LETTER TO THE EDITOR

The influence of the clustering of Mn impurities on the magnetic properties of (GaMn)As

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Abstract
Diluted magnetic semiconductors currently attract immense experimental and theoretical attention as one of the most promising classes of materials for spintronic applications. We report a detailed density-functional-theory study of the influence of the clustering of the substitutional Mn impurities on the electronic structure, exchange interactions and Curie temperature of (GaMn)As. We demonstrate that the strong intra-cluster interaction of the Mn 3d states results in the change of the structure of the impurity band. The influence of this change on the exchange interactions and Curie temperature is revealed.

(Some figures in this article are in colour only in the electronic version)

One of the requirements of magnetic materials for the realization of semiconductor spintronic devices is a Curie temperature well above the room temperature. After the detection of the ferromagnetism of (GaMn)As with a Curie temperature as high as 110 K [1], diluted magnetic semiconductors (DMSs) are considered as one of the most promising classes of materials for such applications. Recently the Curie temperature of (GaMn)As samples has been increased to 160 K [2]. Many efforts are devoted to understanding the mechanisms of the exchange interaction in this system that should provide guidelines for the design of materials with higher Curie temperature [3].

Among the important issues that are still insufficiently understood is the influence of impurity clustering on the magnetism of DMSs. A number of theoretical studies have shown that the formation of the substitutional Mn clusters in DMS materials is energetically favourable [4–6]. In a recent letter, Rao and Jena formulated an interesting hypothesis that the Mn clusters in (GaMn)N carry giant magnetic moments and, therefore, can be the reason for the high Curie temperature detected in some of the (GaMn)N samples [5].

In this letter we report a detailed density-functional-theory (DFT) study of the influence of the Mn clustering on the magnetism of (GaMn)As. We calculate the exchange interactions

and the Curie temperature for systems with various cluster sizes. The comparison with the calculations for uniformly distributed defects helps to single out the role of clustering.

We show that the assumption of Rao and Jena concerning the formation of giant cluster moments is well fulfilled in (GaMn)As. We demonstrate, however, that the effect of the Mn clustering on the Curie temperature is peculiar and is governed by the details of the influence of the clustering on the electron structure.

The calculations are based on the supercell approach, where one or several Ga atoms in a supercell of the zinc blende GaAs are replaced by Mn atoms. For details of the calculational scheme the reader is referred to our previous publications [7]. Two types of impurity patterns are considered. The first is a uniform pattern with one Mn atom per supercell. The second is a clustered pattern where two, three or four Mn impurities per supercell replace, respectively, two, three or four Ga atoms in the vertices of the Ga tetrahedron formed by the nearest neighbours of an As atom. All calculations of the clustered systems are performed for the $2a \times 2a \times 2a$ supercell where a is the lattice parameter of the zinc blende structure. To refer to different systems we use the notation of p-cluster where $p = 1, 2, 3, 4$ is the number of impurities per supercell. The parameter p is referred to as the size of the cluster. We begin the discussion of the calculational results with the consideration of the influence of impurity clustering on the electronic structure of ferromagnetically ordered (GaMn)As. In the next step, the stability of the ferromagnetic state is evaluated by calculating Heisenberg's exchange parameters and the Curie temperature.

The calculated values of the Mn atomic moment depend weakly on both Mn concentration and clustering and vary in a narrow interval, from 3.85 to 3.95 μ_B. Therefore the magnetic moment of a cluster is roughly proportional to the size of the cluster and for the 4-cluster has a large value of 15.5 μ_B. This large value is, however, not sufficient to draw the conclusion about the formation of the giant cluster moments as is proposed by Rao and Jena for (GaMn)N. This conclusion is justified only in the case that the thermodynamics of the system can be described in terms of cluster moments. Therefore the thermal fluctuations of the relative directions of the Mn atomic moments belonging to the same cluster must be much smaller than the fluctuations of the relative directions of the atomic moments belonging to different clusters. This problem will be addressed below.

In figure 1, the calculated Mn 3d DOS of different systems is shown. In gross features the DOS is similar in all cases. The main part of the spin-down Mn 3d DOS lies above the Fermi level. There are no spin-down states at the Fermi level that makes the system half-metallic. The Mn 3d spin-up DOS can be characterized as one big nonsymmetric peak with the maximum about 0.2 Ryd below the Fermi level. The gradual slope on the right of the peak is spread up to the energies above the Fermi level. The similarity of the main structure of the Mn 3d DOS for different concentrations and different spatial distributions of the impurities reveals the primary role of the nearest As surrounding of the Mn atoms. This surrounding is the same in all cases studied. On the other hand, a strong variation from system to system is obtained in the detailed structure of the upper part of the Mn 3d spin-up DOS. These states lie in the energy region about the Fermi level. Since the states situated close to the Fermi level play an important role in the formation of the physical properties of condensed matter systems we consider this part of the electron structure in more detail.

First, we compare the DOS of two uniform Mn distributions with $x = 3.125\%$ and 12.5%. In the case of $x = 3.125\%$ we obtain at the Fermi level a peak that is separated from the lower-lying part of the DOS by a deep minimum. The upper edge of the peak lies about 0.02 Ryd above the Fermi level. The increase of the Mn concentration to 12.5% leads to a strong broadening of the peak that now merges in one common structure with the lower-energy states of the valence band. The broadening of the DOS reflects an increased interaction between impurity states with decreasing distance between nearest impurity atoms.
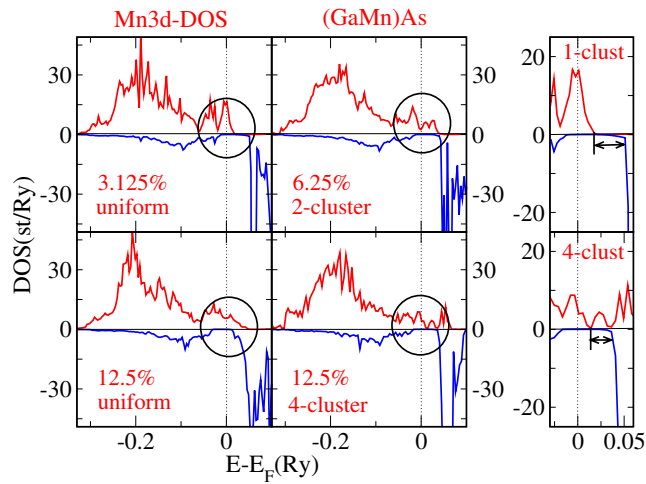
Figure 1. Spin-resolved Mn 3d DOS. Encircled is the part of the DOS about the Fermi level that plays an important role in the formation of the magnetic properties. At the right-hand side this part of the DOS is shown in a larger scale for 1- and 4-cluster systems. The distance between the top of the partially filled spin-up peak and the bottom of the empty spin-down band is marked and is substantially smaller in the 4-cluster case than in the 1-cluster case.
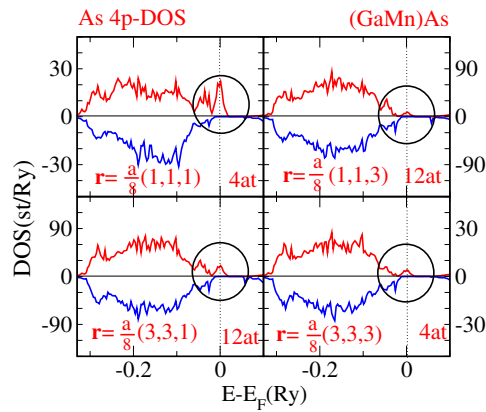
Figure 2. Spin-resolved As 4p DOS for $x = 3.125\%$. The vectors connecting the Mn atom with one of the As atoms of a given coordination sphere and the number of atoms in the sphere are shown. The DOS is given per coordination sphere. Encircled is the part of the DOS about the Fermi level.

The clustering of the Mn atoms leads to a new effect: the appearance of a distinct additional structure in the upper part of the Mn 3d spin-up DOS. For instance, a comparison of the uniform and clustered impurity distributions for the Mn concentration of $x = 12.5\%$ shows that one broad feature of the uniform case (figure 1) is replaced in the clustered system by a number of well-separated subpeaks. Compared to the uniform Mn distribution of 3.125% the 4-cluster system is characterized by both splitting of the peak and spreading the states over a larger energy interval. To understand the physical origin of the splitting caused by the clustering we consider in figure 2 the partial 4p DOS of As atoms for (GaMn)As with $x = 3.125\%$ (1-cluster case). The As atoms neighbouring the Mn impurities contribute strongly to the

impurity-band states. This reveals strong Mn 3d–As 4p hybridization of the neighbouring Mn and As atoms for this part of the electron structure. On the other hand, the As 4p contribution into the impurity band decays with increasing distance of the As atom from the Mn impurity. The spatial decay is characteristic for impurity states lying in the semiconducting gap.

The following explanation of the clustering-caused splitting in the impurity band can now be suggested. The spatial closeness of the Mn atoms belonging to the same cluster and strong Mn 3d–As 4p hybridization with neighbouring As atoms lead to a strong effective interaction between the Mn 3d states within the cluster. Like in a molecule, the degenerate atomic levels split as a result of the inter-atomic intra-cluster interactions. The number of subpeaks and the energy distances between them have a tendency to increase with increasing number of interacting atoms. Because of the spatial decay of the states the broadening through the inter-cluster interaction is not sufficient to merge the levels split by the intra-cluster interaction in one group. These features of the electron structure are important for understanding the character of the Mn–Mn exchange interactions.

To estimate the parameters of the interatomic exchange interactions we map the results of the DFT calculations on an effective Heisenberg Hamiltonian of classical spins

$$H_{\text{eff}} = -\frac{1}{N} \sum_{(m\nu)\neq(m'\nu')} j_{mm'}^{\nu\nu'} \mathbf{e}_m^\nu \cdot \mathbf{e}_{m'}^{\nu'} \tag{1}$$

where ν, ν' label the Mn sublattices and m, m' label the cells. We use the calculational scheme based on the frozen-magnon approach as described earlier [7]. A frozen-magnon state of a translationally periodical set of atoms is characterized by a certain wavevector $\mathbf{q}$. Calculating the total energies of the frozen-magnon states for a regular $\mathbf{q}$ mesh one obtains Fourier transforms of the exchange parameters. The back Fourier transformation gives the Heisenberg exchange parameters.

For the clustered systems considered, the determination of the exchange parameters consists of two steps. In the first step, the frozen-magnon calculations are performed for cluster moments. In the second step, the frozen-magnon calculations are done for one of the Mn sublattices. These two calculations give the exchange interactions between, respectively, cluster moments and the atomic moments belonging to one sublattice. Since all p Mn sublattices are equivalent, these calculations are sufficient for determining the Heisenberg exchange parameters in the system.

In the mean-field approximation the effective exchange fields acting on a given Mn moment from the Mn atoms outside the given cluster and from the Mn atoms belonging to the same cluster are determined by the parameters

$$j_0^{\text{inter}} = \frac{1}{p} \sum_{m\neq 0} \sum_{\nu\nu'} j_{0m}^{\nu\nu'}, \qquad j_0^{\text{intra}} = \frac{1}{p} \sum_{\nu\neq\nu'} j_{00}^{\nu\nu'}. \tag{2}$$

The following j_0^{inter} and j_0^{intra} have been obtained: 1.26 and 2.72 mRyd (2-cluster), 0.333 and 4.18 mRyd (3-cluster), 0.42 and 5.14 mRyd (4-cluster). The ferromagnetic character of the intra-cluster exchange is in agreement with previous estimations of this quantity [4]. Much stronger intra-cluster ferromagnetic exchange interaction compared to the inter-cluster interactions (especially in the cases of 3- and 4-clusters) allows us to treat the thermodynamics of the system in terms of the rigid giant cluster moments. The Curie temperature of the system can be estimated as $k_B T_C^{\text{MF}} = \frac{2}{3} p j_0^{\text{inter}}$.

The result of the calculation of the Curie temperature (figure 3) does not support the prediction by Rao and Jena that the formation of the giant cluster moments leads to a high Curie temperature of the system. For the concentration of 6.25% both uniform and clustered impurity distributions give similar values of the Curie temperature. However, for higher impurity
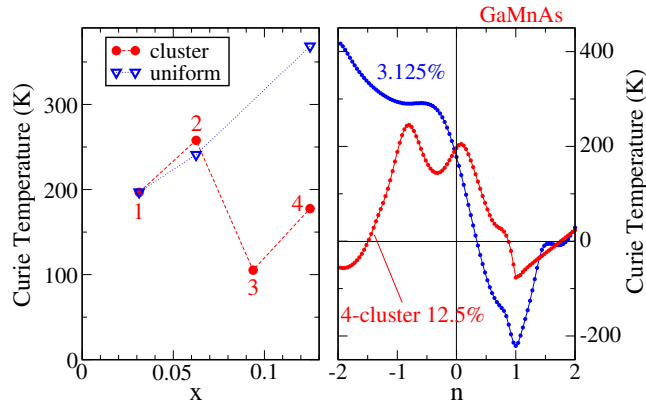
Figure 3. Left panel: the Curie temperature as a function of the Mn concentration. Numbers at the calculated points show the size of the clusters. Right panel: the Curie temperature as a function of the band occupation. $n = 0$ corresponds to the nominal number of electrons.

concentrations the Curie temperature of the clustered system is substantially lower than for the system with uniform distribution of the same number of impurity atoms. Remarkably, the Curie temperature for 3-cluster and 4-cluster systems is lower than in the 1-cluster system. Therefore the replacement of isolated Mn impurities by the 3- and 4-clusters carrying giant magnetic moments does not lead to the increase of the Curie temperature despite a strong increase of the Mn content. To understand the physical origin of this puzzling property we present below a detailed comparative analysis of the formation of the Curie temperature in 1-cluster and 4-cluster cases.

It is common to treat the magnetism of DMSs in terms of the competition between ferromagnetic exchange interactions initiated by the presence of the partially filled bands and antiferromagnetic exchange interactions through filled energy bands [3, 8, 9]. To verify the usefulness of this concept for the interpretation of the properties of exchange interactions in clustered systems obtained in the present DFT calculations, we study the dependence of the Curie temperature on electron number (figure 3, right panel).

In both 1-cluster and 4-cluster systems, the increase of the electron number above the nominal value ($n = 0$ in figure 3) leads to a decrease of T_C. At $n = 1$, in both cases, the Curie temperature reaches its minimum. In the 1-cluster system, $n = 1$ corresponds to the completely filled valence-band and spin-up impurity band and empty conduction band and spin-down impurity band. The absence of carriers for $n = 1$ is consistent with the expectation that one Mn atom produces one hole. The hole is compensated by one additional electron per supercell. The deviation from $n = 1$ to smaller or larger n values produces, respectively, hole or electron carriers that leads to a ferromagnetic contribution into inter-cluster exchange interactions.

For the 4-cluster system the situation differs strongly. Since in this case there are four Mn atoms per unit cell the spin-up impurity band has place for four electrons. The reason for the minimum of $T_C(n)$ already after adding one further electron is in the splitting of the impurity band caused by the intra-cluster Mn–Mn interaction (figure 1). This splitting separates a subpeak of the DOS that becomes filled at $n = 1$.

For more detailed comparison of 1-cluster and 4-cluster cases it is useful to present the Curie temperature at the nominal electron number in the form $T_C(0) = T_{fm} + T_{afm}$, where $T_{fm} = T_C(0) - T_C(1)$ reflects the ferromagnetic contribution of the holes whereas $T_{afm} = T_C(1)$
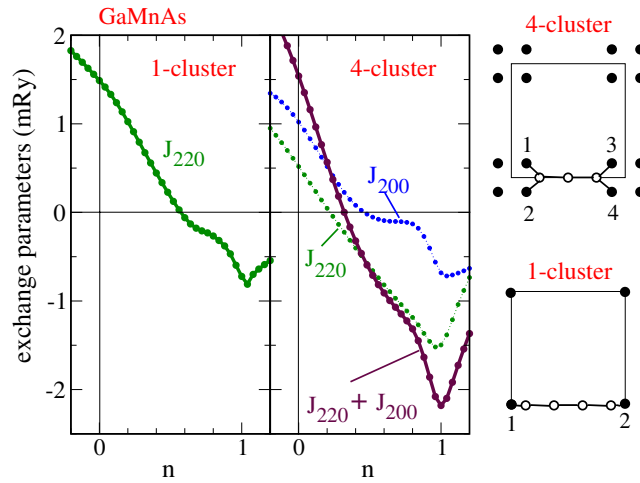
Figure 4. The leading exchange parameters in the case of 1- and 4-cluster systems. The parameters are multiplied by the coordination number corresponding to the symmetry of the corresponding lattice vector. In the right-hand part, the projections of the Mn atoms (filled circles) on the xy plane are shown schematically. The empty circles show the projections of the As atoms realizing the exchange path corresponding to the J_{200} parameter.

gives an antiferromagnetic contribution corresponding to the exchange through completely occupied bands. As is seen in figure 3, a small difference of $T_C(0)$ of the 1-cluster and 4-cluster systems is the result of the compensation of the changes in both contributions: an increased ferromagnetic contribution of T_{fm} and increased antiferromagnetic contribution of T_{afm}.

To understand the origin of the increase of both contributions to $T_C(0)$ we consider in figure 4 the leading exchange parameters determining the n-dependence of the Curie temperature in the interval $0 \geqslant n \leqslant 1$. In the 1-cluster case this is one parameter (J_{220}) that reproduces well the behaviour of the corresponding Curie temperature, whereas in the 4-cluster case these are two parameters, J_{220} and J_{200}, the sum of which determines the behaviour of T_C (figure 4). The contribution of J_{200} determines the larger T_{fm} in the 4-cluster case. The increased importance of J_{200} parameter in the 4-cluster system is the consequence of the geometrical factor illustrated in the right-hand side of figure 4, where the projection of the Mn impurities on the xy plane is presented schematically. As is seen in the figure, for two clusters separated by vector $a(200)$ there are two pairs of Mn atoms—1, 2 and 3, 4—with reduced length of the inter-cluster exchange path compared with the 1-cluster case. The exchange path goes through As atoms [7]. In the 4-cluster system the path includes three As atoms in contrast to four As atoms in the 1-cluster system. The inter-atomic exchange interaction increased because of the shorter exchange path enters J_{200} with an additional factor four.

On the other hand, the increase of T_{afm} in the 4-cluster system is explained by the properties of the J_{220} parameter. Indeed, the ferromagnetic contribution $J_{220}(0) - J_{220}(1)$ to $J_{220}(0)$ is similar in both 1-cluster and 4-cluster cases, whereas the antiferromagnetic contribution $J_{220}(1)$ is much larger in the 4-cluster case. To interpret the increase of the antiferromagnetic contribution it is useful to make contact with the concept of the Anderson superexchange through occupied bands. The simple Anderson formula for the antiferromagnetic super-exchange interaction $J = -\frac{b^2}{\delta}$ [10] is, in its essence, a standard second-order perturbation expression for the energy of a non-degenerate level where δ is the energy distance to the first

excited state and b is a small parameter describing the efficiency of the inter-level interaction caused by the perturbation. The expression is always negative since the interaction takes the form of hybridizational repulsion where the lower level is bonding and decreases its energy.

Since the frozen magnons used in the calculation of the exchange parameters are noncollinear magnetic configurations they lead to the hybridization of the spin-up and spin-down electron states, with the strength of the hybridization increasing with increasing noncollinearity. Because the lower spin-up state is occupied and the upper spin-down state is empty, the repulsion decreases the energy of the system and gives a negative (antiferromagnetic) contribution to the interatomic exchange parameters. The inspection of the DOS of the 1- and 4-cluster cases shows that the clustering leads to a decreased distance between interacting spin-up and spin-down states (figure 1). The smaller energy distance between interacting states leads to a larger antiferromagnetic exchange interaction in the 4-cluster case.

Thus, by a comparative analysis of the 1-cluster and 4-cluster cases we have demonstrated that the puzzling property that the replacement of single Mn impurities by clusters carrying giant magnetic moments does not increase the Curie temperature in the system is explained by the character of the influence of the clustering on the electron structure.

One further important consequence of the clustering is an increased sensitivity of the Curie temperature to the presence of uncontrolled donor defects. Indeed, the compensation of 33% of the holes changes, in the 4-cluster case, the inter-cluster exchange from ferromagnetic to antiferromagnetic (figure 3). Since the effective number of the holes is already four-times reduced by the band splitting, this level of compensation is very low. Therefore, the clustering of the Mn impurities can be the reason for the reduced Curie temperature obtained for many (GaMn)As samples.

Summarizing, we report a detailed study of the influence of the clustering of the substitutional defects on the exchange interactions and Curie temperature of (GaMn)As. We show that the thermodynamics of the system can be described in terms of giant cluster moments. However, we demonstrate that the formation of the giant moments does not automatically lead to an increase of the Curie temperature. The important role of the splitting of the impurity band caused by strong intra-cluster interaction is revealed. By detailed comparison of 1-cluster and 4-cluster cases we demonstrate the usefulness of invoking the concepts of double- and super-exchange for qualitative understanding of the results of the realistic density-functional-theory calculations of the exchange interactions in diluted magnetic semiconductors.

It is worth noting that our calculations did not take into account disorder in the system as well as the possible coexistence of different-size clusters and the presence of other types of defects like anti-sites or interstitial Mn impurities. Obviously, these features can lead to considerable deviation of the Curie temperature from the values presented in this paper. We argue, however, that the study of the clustering of the substitutional Mn impurities reported here provides an important insight into the formation of the electron structure, exchange interactions and Curie temperature, and constitutes a necessary ingredient for understanding the magnetism of more complex samples.

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