Diffusion of Interstitial Mn in the Dilute Magnetic Semiconductor (Ga,Mn)As: The Effect of a Charge State

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Migration barriers for diffusion of interstitial Mn in the dilute magnetic semiconductor (Ga,Mn)As are studied using first-principles calculations. The diffusion pathway goes through two types of interstitial sites: As coordinated and Ga coordinated. The energy profile along the path is found to depend on the ratio of concentrations between substitutional and interstitial Mn in GaAs. Two regions of distinctly different behavior, corresponding to n-type and p-type (Ga,Mn)As, are identified. The difference in mobility is a reflection of the change in the charge state of Mn interstitials (double donors) that occurs in the presence of substitutional Mn impurities (acceptors). In addition, substitutional Mn impurities are shown to act as traps for interstitial Mn. The effective migration barrier for the positively doubly charged Mn interstitials in p-type (Ga,Mn)As is estimated to vary from 0.55 to about 0.95 eV.

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Semiconducting materials with electrically tunable ferromagnetism above room temperature are of strong interest for spintronics as they may open up new possibilities to fabricate functional spintronic devices. In this respect, magnetically doped Si and GaAs have a great potential for applications, as these host semiconductor materials are well understood and already play a crucial technological role. The discovery of ferromagnetic ordering in Mn-doped GaAs [1] and InAs [2] by Ohno *et al.* at temperatures above 100 K has stimulated intensive research into the III-V dilute magnetic semiconductors. The magnetic properties of these materials are very sensitive to the presence of compensating defects, such as antisite defects ($\mathrm{As}_{\mathrm{Ga}}$) [3] or Mn interstitials (Mn_{I}) [4] in (Ga,Mn)As. Indeed, these defects decrease the Curie temperature T_C by acting as double donors and compensating the holes provided by the substitutional Mn atoms that induce ferromagnetism.

It would be ideal for the magnetic properties if the Mn impurities formed a random substitutional solid solution and resided solely on the Ga sublattice in GaAs. However, it was experimentally found that in the as-grown samples a significant fraction (up to 17%) of the doped Mn atoms reside on the interstitial sites [5]. Further experimental studies of (Ga,Mn)As thin films showed a marked increase in the T_C upon low-temperature annealing. This increase was attributed to outdiffusion of the Mn interstitials towards the surface [6,7].

Also, it has been found that by varying the temperature or the duration of annealing one may produce changes of T_C in both directions [5], most probably because the annealing promotes both the migration of interstitial Mn and the formation of defect clusters involving substitutional Mn atoms. The clustering is governed by a diffusion barrier of 2.2–2.3 eV [8] and reduces the Curie temperature. Hence, understanding the impurities' behavior is needed for carefully controlling the outdiffusion of interstitial Mn, while preventing the clustering of substitutional Mn, in order to achieve high critical temperatures of ferromagnetic ordering in (Ga,Mn)As.

The diffusion mechanisms of substitutional Mn impurities in GaAs have been thoroughly studied using atomistic modeling based on a first-principles approach [8,9]. Interstitial diffusion of Mn in (Ga,Mn)As has been studied both experimentally and theoretically by Edmonds *et al.* in Ref. [6]. An experimental estimate of the energy barrier for diffusion of Mn interstitials through GaAs was derived, 0.7 ± 0.1 eV, whereas theoretical estimates obtained in the same study were as high as 0.8–1.25 eV [6]. In the present study, we obtain new theoretical estimates of the energy barriers for diffusion of Mn interstitials in (Ga,Mn)As, for the three possible charge states of the diffusing species: neutral (0), singly charged (+1), and doubly charged (+2). For the positively doubly charged state of Mn_{I} (the only charge state considered by Edmonds *et al.*) our estimates are closer to the experimentally derived values of Ref. [6]. Importantly, our calculations show that the migration barrier of an interstitial Mn impurity in the singly charged state or in the neutral state becomes much lower than that in the doubly charged state.

The gradient-corrected [10,11] total energy calculations reported in this Letter have been done using a supercell approach and employed two electronic structure techniques, the locally self-consistent Green's function (LSGF) method [12,13] and the Vienna *ab initio* simulation package (VASP) [14]. LSGF is a most efficient all-electron technique for performing massive supercell calculations, as it gives a linear scaling of computer time with the number of atoms in the supercell. In this study, we used LSGF supercell calculations [15] in order to make an extensive and quick search for the optimal atomic and magnetic configurations of native defects and impurities in GaAs. We took advantage of the VASP technique [17] when obtaining the fully relaxed geometry for supercells with defect configurations of our interest for the present study. Whenever possible, we made comparisons of, and found good agreement between, the energy differences calculated using both methods.

For example, in Fig. 1 we show the total energy difference between two defect configurations in which the interstitial Mn is situated on either of the two interstitial sites in the GaAs crystal structure (Ga-coordinated site I:Ga and As-coordinated site I:As) [19], $E(\mathrm{Mn}_{\mathrm{I:Ga}}) - E(\mathrm{Mn}_{\mathrm{I:As}})$. Hereafter, this energy difference is referred to as the site-preference energy. Figure 1 shows *unrelaxed* energies, calculated using both the LSGF and VASP techniques at the experimental lattice parameter and with all the atoms kept at the ideal lattice positions (unrelaxed geometry). When setting up the atomic configurations, we placed the interstitial and substitutional Mn impurities as far away from each other as possible within the chosen supercell, in order to exclude, for the moment, the effects of strong nearest-neighbor interactions between the two kinds of impurities. These effects will be considered separately below.

VASP calculations were employed to simulate the migration of a Mn interstitial through the zinc blende lattice of GaAs. The diffusion occurs by means of nearest-neighbor jumps, –I:Ga–I:As–I:Ga–I:As–, between the interstitial positions. Therefore, we considered the extra Mn atom, subsequently, on a Ga-coordinated site and on an As-coordinated site, as well as in the position midway between two nearest-neighbor interstitial sites [19]. In these simulations, unlike in the site-preference energy calculations presented in Fig. 1, the energies were calculated within a fully relaxed geometry, by letting the volume and the internal atomic positions of the supercell freely adjust while constraining the supercell shape and the migrating atom's coordinates (when the ion is considered in the intermediate position).

All these atomic configurations were considered in a magnetic configuration with the magnetic moments on substitutional $\mathrm{Mn}_{\mathrm{Ga}}$ ions oriented parallel to each other and antiparallel to the magnetic moment of interstitial Mn. The energy of this magnetic configuration had been found in our LSGF calculations to be the lowest among the collinear configurations for systems composed of one Mn_{I} and up to six $\mathrm{Mn}_{\mathrm{Ga}}$ impurities in the otherwise pure GaAs 64-atoms supercell.

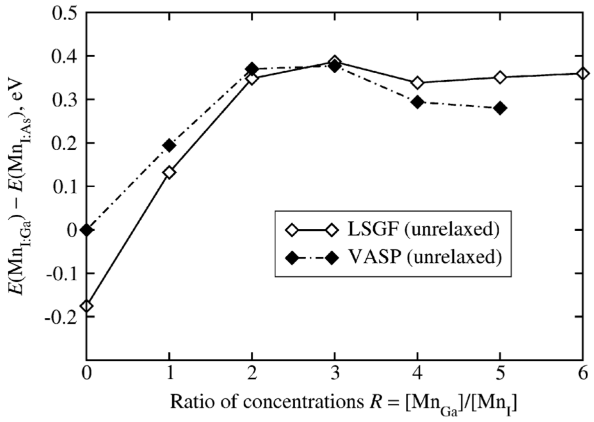

FIG. 1. *Unrelaxed* site-preference energy of an interstitial Mn in the 64-atoms supercells of (Ga,Mn)As, as a function of the relative concentration of substitutional $\mathrm{Mn}_{\mathrm{Ga}}$.

Our LSGF and VASP calculations consistently show (see Fig. 1) that the site-preference energy of an *interstitial* Mn impurity in GaAs depends rather strongly on the concentration of *substitutional* Mn, but only up to a certain point at which a break occurs in the concentration dependence. For concentrations above the break point, which corresponds to a concentration ratio of $R \equiv [\mathrm{Mn}_{\mathrm{Ga}}]/[\mathrm{Mn}_{\mathrm{I}}] = 2$, the As-coordinated site becomes strongly preferred by an interstitial Mn impurity, but concentration dependence of the site-preference energy becomes rather weak. (Hereafter square brackets denote the site fraction of the impurity.) On the other side of the breakpoint, in the limit of complete absence of substitutional Mn where $R = 0$, the calculated site-preference energy becomes very small; the LSGF value even turns slightly negative.

In order to explain the concentration dependence of site-preference energy, as well as that of diffusion barriers (will be presented below), one should take into account the electronic structure of the interstitial and substitutional Mn impurities. The substitutional $\mathrm{Mn}_{\mathrm{Ga}}^{\times}$ impurities in GaAs are single acceptors, whereas the interstitial $\mathrm{Mn}_{\mathrm{I}}^{\times}$ impurities are double donors. When Mn impurities of both kinds are present in Mn-doped GaAs, the electrons and the holes brought by the impurities recombine with each other to produce charged defect species: negatively charged substitutional impurities $\mathrm{Mn}_{\mathrm{Ga}}^{\prime}$ as well as singly, $\mathrm{Mn}_{\mathrm{I}}^{\bullet}$, or doubly, $\mathrm{Mn}_{\mathrm{I}}^{\bullet\bullet}$, positively charged interstitial impurities. Hereafter we use the Kröger-Vink notations (superscripts $\times$, $\bullet$, and $/$) to denote, respectively, the charge-neutral, positively charged, and negatively charged states of defects. The breakpoint occurs at a concentration ratio of $R = 2$, which corresponds to the compensation point separating the *n*- and *p*-type doping regions of (Ga, Mn)As.

The interstitial site preference may be considered to be a result of competition between the following main contributions: (1) atomic size contribution, which favors the occupancy of an interstitial site coordinated by the relatively small Ga cations, (2) electronegativity (or ionic) contribution, which stabilizes a Mn cation at a site coordinated by the negatively charged As anions.

For the *charge-neutral* state of an interstitial Mn_{I} (the case of $R = 0$ in Fig. 1) this competition results in a very weak site preference, implying that the atomic size contribution and the electronegativity contribution are nearly balancing each other. On the other side of the compensation point (the case of $R \geq 2$ in Fig. 1) the interstitial Mn impurity is doubly *positively charged* and, therefore, the ionic contribution dominates.

The effect of full relaxation on the VASP-calculated site-preference energy comes mainly from the lowering of the first contribution, which is due to the fact that structural relaxation makes the difference in size between the two interstitial positions in GaAs less important, thereby making the second (ionic) contribution relatively more important. Figure 2 shows the calculated lattice parameter of the $(\mathrm{Ga,Mn})\mathrm{As} + \mathrm{Mn}_{\mathrm{I:As}}$ and $(\mathrm{Ga,Mn})\mathrm{As} + \mathrm{Mn}_{\mathrm{I:Ga}}$ supercells as a function of the ratio of substitutional and interstitial Mn concentrations. Apart from a weak lattice parameter anomaly in $(\mathrm{Ga,Mn})\mathrm{As} + \mathrm{Mn}_{\mathrm{I}}$ at the compensation point, the concentration dependencies for $\mathrm{Mn}_{\mathrm{I:As}}$ and $\mathrm{Mn}_{\mathrm{I:Ga}}$ are monotonic and almost parallel to each other, indicating that the size contribution is nearly independent of the concentration ratio. The lattice parameter of $(\mathrm{Ga,Mn})\mathrm{As} + \mathrm{Mn}_{\mathrm{I:As}}$ is calculated to always be above that of $(\mathrm{Ga,Mn})\mathrm{As} + \mathrm{Mn}_{\mathrm{I:Ga}}$, showing that interstitial Mn impurity pushes out the host atoms much stronger when it is situated at a tighter As-coordinated site, rather than at a relatively loose Ga-coordinated site, thereby reducing the size difference between the sites.

In summary, the site preference of an interstitial Mn impurity in GaAs is mainly determined by the *ionic* contribution, due to which the total energy is a minimum when the impurity occupies an As-coordinated site. Because of the dominant ionic contribution, the site-preference energy takes on different values for different charge states of the impurity. These conclusions are illustrated by Fig. 3, where we show the calculated total energy profiles for an interstitial Mn_{I} moving along the I:As–I:Ga–I:As migration path in (Ga,Mn)As. All the total energy profiles exhibit a deeper minimum when the Mn impurity is located at an As-coordinated interstitial site.

A very shallow energy profile is exhibited by the interstitial impurity in the charge-neutral state $\mathrm{Mn}_{\mathrm{I}}^{\times}$, which is realized in supercells that do not contain substitutional Mn impurities. The profile has a maximum at the Ga-coordinated site; therefore, the migration barrier for a charge-neutral interstitial impurity is equal to the modulus of site-preference energy. Interstitial Mn impurities become singly positively charged, $\mathrm{Mn}_{\mathrm{I}}^{\bullet}$, at a concentration ratio of $R = 1$ and doubly positively charged, $\mathrm{Mn}_{\mathrm{I}}^{\bullet\bullet}$, for the concentration ratios above the compensation point, $R \geq 2$. For these charged states of Mn_{I} the total energy profiles have shapes that are qualitatively different from that for a charge-neutral impurity, with minima at interstitial sites of both kinds and maxima in the intermediate positions. Figure 3 also shows that within the practically most relevant range of concentrations, $2 \leq R \leq 5$, the calculated height of diffusion barrier is 0.55 ± 0.03 eV, almost independently of the substitutional $\mathrm{Mn}_{\mathrm{Ga}}$ concentration. The obtained dependence of the diffusion barrier on the charge state of an interstitial Mn impurity in GaAs is most naturally explained by the electrostatic interaction of the migrating impurity ion with the crystal field imposed by the host. It is the electrostatic interaction of an interstitial Mn impurity with the cationic (Ga) and anionic (As) sublattices that creates high additional barriers for its migration when the impurity is charged; a neutral $\mathrm{Mn}_{\mathrm{I}}^{\times}$ impurity makes its way through GaAs relatively easily.

Experimental measurements [5] have shown that a significant fraction of interstitial Mn remains in the sample after the annealing at 282 °C. The measured magnetization of annealed samples [7] is still less than the theoretically expected $4\mu_B$ per Mn atom [3], which may be explained by the presence of residual donor defects that have formed charge-neutral paramagnetic complexes like $\{2\mathrm{Mn}'_{\mathrm{Ga}} + \mathrm{Mn}_{\mathrm{I}}^{\bullet\bullet}\}^{\times}$. We have studied the stability of such complexes using VASP calculations. The dissociation energies have been computed relative to the final configuration in which the substitutional and interstitial Mn atoms are removed from each other to a maximum separation distance within the 64-atoms cubic supercell.

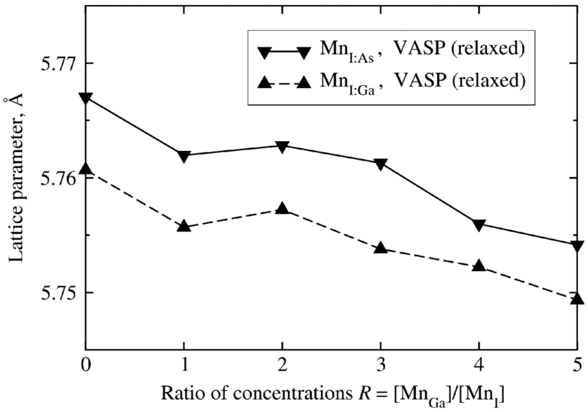

FIG. 2. Relaxed lattice parameter of (Ga,Mn)As supercells, each containing one interstitial impurity ($\mathrm{Mn}_{\mathrm{I:As}}$ or $\mathrm{Mn}_{\mathrm{I:Ga}}$), as a function of the relative concentration of substitutional $\mathrm{Mn}_{\mathrm{Ga}}$.

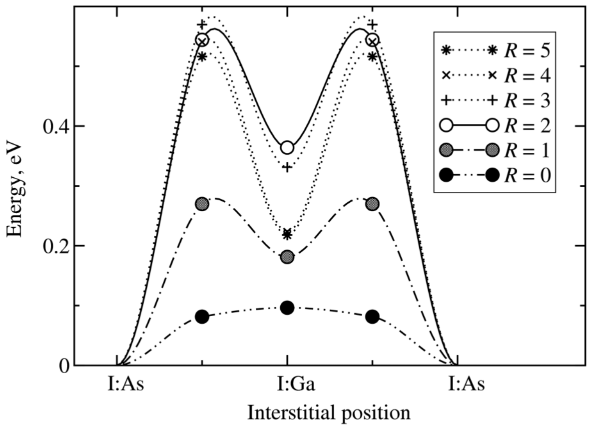

FIG. 3. Calculated energy of a migrating Mn interstitial along the I:As–I:Ga–I:As path in (Ga,Mn)As for six different values of concentration ratio $R \equiv [\mathrm{Mn}_{\mathrm{Ga}}]/[\mathrm{Mn}_{\mathrm{I}}]$. The lines are guides to the eye.

The calculated dissociation energies of $\{2\mathrm{Mn}'_{\mathrm{Ga}} + \mathrm{Mn}^{\bullet\bullet}_{\mathrm{I:As}}\}^{\times}$, $\{\mathrm{Mn}'_{\mathrm{Ga}} + \mathrm{Mn}^{\bullet}_{\mathrm{I:Ga}}\}^{\times}$, and $\{\mathrm{Mn}'_{\mathrm{Ga}} + \mathrm{Mn}^{\bullet}_{\mathrm{I:As}}\}^{\times}$ defect complexes in GaAs are 0.81, 0.29, and 0.49 eV, respectively. The most stable of these defect complexes corresponds to a fully compensated state of three Mn impurities. In order for the interstitial Mn ion to move away from such a complex, an activation energy of $0.81 + 0.55 = 1.35$ eV is needed. This high energy prevents outdiffusion of a part of Mn_{I} atoms that are bound in these complexes, which explains why some Mn_{I} remain in the specimen after a low-temperature annealing. The "effective" activation energy, which includes an average dissociation energy of a $\mathrm{Mn}'_{\mathrm{Ga}} + \mathrm{Mn}^{\bullet}_{\mathrm{I}}$ defect pair, is then 0.95 ± 0.1 eV. The outdiffusion path of a Mn interstitial involves many steps and may be complicated. The probability for the interstitial ion to be trapped into pair complexes on its way out is quite high. The experimentally observed activation energy for diffusion should then be viewed as an average of the migration barriers at individual diffusion steps. Treating the $\mathrm{Mn}_{\mathrm{Ga}}$ impurities as reversible traps [20] for interstitial Mn, one can expect, depending on the concentration and distribution of $\mathrm{Mn}_{\mathrm{Ga}}$, the activation energy for Mn_{I} diffusion to be within the range 0.55–0.95 eV, in agreement with the experimental value of 0.7 ± 0.1 eV obtained by Edmonds *et al.* [6].

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