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Lattice constant in diluted magnetic semiconductors (Ga,Mn)As

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We use the density-functional calculations to investigate the compositional dependence of the lattice constant of (Ga,Mn)As containing various native defects. The lattice constant of perfect mixed crystals does not depend much on the concentration of Mn. The lattice parameter increases if some Mn atoms occupy interstitial positions. The same happens if As antisite defects are present. A quantitative agreement with the observed compositional dependence is obtained for materials close to the complete compensation due to these two donors. The increase of the lattice constant of (Ga,Mn)As is correlated with the degree of compensation: the materials with low compensation should have lattice constants close to the lattice constant of a GaAs crystal.

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Diluted magnetic III-V semiconductors, such as $Ga_{1-x}Mn_xAs$, combine semiconducting and ferromagnetic properties,[1–4] and are interesting for applications in spin electronics. These materials have been extensively studied in the past years, both experimentally and theoretically.

There is, however, still not much known about the details of the crystal structure of these materials and about the incorporation of Mn atoms. It is generally believed that in well-defined samples the volume of the MnAs precipitates is reduced to zero, and that Mn simply substitutes for the host cation in a tetrahedral (zinc-blende or wurtzite) crystal structure. Only recently it was suggested[5,6] and experimentally proved[7] that a portion of Mn occupies interstitial rather than substitutional positions in the zinc-blende lattice of (Ga,Mn)As. The interstitial Mn atoms act as double donors,[5,6,8,9] in contrast to Mn atoms in the substitutional positions that are known to be acceptors.

Almost unnoticed remains the surprising fact that the lattice constant of (Ga,Mn)As increases with the increasing concentration of Mn.[10] According to the atomic radii,[11] Mn atoms are smaller ($R_{\mathrm{Mn}}=1.17$ Å) than Ga atoms ($R_{\mathrm{Ga}}=1.25$ Å) and, in the simplest approximation, the lattice constant should be expected to decrease rather than to increase. This is also a result of a recent theoretical study[12] of the structure of zinc-blende α-MnAs. According to these calculations, the lattice constant of α-MnAs is smaller than the lattice constant of GaAs.

On the other hand, the lattice constant of GaAs is well known to increase in the presence of As antisite defects.[13,14] The molecular-beam epitaxy grown GaAs crystals may contain up to 1 at. % of these defects and a large amount of the antisite defects is expected also in (Ga,Mn)As.[15] Being donors, they have an important role in the compensation of Mn acceptors. It was also shown recently[16] that the formation energy of an As antisite defect in (Ga,Mn)As decreases remarkably with the increasing content of Mn, and that the concentration of As antisites should be correlated with the concentration of Mn atoms. This indirect mechanism, i.e., the increasing number of the As antisites due to the addition of Mn, could be a possible explanation for the observed increase of the lattice constant of (Ga,Mn)As.

Also the presence of the interstitial Mn atoms can be the reason for the observed expansion of the lattice,[6] assuming only that the number of the interstitials increases proportionally to the total concentration of Mn.

In this paper, we put these intuitive considerations on serious grounds by using the density-functional calculations. We consider a GaAs crystal with small but finite concentration of various impurities, such as Mn atoms in either substitutional or interstitial positions and As atoms in the cationic sublattice. We use a tight-binding linear muffin-tin orbital method to describe the electronic structure of these imperfect crystals. The charge self-consistency is treated in the framework of the local spin-density approximation with the Vosko-Wilk-Nusair parametrization[18] for the exchange-correlation potential. The crystal potential is considered within the atomic-sphere approximation (ASA) with empty spheres in tetrahedral interstitial positions for a good space filling.

The substitutional disorder due to the random distribution of either Mn or As atoms on the cationic sublattice as well as the random distribution of Mn atoms in the interstitial positions are treated in the coherent-potential approximation (CPA)—for details, see Ref. 17. The advantage of the CPA is that it is well suited for systems with low concentrations of impurities, assuming the unperturbed, zinc-blende symmetry of the mixed crystals. The CPA treatment, on the other hand, neglects the relaxation of the lattice around the impurities.

The lattice constant a is used as a variable parameter and the total energy is calculated for approximately ten values of a around the calculated lattice constant 5.57 Å of the pure GaAs. The minimum of the total energy from the density-functional calculations with respect to a is found by using a cubic interpolation scheme.

We start with ideal mixed crystals $Ga_{1-x}Mn_xAs$, where all Mn atoms are in the substitutional positions. We calculated the lattice constants for a series of materials with $x=0.01$, 0.02, 0.03, 0.04, 0.05, and 0.10. The calculated dependence of the lattice constant on the concentration is linear up to $x=0.10$:

$$a(x)=a_0+0.02x \quad (\text{Å}). \tag{1}$$

It is in a good agreement with the Vegard law. The calculated lattice constant of GaAs crystal, $a_0=5.569$ Å, is smaller than the observed value $a_0^{\mathrm{exp}}=5.653$ Å.[19] This is a result of

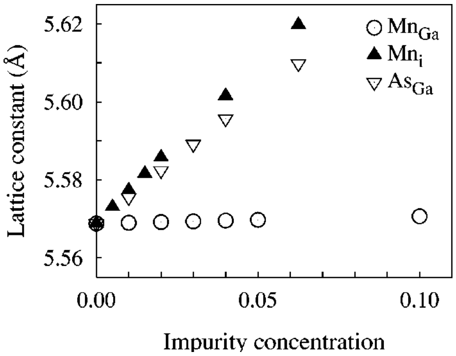

FIG. 1. Calculated lattice constant as a function of the concentration of the impurities: (a) Mn atoms in the substitutional positions (circles), (b) Mn atoms in the interstitial positions (full triangles), and (c) As antisite defects (empty triangles).

the local spin-density approximation (LSDA) combined with the ASA. In our study, however, we are not primarily interested in the absolute values of the lattice constant, but in its variation due to the changes of the chemical composition. We assume that this systematic underestimation has only a minor effect on the compositional dependence of the lattice constant a, characterized by the linear coefficient in Eq. (1). This coefficient is very small. Even at the highest concentration of Mn atoms ($x=0.1$), the lattice constant of the mixed crystal $a=5.571$ Å does not differ from the lattice constant of the pure GaAs by more than 0.05%.

This means that the calculated changes of $a(x)$ are by an order of magnitude smaller than the observed values.[10] This result is in a good correspondence with the recent finding that the local relaxations around the substitutional Mn impurity are very small and have only a small impact on its electronic configuration.[20] According to Zhao *et al.*,[12] the lattice constant of $Ga_{1-x}Mn_xAs$ may even decrease with increasing x. From this point of view, we conclude that the substitution of Mn atoms into the cationic sublattice has a negligible effect on the lattice constant of $Ga_{1-x}Mn_xAs$, and that the observed expansion of the lattice of the (Ga,Mn)As mixed crystals should be ascribed to other lattice defects.

To estimate the effect due to the interstitial Mn atoms, we first consider hypothetical materials $GaMn_zAs$, in which all Mn atoms are in the interstitial positions. We assumed only the interstitial positions surrounded by As atoms (cf. Ref. 5) that are thermodynamically more favorable than the positions with neighboring Ga atoms. As shown in Fig. 1, the calculated lattice constants of $GaMn_zAs$ with $z=0.01$, 0.02, 0.03, and 0.04 lie on a straight line

$$a(z)=a_0+0.86z \quad (\text{Å}). \tag{2}$$

The change of the lattice constant due to the addition of Mn atoms is in this case much stronger as compared to the case of substitution. Assuming for simplicity that the increase of the lattice constant is only due to the presence of the interstitial Mn atoms, we can use Eq. (2) to estimate the number of these defects in the material. The experimental compositional dependence of the lattice constant of (Ga,Mn)As is[10]

$$a(\tilde{x})=a_0^{\exp}+0.32\tilde{x} \quad (\text{Å}), \tag{3}$$

where $\tilde{x}$ denotes the total concentration of Mn atoms ($\tilde{x}=x+z$). Combining Eqs. (1)–(3), we get $z\approx\tilde{x}/3$. This result is close to the experimental finding[7] and to a simple estimate of Ref. 6. It is important to point out that materials with such a ratio between acceptors and donors are almost completely compensated, with a strongly reduced doping efficiency of Mn.

It should be noted that the hypothetical materials used to obtain Eq. (2) contain no substitutional Mn and are *n*-type semiconductors. This is the reason why we have performed additional calculations also for *p*-type materials containing 5 at. % of the substitutional Mn. We consider the z dependence of the lattice constant for $Ga_{0.95}Mn_{0.05}Mn_zAs$ mixed crystals. In this case we obtain that the linear coefficient in $a(z)$ is 1.26 instead of 0.86 as in Eq. (2). The real concentrations of the interstitial Mn atoms are, however, small ($z<0.01$), so that both values of the linear coefficient describe the increase of the lattice constant with a reasonable accuracy. In the following, we shall consider a simple modification of Eq. (2), with the average value 1.05 of the linear coefficient instead of introducing corrections proportional to the product xz.

The dependence of the lattice constant on the concentration of As antisite defects was treated in the same way. We considered a series of hypothetical nonstoichiometric crystals $Ga_{1-y}As_yAs$ with a random distribution of the additional As atoms on the cationic sublattice. In Fig. 1 we show that the lattice constant increases with the increasing concentration y of the antisite defects. The data for $y=0.01$, 0.02, 0.03, and 0.04 can be fitted by a linear function

$$a(y)=a_0+0.69y \quad (\text{Å}). \tag{4}$$

The substitution of As atoms into the Ga sublattice has a much stronger effect on the lattice expansion as compared to the substitution of Mn. The value of the linear coefficient compares well with the lattice expansion of GaAs due to As antisite defects obtained recently using the large-unit-cell calculations.[14] The coefficient in the experimental function (3) is approximately one-half of the linear coefficient in Eq. (4). This means that the number of the antisite defects necessary to explain the observed increase of the lattice constant is, with a good accuracy, proportional to the total concentration of Mn, namely, $y\approx\tilde{x}/2$. This result is not surprising because it implies an almost complete compensation, which is actually observed in (Ga,Mn)As.

Finally, Eqs. (1), (4), and a modified Eq. (2) can be summarized to a simple formula for the compositional dependence of the lattice constant of (Ga,Mn)As,

$$a(x,y,z)=a_0+0.02x+0.69y+1.05z \quad (\text{Å}). \tag{5}$$

The additivity of three contributions on the right-hand side of

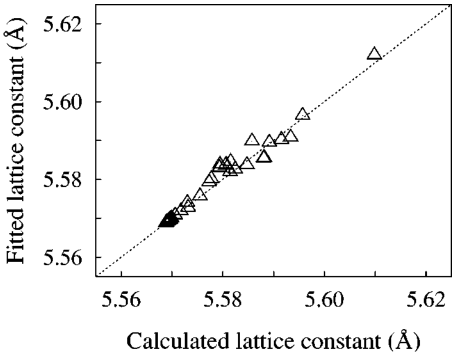

FIG. 2. Correlation plot for the lattice constant. The values obtained according to Eq. (5) (y axis) are plotted against the results of the density-functional calculations (x axis).

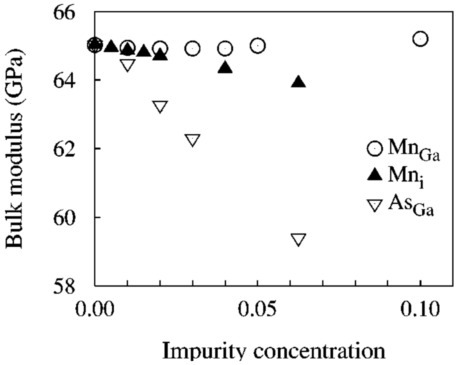

FIG. 3. Calculated bulk modulus as a function of the concentration of the impurities: (a) Mn atoms in the substitutional positions (circles), (b) Mn atoms in the interstitial positions (full triangles), and (c) As antisite defects (empty triangles).

Eq. (5) was checked by calculations of the lattice constant for several compositions with different values of concentrations x, y, and z. The validity of the formula (5) is illustrated in Fig. 2, in which we present a correlation plot of the values of $a(x,y,z)$ as obtained from Eq. (5) against the results of the density-functional calculations. Most of the points are found close to the diagonal. This means that Eq. (5) is applicable with a reasonable accuracy to the whole low-concentration range of the mixed (Ga,Mn)As crystals.

The observed dependence of the lattice constant can be obtained assuming that the concentration of either interstitial Mn atoms or As antisites increases proportionally to the nominal concentration of Mn. A rough estimate of the proportionality coefficients shows that in both cases number of native defects is such that the system is highly compensated.

Combining the calculated linear coefficients in Eq. (5) with the condition $x+z=\tilde{x}$ and with the expression

$$\eta\tilde{x}=x-2y-2z \tag{6}$$

for the doping efficiency η, we can speculate about the values of x, y, and z. For a realistic degree of compensation, $0.1\leqslant\eta\leqslant0.2$, the fit of Eqs. (3)–(5) does not result to a preferential occurrence of either Mn interstitials or As antisites. This result indicates that both donors are equally important for the compensation in (Ga,Mn)As. It is also in a good correspondence with the fact that the formation energies of both Mn interstitials[9] and As antisites[21] have roughly the same value (≈ 2 eV).

The dependence of the total energy $E_{tot}(a)$ on the lattice constant a can also be used to determine the elastic modulus

$$B=\frac{1}{9a}\,\frac{d^2E_{tot}(a)}{da^2} \tag{7}$$

for (Ga,Mn)As mixed crystals and its compositional dependence. Our results indicate that the bulk modulus B does not depend much on the concentration of substitutional Mn atoms, as shown in Fig. 3. It decreases in the presence of interstitial Mn atoms and in particular in the presence of As antisites. The softening of the lattice is not surprising because these defects disturb the crystal bonding. It should be noticed, however, that the elastic modulus, as compared to the lattice constant, is much more sensitive both to the (neglected) lattice relaxation and to the detailed shape of the potential.

We also performed complementary full-potential LAPW (Ref. 22) calculations of the lattice constants for supercells $Ga_{15}MnAs_{16}$ and $Ga_{16}MnAs_{16}$ with Mn in either substitutional or interstitial positions. Both linearized-augmented-plane-wave and generalized gradient approximation versions of the density functional were used. The results of the supercell calculations confirm the basic finding of the CPA study that the substitution of Mn in the cationic lattice has a negligible effect on the lattice constant. In the case of interstitial Mn, a remarkable increase of the lattice constant is found, similar to Eq. (2). In this case, the preliminary calculations also indicate, in contrary to the case of substitution,[20] the importance of the lattice relaxations around the Mn impurity. The detailed discussion of the Mn interstitials in (Ga,Mn)As will be given elsewhere.

We conclude that the lattice constant can be used as a simple indication of the quality of the diluted (Ga,Mn)As mixed crystal. The lattice constant increasing with the content of Mn seems to be an inherent property of materials with a large number of Mn-induced native defects. These defects lower the doping efficiency of Mn in mixed (Ga,Mn)As crystals and, in turn, also the Curie temperature. On the other hand, the desirable samples with low concentrations of compensating donors and with most of Mn atoms substituted into the cationic sublattice are expected to have almost the same lattice constant as the underlying GaAs crystal.

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