn_{int}. The same is valid also for the formation energy of the As antisite defect.

Figure 3 shows the formation energies of the two native defects, i.e. As_{Ga} and Mn_{int}, in the mixed crystal with varying number of the substitutional Mn in the Ga sublattice. Notice that both relative quantities, being pinned to zero for the reference material with 4% of Mn_{Ga}, are almost identical. In both cases, the formation energy is a decreasing function, indicating an increasing probability of formation of these defects in materials with a higher concentration of Mn.

This self-compensation tendency is a very important mechanism controlling the basic physical properties of (Ga,Mn)As mixed crystals. It is the reason for the observed low doping efficiency of Mn in GaAs [14]. The increasing number of both As_{Ga} and Mn_{int} also explains the expansion of the lattice of (Ga,Mn)As with an increasing concentration of Mn [15].

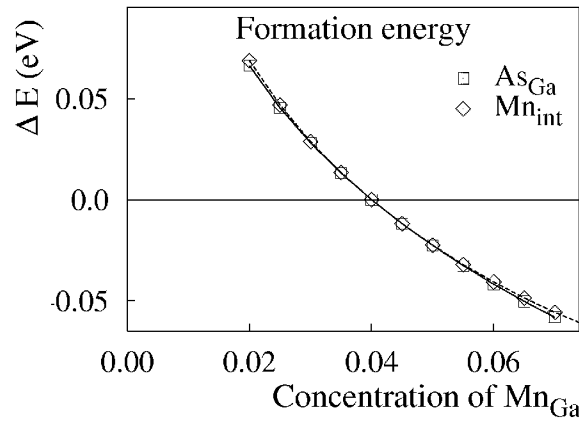

Fig. 3. The formation energy of the interstitial Mn and As antisite defect in $Ga_{1-x}Mn_xAs$ as a function of the concentration x of Mn atoms substituted in the Ga sublattice. The formation energies are referred to the values corresponding to $Ga_{0.96}Mn_{0.04}As$.

3. Dynamical equilibrium between Mn_{Ga} and Mn_{int}

In this Section, we use the calculated formation energies to simulate the incorporation of Mn into the (Ga,Mn)As mixed crystal. We assume that the probabilities that an Mn atom occupies either substitutional or interstitial position are related to the corresponding formation energies E_S and E_I also in the non-equilibrium epitaxial growth. As a simplest approximation, we characterize the deposition condition with some effective temperature T_{eff} and use the corresponding Boltzmann weighting factors.

To this purpose, the absolute formation energies of Mn in the two crystallographic positions, i.e. Mn_{Ga} and Mn_{int}, are required. They are obtained for the reference system $Ga_{0.96}Mn_{0.04}As$ including the additive terms from Eq. (1). For the epitaxial growth, it is reasonable to use E^{atom} calculated for isolated atoms as stated above. A linear interpolation for the dependence of E_S and E_I on the corresponding partial concentrations x_S and x_I is used

$$E_S(x_S, x_I) = E_S^0 + \kappa_{SS} x_S + \kappa_{SI} x_I, \tag{3}$$

$$E_I(x_S, x_I) = E_I^0 + \kappa_{IS} x_S + \kappa_{II} x_I \tag{4}$$

with $E_S^0 = 0.31$ eV, $E_I^0 = 0.42$ eV, $\kappa_{SS} = -0.17$ eV, $\kappa_{SI} = \kappa_{IS} = -6.03$ eV, and $\kappa_{II} = 10.33$ eV.

The composition dependent formation energies, Eqs. (3, 4), define the thermodynamic probabilities p_S and p_I that extra Mn atoms occupy substitutional or interstitial position in the mixed crystal with a given composition. They are

$$p_{S,I} = \frac{\exp(-E_{S,I}/kT_{\text{eff}})}{\exp(-E_S/kT_{\text{eff}}) + \exp(-E_I/kT_{\text{eff}})}. \tag{5}$$

On the other hand, these probabilities determine the number of Mn atoms that substitute for Ga or occupy the interstitial positions. The resulting changes of the partial concentrations x_S and x_I due to the variation dx of the total concentration x of Mn are as follows:

$$\mathrm{d}x_S = p_S \mathrm{d}x, \ \mathrm{d}x_I = p_I \mathrm{d}x, \tag{6}$$

and the dependence of x_S and x_I on x can be obtained by the integration of Eq. (6).

Figure 4 shows the solution of Eq. (6) for $T_{\text{eff}} = 500$ K. For the lowest concentrations ($x < 0.015$), Mn atoms occupy preferentially the substitutional positions which have a lower formation energy (cf. Eqs. (3, 4)). For a higher concentration of Mn, however, the difference of $E_I(x_S, x_I) - E_S(x_S, x_I)$ decreases and approaches zero. From this point, both positions can be occupied with a comparable probability, and the partial concentrations of both $\mathrm{Mn_{Ga}}$ and $\mathrm{Mn_{int}}$ increase proportionally to x. Any deviation from the situation with $E_S = E_I$ changes the formation energies of $\mathrm{Mn_{Ga}}$ and $\mathrm{Mn_{int}}$ in such a way that the dynamical equilibrium is restored. As a result, the high-concentration regime with co-existing $\mathrm{Mn_{Ga}}$ and $\mathrm{Mn_{int}}$ is stabilized. This finding does not depend much on T_{eff} over a wide temperature range. We can conclude that the partial concentrations of Mn are simply given by the following equation:

$$E_S(x_S, x_I) = E_I(x_S, x_I), \tag{7}$$

together with the condition $x_S + x_I = x$. Combining Eqs. (3, 4) with (7) we find that the proportion of $\mathrm{Mn_{Ga}}$ and $\mathrm{Mn_{int}}$ atoms is roughly 3:1, in a very goodagreement with both experiment [4] and theoretical expectations [6, 15] for the as-grown materials.

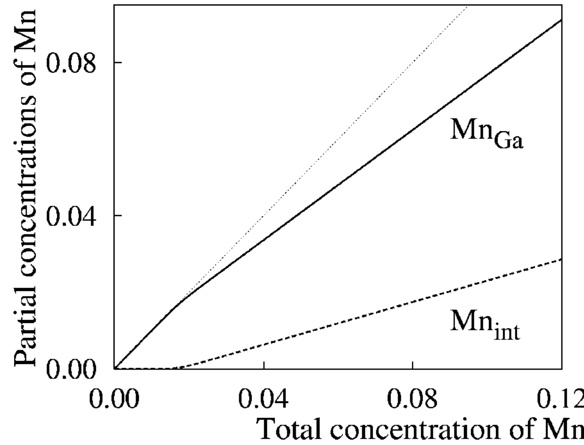

Fig. 4. The partial concentrations of $\mathrm{Mn_{Ga}}$ (solid) and $\mathrm{Mn_{int}}$ (dashed) as a function of the total concentration of Mn in (Ga,Mn)As for $T_{\text{eff}} = 500$ K. The influence of other dopants is not considered.

It is important to point out that according to Eqs. (3, 4, 7) both Mn_{Ga} and Mn_{int} atoms remain metastable with the activation energy $\approx$ 0.3 eV in the whole concentration range shown in Fig. 4. The formation energies used in our dynamical-equilibrium approach control the preferential incorporation of Mn atoms during the growth. The annealing process, on the other hand, depends on the barriers preventing the Mn atoms to leave their metastable positions. The barriers are lower for Mn_{int} than for Mn_{Ga} position [16], so that the post-growth treatment can substantially reduce the number of the interstitial Mn atoms without a remarkable change of the number of Mn_{Ga}.

4. Summary

We have shown that the formation energies of Mn in either substitutional or interstitial position depend strongly on the partial concentrations of both Mn_{Ga} and Mn_{int}, and also on the number of compensating donors. Also the formation energy of As_{Ga} antisite, the main native defect in (Ga,Mn)As, is very sensitive to the concentration of Mn.

The composition dependence of the formation energies represents a feedback mechanism which defines a dynamical equilibrium between Mn_{Ga}, Mn_{int}, and other defects and impurities during the growth. In particular, we found that at higher Mn concentrations the number of both Mn_{Ga} and Mn_{int} increases proportionally to the total concentration of Mn in the as-grown (Ga,Mn)As mixed crystal.

In addition, the concentration dependence of the formation energy of the As_{Ga} antisite defects indicates that an increasing number of these donors also participate in the compensation of the regular Mn_{Ga} acceptors for higher Mn concentrations.

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