Defect-Induced Magnetic Structure in $(Ga_{1-x}Mn_x)As$

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We show that magnetic structures involving partial disorder of local magnetic moments on the Mn atoms in $(Ga_{1-x}Mn_x)As$ lower the total energy, compared to the case of perfect ferromagnetic ordering, when As defects on the Ga sublattice are present. Such magnetic structures are found to be stable for a range of concentrations of As antisites, and this result accounts for the observed magnetic moments and critical temperatures in $(Ga_{1-x}Mn_x)As$. We propose an explanation for the stabilization of the partially disordered magnetic structures and conclude that the magnetization and critical temperatures should increase substantially by reducing the number of As antisite defects.

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Magnetically doped semiconductors have been argued to be of tremendous scientific and technological importance [1]. Substitution of Mn for Ga in GaAs has been shown to result in a particularly promising material and the observation of ferromagnetism at temperatures up to 100 K (Ref. [2]) has spurred intense experimental [1–3] and theoretical [4–11] activity. Typically these materials are produced by thin film growth since Mn has limited solubility in bulk GaAs.

In order to facilitate a technological breakthrough using magnetic semiconductors with a critical temperature above room temperature, an understanding of their magnetic properties and a correlation to the electronic structure must be achieved. However, even the origin of the ferromagnetism in these systems is under discussion, and alternative viewpoints have been put forward, including the RKKY model [5], the competition between the double- and superexchange mechanisms [4], or a double resonance mechanism [6]. Experimental and theoretical work agree so far upon the conclusion that for $(Ga_{1-x}Mn_x)As$ the critical temperature depends on the hole concentration and that the hole concentration correlates to the concentration of Mn atoms that has substituted Ga [3–5]. The latter is expected for divalent Mn substituting trivalent Ga in GaAs. However, the correlation between Mn concentration and hole concentration is not one-to-one [3], suggesting that Mn substitution is accompanied by lattice defects on the Ga and/or As sublattice. In particular so called As antisites, i.e., As atoms substituting on the Ga sublattice (denoted As_{Ga}), are found to be the most common defects [12]. Because of a high equilibrium vapor pressure of As, epitaxial growth of GaAs is usually performed at a certain As overpressure that produces an As-rich GaAs [13]. Combined with the high concentration of Mn atoms (acceptors), such experimental conditions make the formation of As antisites (donors) energetically favorable.

With the aim of achieving room temperature magnetic semiconductors one could try to increase the value of the critical temperature by increasing the Mn concentration. However, growth of the $(Ga_{1-x}Mn_x)As$ films with higher Mn concentration than $\sim$10% (atomic percentage on the Ga sublattice will be used throughout the paper) has been difficult [14]. Another avenue to increase the value of T_c would be via the influence on the hole concentration and possibly via the influence of defects, such as the mentioned As_{Ga} antisites, but in order to do this one needs to elucidate how the holes or the As_{GA} concentration influence the magnetic properties. In order to illuminate the problem, we would like to point out that first-principles calculations give magnetic moments of $4\mu_B$ for ferromagnetically coupled Mn impurities on the Ga sublattice in GaAs. The conventional assumption that electrons of the As_{GA} antisite simply compensate some of the holes introduced by Mn impurities leads to that the saturation magnetization is expected to be between 4 and $5\mu_B$ per Mn atom. However, this is in sharp contrast to the experimental results obtained by saturation magnetization measurements that, as we shall show below, are significantly smaller. Thus, there is a marked disagreement between experimental saturation magnetization data and the theory, which is serious (it is well known that first-principles calculations typically reproduce the magnetic moments of any material within a few percent) and casts doubt on the theoretical understanding of the magnetism and its connection to the electronic structure of $(Ga_{1-x}Mn_x)As$.

In this manuscript we address this problem by a combined experimental and theoretical study and we demonstrate that an almost perfect agreement between experiment and theory is obtained provided one considers the influence of As antisites and a magnetic ground state where *only a part* of the randomly distributed Mn atoms are ferromagnetically aligned while the rest of the Mn atoms have orientations of their magnetic moments antiparallel to each other, in a so-called disordered local moment (DLM) configuration [15]. We also provide a microscopic explanation of the correlation between magnetic moment disorder and the concentration of As_{GA}.

The details of the experimental work are the following. High-quality $(Ga_{1-x}Mn_x)As$ films, with the concentration of manganese ranging from 1% to 7% have been grown on GaAs (001) substrates using low-temperature molecular beam epitaxial growth [14]. Magnetization vs temperature and magnetic field measurements were performed in a superconducting quantum interference device (SQUID) magnetometer. The saturation magnetization of the different samples was estimated at the temperature $T = 10$ K and in an applied field of $H = 2$ kOe.

The electronic structure and total energy calculations for disordered $(Ga_{1-x-y}Mn_xAs_y)As$ alloys were based on the density functional theory [16] and we made use of the local density approximation [17]. We employed a basis set of the linear muffin-tin orbitals (LMTO) [18,19] with $l_{max} = 2$, in conjunction with the multipole-corrected atomic sphere approximation [20]. We used equal Wigner-Seitz sphere radii for all the atoms on the Ga and As sublattices, as well as for the empty spheres representing the two types of interstitial sites in the zinc blende structure of GaAs. The substitutional and magnetic disorder on the Ga sublattice were treated within the coherent potential approximation [21]. The Mn atoms were allowed to have collinear, but random spin up or spin down orientations of their local spin moments by means of the DLM model [15]. In our theoretical treatment we have minimized the total energy with respect to the fraction of the Mn ↑ and Mn ↓ atoms and the system may obtain a ferromagnetic component in a state that is intermediate between a saturated ferromagnetic state and a DLM state [22].

We first show the results of our magnetization measurements (Fig. 1) of the $(Ga_{1-x}Mn_x)As$ films for concentrations x of Mn between 1% and 7%. The temperature dependent magnetization was measured in a field larger than the coercive field at $T = 10$ K. As may be noted from the main frame of this figure the saturation magnetization corresponds to a magnetic moment between $1.5\mu_B$ and $2.2\mu_B$ per Mn atom. As noted above this number is significantly lower than the data calculated from first principles, $4\mu_B$ for ferromagnetic $(Ga_{1-x}Mn_x)As$ without As antisites [9–11]. The disagreement is particularly alarming since the integer moment in the calculations can be understood only if the system is semiconducting or half metallic. A possible explanation for this disagreement is that the magnetic and electronic states considered in previous theory are more complex, and next we will explore this possibility. Before doing this, however, we note in passing that the measured moment of $4\mu_B$ per Mn atom, quoted by Ohno *et al.* [1–3], is incompatible with our own measurements.

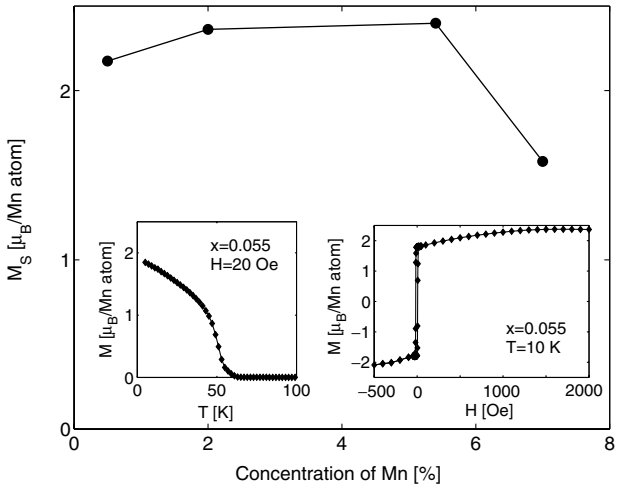

FIG. 1. Mn moment estimated from the measured saturation magnetization vs Mn concentration for $(Ga_{1-x}Mn_x)As$. The two insets show the temperature dependence of the Mn moment (left-hand inset) and the hysteresis loop measured at $T = 10$ K (right-hand inset) for a $(Ga_{1-x}Mn_x)As$ sample with $x = 0.055$.

In Fig. 2 we display the calculated total energy for GaAs when 4% Mn has substituted Ga atoms. In the calculations the system was allowed to form either a pure ferromagnetic state or a ferromagnetic state with a certain degree of local moment disorder. In the later case part of the Mn atoms had the atomic moments pointing towards the global magnetization direction, while another part was pointing in the opposite direction. In the figure the fraction of the Mn atoms that are still ferromagnetically aligned is shown as the order parameter, $\eta = M_{tot}/|M_{loc}|$, where M_{tot} is the averaged, net magnetic moment of the system and M_{loc} is the value of the local moment per Mn atom. Hence, for example, a value of $\eta = 1(-1)$ corresponds to a saturated ferromagnetic state, while if $\eta = 0$ the system has an equal amount of up and down orientations of the magnetic moments. We now allow the order parameter to vary continuously between these two limiting cases. Note also that in our study we calculate the energies of all these different magnetic solutions for different concentrations of the As antisites. As is evident from Fig. 2 the sample is an ideal ferromagnet without spin disorder when there are no As antisites and it is in a spin-disordered state when the concentration of As antisites is above 2%, corresponding to the situation when all the holes introduced by the transition metal are compensated. However, for intermediate concentrations of As_{Ga} antisites, 1%–2%, a DLM state with only partial magnetic order is found to have the lowest total energy.

In Fig. 3 we display the calculated net magnetization as a function of the As_{Ga} concentration, determined for

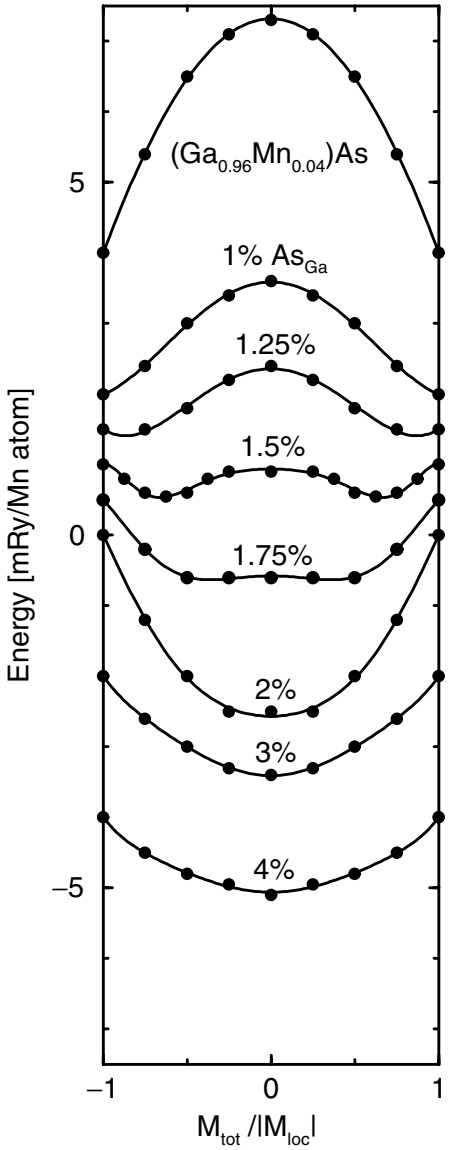

FIG. 2. Calculated total energy as a function of the order parameter $M_{\mathrm{tot}}/|M_{\mathrm{loc}}|$ for various As antisite ($\mathrm{As_{Ga}}$) concentrations. The curves are shifted along the y axis to avoid overlap.

magnetic configurations which minimize the total energy in Fig. 2. In Fig. 3 we also show values of the local moment of the Mn atoms. Note that, in agreement with intuitive chemical arguments, the value of the local moment increases with increasing concentration of $\mathrm{As_{Ga}}$, until a complete compensation of holes takes place at 2% of As antisites. This is so because holes which have spins antiparallel to the d moment of Mn are compensated by the electrons of the As antisites. At the same time, the original increase of the net magnetization is followed by a sharp drop of the average magnetic moment at $\mathrm{As_{Ga}}$ concentrations above 1%. The inset in Fig. 3 shows an estimate of the effective exchange constant [23], J_0, obtained on the basis of the total energy difference between the disordered (DLM) and (partially) ordered (FM) magnetic configurations shown in Fig. 2,

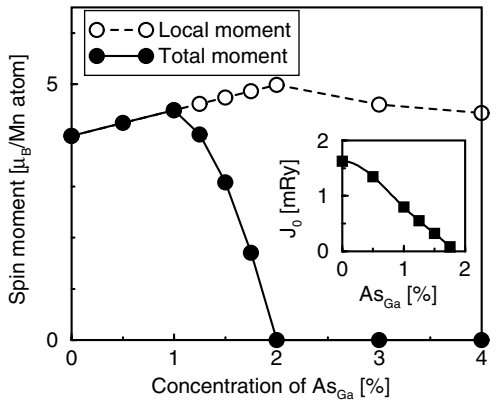

FIG. 3. Calculated net total spin moment, M_{tot}, and local Mn moment, M_{loc}, as a function of $\mathrm{As_{Ga}}$ concentration. The inset shows estimated effective exchange constant J_0.

as $J_0 = (E_{\mathrm{DLM}} - E_{\mathrm{FM}})/2|\eta_{\mathrm{min}}|$. Here η_{min} is the value of the order parameter corresponding to the total energy minimum. The estimated J_0, which may be considered as proportional to the temperature of ferromagnetic ordering, rapidly decreases with increasing the antisite concentration and vanishes in the completely compensated case. In the experimental samples we estimate that the $\mathrm{As_{Ga}}$ concentration is approximately $1.7\% \pm 0.2\%$, in reasonable agreement with direct measurements of this concentration by means of cross-sectional scanning tunneling microscopy [12]. Note that for this $\mathrm{As_{Ga}}$ concentration our theoretical calculations (Fig. 3) result in a magnetization that is in very good agreement with the experimental values shown in Fig. 1. Hence allowing for the system to form a DLM state with a partial magnetic order resolves the discrepancy between previous theory and experiment.

Let us now analyze, in terms of the electronic structure, why the presence of $\mathrm{As_{Ga}}$ antisites in these materials leads to a formation of the partially disordered magnetic state. In Fig. 4 we present the calculated DOS of $(\mathrm{Ga_{0.96}Mn_{0.04}})\mathrm{As}$ (with and without $\mathrm{As_{Ga}}$ atoms) in the DLM configuration where a small (0.25%) fraction of Mn atoms have flipped their magnetic moments against the total magnetization direction. In the figure the DOS is shown for the majority spin channels only. Note that for Mn $\downarrow$ atoms the majority spin channel is the spin $\downarrow$ channel. Without $\mathrm{As_{Ga}}$ antisites (see Fig. 4a) the Mn $\downarrow$ d states form a very narrow impurity subband that is situated exactly at the Fermi level, an energetically very unfavorable situation. Therefore, a flip of a Mn local moment in $(\mathrm{Ga_{0.96}Mn_{0.04}})\mathrm{As}$ is energetically very costly, which is why the Mn atoms order ferromagnetically. The presence of As antisites in $(\mathrm{Ga_{0.945}Mn_{0.04}As_{0.015}})\mathrm{As}$ changes the situation. Figure 4(b) shows that the two extra electrons donated by each As antisite defect have recombined with the Mn-induced holes, so that the impurity s states of $\mathrm{As_{Ga}}$ are unoccupied. As Fig. 4(b) shows, the impurity subband of the Mn $\downarrow$ atoms is now entirely below the Fermi level, due to the band filling effect driven by the As antisites. This reduces the large energy cost of the DLM state, compared to the ferromagnetic state.

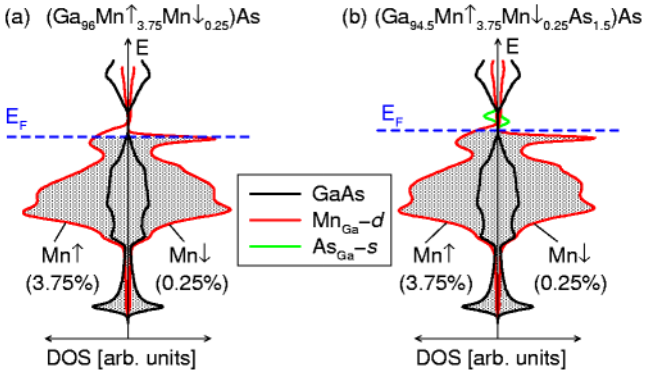

FIG. 4 (color). Density of electron states (per atom) in (GaMn)As alloys containing 4% Mn atoms (3.75% Mn ↑ and 0.25% Mn ↓) on the Ga sublattice, (a) without and (b) with 1.5% As_{Ga} antisites. Shaded areas denote occupied states. Black solid lines show the total DOS of the host, GaAs, whereas colored lines show the DOS for Mn d- (red) and As_{Ga} s- (green) impurity states. Only the majority spin component of the DOS is shown for the Mn ↑ (spin up states) and Mn ↓ (spin down states).

To summarize we have, by combining first principles theory and experimental work, resolved the conspicuous disagreement between previously calculated and measured magnetic moments in $(Ga_{1-x}Mn_x)As$. A novel magnetic structure involving disordered magnetic moments is demonstrated to both minimize the total energy in our theoretical calculations, as well as to reproduce the experimental magnetic moments, provided a concentration of ~1.7% As antisites is considered. This concentration is in agreement with the expected concentration of As antisites in (Ga,Mn)As films [12]. Although the present paper is focused on $(Ga_{1-x}Mn_x)As$ films, our results are most likely applicable to any magnetically doped semiconductor with defects as well as to diffuse interfaces between a semiconductor and a metallic ferromagnet. Our calculations show that as long as GaAs (and most likely any semiconductor) has defect donor states that lie in the band gap, the magnetic coupling of the Mn atoms cannot be purely ferromagnetic, some Mn atoms couple antiferromagnetically or even in a noncollinear fashion. As a result the transport properties would normally not originate from electrons of only one spin projection, an important aspect when these materials are considered for spin injection.

Finally, we propose that the magnetic moments and critical temperatures of magnetically doped semiconductors could be increased substantially by elimination of defects, especially As antisites, putting high demands on the film preparation of these materials. Indeed, recent experiments [24] show that the saturation magnetization increases when the $(Ga_{1-x}Mn_x)As$ films are heat treated. This supports the picture given in the present report.

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