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Ferromagnetic transition temperature enhancement in (Ga,Mn)As semiconductors by carbon codoping

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We present a theoretical study of (Ga,Mn)(As,C) diluted magnetic semiconductors with high C acceptor density that combines insights from phenomenological model and microscopic approaches. A tight-binding coherent-potential approximation is used to describe the electronic structure in the presence of Mn_{Ga} and C_{As} impurities. We find only a small effect of C on the distribution and coherence of electronic states close to the top of the valence band and on the coupling between Mn moments, even at doping levels of several per cent. These results justify applying the model of ferromagnetic Mn-Mn coupling mediated by itinerant holes in the valence band also to C doped samples. The increase of ferromagnetic transition temperature due to the presence of C acceptors is illustrated by calculations that use the $\mathbf{k}\cdot\mathbf{p}$ Kohn-Luttinger description of the GaAs valence band and assume systems where Mn local moment and itinerant hole densities can be varied independently.

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Prospects for new device functionalities in all-semiconductor spin-electronic structures rely on the realization of a ferromagnetic semiconductor operating at room temperature. An important milestone in this material research was the discovery, five years ago,[1] of ferromagnetism in Mn-doped GaAs[2] with the Curie temperature $T_c = 110$ K.[1] In the $Ga_{1-x}Mn_xAs$ diluted magnetic semiconductor (DMS) with $x \approx 1-10\%$, Mn substituting for Ga provides a local moment $S = 5/2$ and a delocalized hole.[3,4] Ferromagnetic coupling between Mn moments is mediated by the itinerant holes via a kinetic-exchange interaction.[5] Recent progress in low-temperature molecular-beam epitaxy growth and postgrowth annealing techniques has led to the increase of the transition temperature in (Ga,Mn)As DMS's by nearly 50 K.[6] This success is attributed to a smaller concentration of carrier and moment compensating defects, especially interstitial Mn, in the optimally annealed samples.[7] The latest observations are consistent with an approximately linear dependence of T_c on x and hole Fermi wave vector predicted by theory.[8–10]

In this Rapid Communication we address theoretically the possibility of increasing T_c in (Ga,Mn)As DMS's by a non-magnetic acceptor codoping, namely, by introducing substitutional C_{As} impurities. Our work is partly motivated by a recent experimental observation of a marked enhancement of the Curie temperature in Mn-implanted GaAs:C samples compared to the Mn-implanted undoped GaAs layers.[11] We focus on two key issues related to high-density carbon doping.

(i) The effect of C impurities on the density of states in the semiconductor valence band is assessed using the tight-binding/coherent-potential-approximation (TB/CPA) description of the disordered semiconductor.

(ii) The strength of the hole-mediated ferromagnetic Mn-Mn coupling is compared for systems with and without C codoping using the TB/CPA results and T_c is then estimated from a model that combines the $\mathbf{k}\cdot\mathbf{p}$ Kohn-Luttinger description of the GaAs valence bands and a mean-field treatment of the kinetic-exchange coupling between Mn local moments and the band holes.

Before we start with the detailed description of the models we use and of the results let us remark that another important issue for hole codoping in (Ga,Mn)As DMS's is the change of the substitutional Mn_{Ga} formation energy caused by the presence of additional non-magnetic acceptors.[12] It is not our intention here to discuss this property in detail, primarily because systematic and quantitatively reliable calculations should be done using *ab inito*, density-functional theory tools which are beyond the scope of this Rapid Communication. In the following paragraph, we make only few qualitative remarks, based on our TB/CPA total energies, that compare effects of C_{As} and Be_{Ga}[13] acceptors on substitutional Mn incorporation in (Ga,Mn)As DMS's.

The TB/CPA results suggest that Be acceptors substituting for the same element as Mn, i.e., for Ga, lead to a strong enhancement of the Mn_{Ga} formation energy. At the same time, the formation energy of interstitial Mn is suppressed and, hence, an increasing fraction of Mn is incorporated in the form of interstitial donors or electrically neutral MnAs or Mn clusters. This scenario, which leads to a decrease rather than an increase of T_c, has recently been established by extensive experimental studies of Be codoped (Ga,Mn)As samples.[13] On the other hand, the TB/CPA calculations indicate that C acceptors lead to a much weaker increase of the Mn_{Ga} formation energy. We surmise that this property stems from the anomalous nature of C_{As} which acts as an acceptor, yet has a larger Pauling's electronegativity than As. The difference between the effects of Be_{Ga} and C_{As} impurities on Mn_{Ga} incorporation is further enhanced at high doping levels where the competition of Be and Mn for the same lattice site starts to play a role.

The above qualitative analysis of formation energies suggests that C_{As} codoping is favorable for achieving high Curie temperatures. Unlike typical acceptors, however, C has a very different atomic size and, as already mentioned, a large electronegativity compared to the atom it substitutes for. The crucial question, addressed in the following paragraphs, is then to what extent doping by several percent of C_{As} changes the semiconductor band structure and whether the model of shallow acceptor carrier-induced ferromagnetism still applies in (Ga,Mn)(As,C).

Our calculations of the electronic structure of GaAs in the presence of Mn_{Ga} and C_{As} impurities are done using the tight-binding version of the coherent-potential approximation (see, e.g., Ref. 14). The CPA, in contrast to supercell calculations, is well suited for the mixed crystals with low concentrations of randomly distributed impurities. It provides estimates for configurationally averaged density of states (DOS) and related quantities. The configurational averaging restores full translational symmetry of the lattice and makes it possible to decompose the DOS into contributions from specific points in the Brillouin zone. The spectral density $A(k,E)$ then includes a detailed information about the dispersion of the electronic states in the reciprocal space. In addition, the width of the peaks of $A(k,E)$ defines the scattering rate of the band quasiparticles in various parts of the Brillouin zone due to the impurities.

The parametrization of the TB Hamiltonian provides correct band gap for a pure GaAs crystal[15] and an appropriate exchange splitting of the Mn *d* states. Local changes of the crystal potential at both Mn and C impurities, represented by shifted atomic levels, are estimated using Ref. 16. Long-range tails of the impurity potentials, which become less important with increasing level of doping, are neglected. (Note that the Thomas-Fermi screening length is only 3–5 Å for typical carrier densities,[17] i.e., comparable to the lattice constant.) Also lattice relaxation effects are neglected within the CPA. This is well justified for Mn_{Ga} impurities[18,19] but becomes a more important issue in the case of C_{As} impurities. Previous density-functional studies found a -0.6% relative change of the GaAs lattice constant in a 64-atom supercell with a single C_{As} impurity.[20] Although the lattice relaxation around C_{As} may change our results quantitatively, we expect that the dominant effects on the band structure and on the spectral broadening arise from the different atomic levels of C compared to As which is readily accounted for in the TB scheme.

In Fig. 1 we plot the spin-polarized DOS in $Ga_{1-x}Mn_xAs_{1-y}C_y$ with $x=y=4\%$ together with local DOS on host (As) and impurity (C_{As}) atoms. Despite the remarkable difference between the atomic levels of As and C, $\Delta\varepsilon_p \approx -1$ eV, the local DOS on C_{As} sites (thin full line) near the valence-band edge does not differ much from the local DOS on the As sites (dashed line). (A still larger full width of the valence band than $\Delta\varepsilon_p$ may partly explain this.) As a result, the total DOS (thick full line) is only weakly affected by the presence of C in this spectral region. In particular, the spin splitting of 0.26 eV of the valence-band edge, directly related to the kinetic-exchange parameter J_{pd}, is nearly the same in systems with and without C_{As} impurities. The shaded region in Fig. 1 shows the DOS of Mn *d* states peaked near the energy of -4 eV which is consistent with results in C free (Ga,Mn)As.[21]

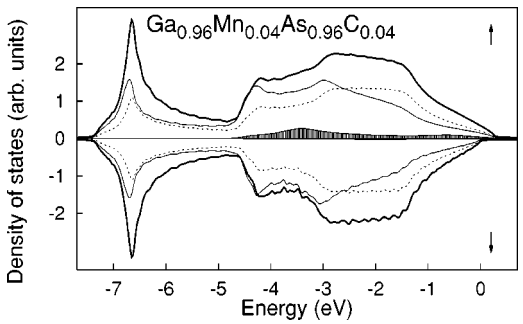

FIG. 1. TB/CPA density of states in $Ga_{1-x}Mn_xAs_{1-y}C_y$ DMS with $x=y=4\%$. Total DOS (thick full line), local DOS on host As (thin dashed line), and impurity C_{As} (thin full line) atoms, and the DOS of Mn *d* states are plotted as a function of energy, measured from the Fermi level.

It is important to point out that the substitution of C also has a very small effect on the linewidth of $A(k,E)$ for the states close to top of the valence band, i.e., electron scattering on C impurities does not disturb substantially the coherence of the Bloch states. This, together with an unchanged value of J_{pd}, implies that the additional disorder due to the codoping with C should not have any marked effect on the carrier mediated coupling between Mn moments. We check this more explicitly using the compatibility of the CPA with the Weiss mean-field theory. The strength of the Mn-Mn coupling is characterized by the energy cost of flipping one Mn_{Ga} moment, which can be calculated for a given chemical composition.[22] In Fig. 2, we plot this quantity as a function of the hole density p for $x=y=4\%$ (solid line) and $x=4\%$ and $y=0$ (dashed line) samples. The hole density is varied in the calculations independently of x and y, i.e., we assume implicitly a compensation whenever p is smaller than the total density of Mn_{Ga} and C_{As} acceptors. The curves are nearly identical for systems with and without C, as anticipated above. This means that, for a given hole concentration, the exchange coupling is quite insensitive to the large amount of the additional C_{As} defects. We conclude our TB/CPA considerations by stating that, as in the Mn_{Ga} acceptor

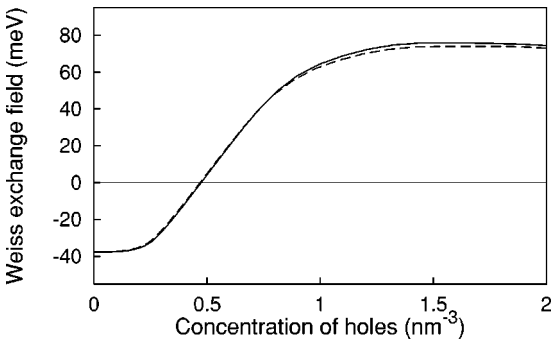

FIG. 2. Energy cost of flipping one Mn_{Ga} moment, obtained from the TB/CPA spectra, is plotted as a function of the hole density for $x=y=4\%$ (solid line), and $x=4\%$ and $y=0$ (dashed line).

case, the main effect of C_{As} doping is a downward shift of Fermi energy with respect to the band edge, i.e., an increase of the number of holes in the valence band. In the following paragraphs we discuss prospects for ferromagnetic transition temperature enhancement by adding extra holes into the DMS valence band.

We use a model in which the itinerant holes are described by the GaAs host bands and the coupling to the local moments by a phenomenological constant $J_{pd}=55$ meV nm^3.[5,23] This theory has been successful in describing semiquantitatively many non-trivial thermodynamic and transport properties of (Ga,Mn)As DMS's.[9,10,24–28] In the simplest, virtual-crystal mean-field version of the model, which assumes ferromagnetic indirect coupling between Mn ions, the energy to flip the Mn_{Ga} moment is proportional to the effective field $H_{eff}=J_{pd}\langle s\rangle$. Here $\langle s\rangle$ is the mean spin-polarization density of the itinerant holes which increases with the hole density. This result is consistent with our TB/CPA calculations, shown in Fig. 2, for hole densities not too much larger than the Mn_{Ga} density. Recall that the concentration of the substitutional Mn ions is given by $N_{Mn}=4x/a_{lc}^3$, where a_{lc} is the GaAs lattice constant ($N_{Mn}=0.88$ nm^{-3} for $x=4\%$, e.g.). For $p>N_{Mn}$, Ruderman-Kittel-Kasuya-Yosida (RKKY) oscillations of the Mn-Mn coupling[5] start to play a role and the increasing number of antiferromagnetically coupled Mn moments leads to a saturation or even to a suppression of T_c, as seen in Fig. 2 for $p>1.3$ nm^{-3}. The mean-field theory that allows only for collinear ferromagnetic states is therefore likely to breakdown in this high hole-density region. Note also that for high N_{Mn} and low p, the direct antiferromagnetic Mn-Mn interaction takes over, as suggested by negative Weiss exchange-field values in Fig. 2, which sets another limit on the validity of the simple mean-field model. This low hole-density region is, however, not important for the high-T_c (Ga,Mn)(As,C) DMS's we focus on in this paper.

We will now use the mean-field model to estimate the Curie temperature as a function of the Mn_{Ga} local moment density and of the density of itinerant holes that can be varied independently. We emphasize that hole doping due to C is relevant also for systems with $p<N_{Mn}$ since most of the experimental (Ga,Mn)As samples show some level of compensation, usually caused by interstitial Mn defects. In the calculations, the GaAs host band structure is obtained from the $\mathbf{k}\cdot\mathbf{p}$ Kohn-Luttinger model.[24] We neglect the $\sim 10\%-20\%$ suppression of T_c due to spin-wave fluctuations since the effect is compensated, to a large extent, by hole-hole exchange enhancement of T_c,[10] also neglected in the present calculations. Details of the model are described elsewhere;[3,8,10,24] here we recall only the general T_c expression we use[5,8,10]

$$k_B T_c = \frac{N_{Mn} S(S+1)}{3} \frac{J_{pd}^2 \chi}{(g\mu_B)^2}, \qquad (1)$$

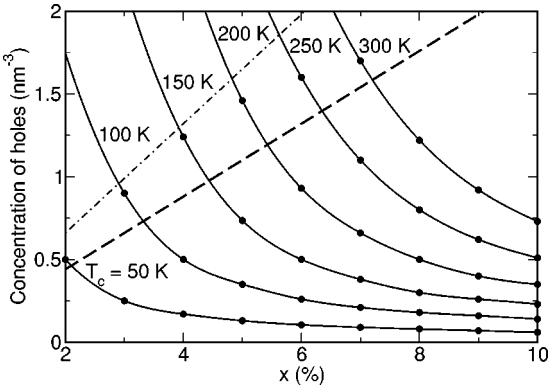

FIG. 3. Mean-field, $\mathbf{k}\cdot\mathbf{p}$ model calculations of constant T_c curves are plotted in the Mn_{Ga} doping (x)—hole-density (p) diagram. Dashed line corresponds to $p=N_{Mn}=4x/a_{lc}^3$ and the dotted-dashed line indicates approximately hole densities at which the mean-field model is expected to breakdown due to RKKY oscillations of the Mn-Mn indirect coupling.

where χ is the band-hole magnetic susceptibility which is roughly proportional to $p^{1/3}$. Figure 3 shows constant-T_c curves calculated for critical temperatures ranging from 50 K to room temperature. The dashed line corresponds to $p=N_{Mn}$ and also indicates approximately the onset of RKKY oscillation effects on T_c. Note that the simple mean-field theory used to calculate the constant-T_c curves is expected to breakdown above the dotted-dashed line where the large number of antiferromagnetically RKKY-coupled Mn moments might lead to a decrease rather than increase of T_c with increasing hole density.

Figure 3 suggests that a substantial enhancement of the ferromagnetic transition temperature may be expected in hole codoped samples with high Mn moment concentration. Assuming, e.g., $x=10\%$, an increase of the hole density from $p\approx 0.1$ nm^{-3} to $p\approx 0.7$ nm^{-3} leads to an increase of the theoretical T_c from 50 K to 300 K. For smaller x, a larger Δp is needed to enhance T_c by the same amount. Recent experiments have demonstrated that good quality (Ga,Mn)As DMS's can be grown with x reaching 8%.[6] Based on the curves in Fig. 3 and our TB/CPA results we conclude that (Ga,Mn)As DMS's codoped with several percent of C should not be overlooked among potential candidates for a room-temperature ferromagnetic semiconductor.

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