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Ab Initio Study of Curie Temperatures of Diluted Magnetic Semiconductors

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The Curie temperature of diluted (Ga,Mn)As magnetic semiconductors in the presence of As antisites is studied from first principles. We map total energies associated with rotations of Mn-magnetic moments onto the effective classical Heisenberg Hamiltonian which is treated in the mean-field approximation to find the Curie temperature. The presence of donors strongly reduces the Curie temperature and gives rise to a ground state with a partial disorder of local moments. We show that the observed dependence of the Curie temperature on the Mn concentration indicates that the concentration of As antisites increases with the Mn content.

KEY WORDS: Curie temperature; Heisenberg model; diluted magnetic semiconductors; ab initio approach; As antisites.

The diluted magnetic semiconductors (DMS) represent a new material with potential technological applications by incorporating ferromagnetic elements into semiconductor devices [1]. The physics of the DMS is interesting because of the interplay between the hole-mediated ferromagnetism and disorder in the tetrahedrally bonded semiconductor compounds. The DMS with Curie temperatures of the order of room temperature are needed for practical applications. The study of the Curie temperature for realistic models is thus of great importance.

We determine the Curie temperature of the DMS from first principles taking the (Ga,Mn)As mixed crystal as a case study. These materials are highly compensated, i.e., the experimentally observed number of holes in the valence band is much less than the concentration of Mn impurities. This indicates the presence of other lattice defects acting as donors of which the As antisites are favorite candidates. It is therefore important to understand the combined effect of Mn impurities and As antisites on the properties of the DMS, in particular on its electronic structure and Curie temperature.

We have determined the electronic structure of the DMS in the framework of the first principles all-electron scalar-relativistic tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic-sphere approximation. We introduce empty spheres into interstitial positions of GaAs semiconductor for a good space filling [2]. The disorder is treated in the coherent potential approximation (CPA) applied to a system consisting of several sublattices. We neglect possible lattice relaxations and a weak dependence of the sample volume on defect concentrations. The details of the method can be found in [3].

Recent studies indicate [4,5] that DMS are characterized also by some degree of the magnetic disorder. We include the magnetic disorder in the framework of the disordered local moment (DLM) model [5,6] that can be naturally treated in the framework of the CPA: different amounts of Mn atoms have collinear, but random spin-up (Mn^+) and spin-down (Mn^-) orientations with corresponding concentrations x^+ and x^-, $x = x^+ + x^-$, where x is the

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concentration of Mn atoms. The amount of the degree of magnetic disorder is characterized by the order parameter $r = x^{-}/x$. In the saturated ferromagnetic (FM) state, $r = 0$, all magnetic moments are pointing in the direction of a global magnetization. The paramagnetic (PM) state, $r = 0.5$, is characterized by a complete disorder of spin directions. To obtain the order parameter r corresponding to the ground state, we varied for each composition (x,y) the ratio r and find the corresponding total energy minimum.

We have determined the magnetic phase diagram for whole range of physically relevant concentrations (x,y). In Fig. 1 we present the cut through this phase diagram along the line $x = 0.05$. The ground state is the saturated ferromagnet for less than 1% of As antisites and a paramagnet for more than 2.25% of As antisites. In between there is an additional phase [5], the partial ferromagnetic (pFM) state, in which some degree of disorder in spin orientations is present. This new phase appears in the region where the number of holes is reduced by the As antisites ($y > 0$) and it exists over a concentration range of As antisites that increases with the Mn doping. The resulting magnetization on Mn sites in the pFM state, $m^{\mathrm{Mn}} = x^{+}m^{\mathrm{Mn}+} + x^{-}m^{\mathrm{Mn}-}$, is strongly reduced as compared to the corresponding FM state. The total magnetic moment per Mn in the FM state increases linearly from 4 μB ($y = 0.0$) to 5 μB ($y = 0.025$).

The evaluation of the Curie temperature on ab initio level is still a challenging task, in particular for a complex system like the DMS. One therefore has to use some approximations in order to calculate it. A particularly simple and yet accurate approach consists in a mapping of the itinerant spin-polarized electron system onto an effective classical Heisenberg model (EHM)

$$H = -\sum_{i \neq j} J_{ij}\, e_i \cdot e_j, \tag{1}$$

and subsequent application of the statistical mechanics to it [7,8]. Here, e_i and e_j are the unit vectors of the local magnetic moments at sites i and j, and J_{ij} denote the (random) effective exchange interactions between any pair of atoms carrying magnetic moments. We treat the DMS as random substitutional alloys and, therefore, we have generalized the theory developed in [7,8] to disordered systems. We calculate J_{ij} directly in the real space by employing the change of energy associated with a constrained rotation of the spin-polarization axes in atomic cells i and j, and the magnetic force theorem. The configurationally averaged $\bar{J}_{ij}$ is determined in the framework of the CPA by employing the vertex-cancellation theorem (VCT) that simplifies calculations significantly [9]. The summation in Eq. (1) is restricted to magnetic atoms and the only nonvanishing exchange interactions are[6]

$$\bar{J}_{ij}^{\mathrm{Mn,Mn}} = \frac{1}{4\pi}\,\mathrm{Im}\int_{-\infty}^{E_{\mathrm{F}}} \mathrm{tr}_L\big[\delta_i^{\mathrm{Mn}}\bar{G}_{ij}^{\mathrm{Mn,Mn}\uparrow}(E) \times \delta_j^{\mathrm{Mn}}\bar{G}_{ji}^{\mathrm{Mn,Mn}\downarrow}(E)\big]dE. \tag{2}$$

Here, tr_L denotes the trace over the angular momentum $L = (\ell m)$, δ_i^{Mn} is the exchange splitting on the Mn atom (see [8] for its definition in the framework of the TB-LMTO method), $\bar{G}_{ij}^{\mathrm{Mn,Mn}\uparrow}(z)$ and $\bar{G}_{ji}^{\mathrm{Mn,Mn}\downarrow}(z)$ are the conditionally averaged site off-diagonal blocks of the system Green function [3], and E_{F} is the Fermi energy.

We employ the mean-field approximation (MFA) to determine the Curie temperature from the EHM. It should be noted that the CPA used for the construction of the EHM is also the mean-field theory. The MFA value of the Curie temperature T_{c} in the FM state is

$$k_{\mathrm{B}}\,T_{\mathrm{c}}^{\mathrm{MFA}} = \frac{2x}{3}\sum_{i \neq 0}\bar{J}_{0i}^{\mathrm{Mn,Mn}}, \tag{3}$$

where x is the concentration of Mn atoms, and k_{B} is the Boltzmann constant [7,8]. Alternatively, a simple

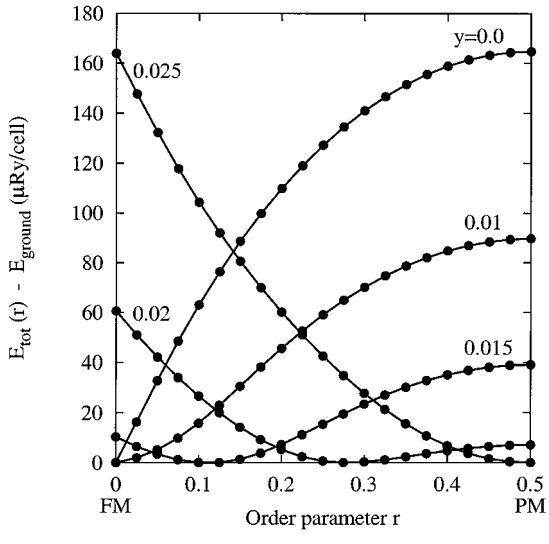

Fig. 1. The differences $E_{\mathrm{tot}}(r) - E_{\mathrm{ground}}$ plotted as a function of the order parameter r for an alloy $(Ga_{0.95-y}Mn_{0.05}As_y)As$ and a set of concentrations y of As antisites. The lines serve as a guide for eye.

[6] Details of derivation and more complete results will be the subject of another paper.

Table I. Curie Temperatures in (Ke) for the Ferromagnetic State[a]

$(Ga_{1-x}Mn_x)As$		$(Ga_{0.95-y}Mn_{0.05}As_y)As$		$(Ga_{0.95-y}Mn_{0.05}As_y)As$		
x	T_c	y	T_c	x_{exp}	T_{exp}	y_e
0.02	220	0.0	289	0.015	30	0.0052
0.04	273	0.0025	258	0.022	41	0.0071
0.06	289	0.005	221	0.035	59	0.0098
0.05	302	0.0075	177	0.043	91	0.0101
0.08	315	0.01	126	0.053	110	0.0111
0.10	320	0.0125	67	0.070	63	0.0157
0.12	319	0.015	1			
0.15	309					

[a]Temperatures were evaluated as a function of concentration of Mn atoms x without As antisites (columns 1 and 2) and as a function of concentration of As antisites y for a fixed $x = 0.05$ (columns 3 and 4). Experimental values T_{exp} of Curie temperatures [1] for a given concentration x_{exp} of Mn atoms (columns 5 and 6) and corresponding concentrations of As antisites y_e (last column) estimated from Eq. (3).

estimate of T_c follows from the energy difference $\Delta(x, y)$ between the paramagnetic DLM state and the FM state which is calculated from first principles. We obtain $k_B T_c = 2\Delta/3x$ if we employ (3) and identify Δ with $x^2 \Sigma_{i\neq 0} \bar{J}_{0i}^{Mn,Mn}$. The values of T_c obtained in this way are higher by 10 to 15% as compared to the values obtained from Eq. (3).

The results of evaluation of T_c are summarized in Table I and the following conclusion can be done: (i) without donors T_c increases with x, reaches the room temperature at $x \approx 0.05$, and saturates for higher Mn concentrations which indicates that the effective exchange interactions decrease for heavy Mn doping[7]; (ii) the Curie temperature rapidly decreases with increasing concentration of donors in a qualitative agreement with predictions of the simple kinetic-exchange model [10]. For example, T_c of 289 K for 5% of Mn impurities without As antisites is reduced to 126 K for 1% of As antisites which is, in turn, close to the experimental value for this Mn content [1]; (iii) for a further analysis we have determined from Eq. (3) the concentration of As antisites y that corresponds to the experimental T_c (see Table I). We observe that values of y obtained in this way follow approximately a straight line, i.e., the number of As antisites increases proportionally to the concentration of Mn atoms. This result indicates that further increase of T_c in GaAs cannot be achieved by increasing the Mn content and either the reduction of the concentration of As antisites or new materials are needed.

In conclusion, we have developed the first-principle description of the Curie temperature in the DMS that separates the electronic and statistical degrees of freedom, which can be then treated independently. The calculated exchange interactions can be used in the future as a stating point for more sophisticated statistical treatments that include the influence of atom clustering and/or the effect of spin fluctuations beyond the simple MFA approach adopted here. The present results for GaMnAs alloys demonstrate a strong influence of As antisites on the Curie temperature and the correlation between concentrations of Mn impurities and As antisites, namely the increase of donor concentration with the increase of the Mn content.

[7]See footnote 6.

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