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First-principles study of the thermal properties of half-metallic ferromagnetic systems

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ABSTRACT

The origin of the half-metallicity is different in diluted magnetic semiconductors and Heusler alloys. I briefly review our earlier work on (GaMn)As and (GaMn)N focusing on the relation between the half-metallicity and the strength of the interatomic exchange interactions. This relation is governed by the properties of the valence-band holes. In Heusler alloys the factors determining the thermal behavior are distinct. Here the relation between half-metallicity and the longitudinal fluctuations of atomic moments is considered. The temperature dependence of the Ni magnetization in NiMnSb is studied.

1. Introduction

The half-metallicity is an interesting state of magnetic systems where the electronic structure of one of the spin-subsystems is metallic whereas the electronic structure of the other is semiconducting. Since the half-metallic materials are characterized by a 100% spin-polarization of the electronic states at the Fermi level they are promising candidates for the applications in the spintronic devices utilizing the spin degree of freedom.

Among the half-metallic materials attracting most research attention are the diluted magnetic semiconductors (DMS) and Heusler alloys. Since the spintronics devices should be operative at room temperature the Curie temperature of the materials suitable for applications must exceed the room temperature considerably. The value of the Curie temperature is determined by exchange interactions in the electron system. The understanding of the mechanisms of the exchange interactions in the half-metallic materials is of primary importance for both fundamental physics and applications.

2. Half-metallic (GaMn)As

The half-metallicity of the DMS and Heusler alloys has different nature. In the DMS, we deal with the systems that, in the absence of the impurities, are semiconducting and nonmagnetic. The origin of the gap between occupied and empty electron states in this case does not have a magnetic character and is a consequence of the hybridization of the electron states of the nonmagnetic matrix. A magnetic impurity contributes differently to the two spin channels of the electron structure. The formation of a half-metallic state is connected with establishing of the long-range magnetic order of impurity moments.

Taking as an example (GaMn)As with Mn impurities substituting Ga atoms in GaAs one finds (Fig. 1) that a strongly spin-polarized Mn atom contributes five additional states into the energy region of the valence band of GaAs and only four additional electrons. Therefore, there is one hole per Mn atom at the top of the valence band. The minority-spin 3d states of the Mn atom are shifted to higher energies by the intra-atomic Mn exchange splitting. They are empty and do not overlap with the valence band of GaAs. If the Mn moments are ferromagnetically ordered the majority-spin electronic structure of (GaMn)As is metallic whereas the minority-spin electronic structure remains semiconducting.

The frozen-magnon calculations [1] show that the ferromagnetic half-metallic state corresponds to the minimum of the total energy of the system. These calculations allow the mapping of the system on an effective Heisenberg Hamiltonian and the estimation of the Curie temperature T_C. In Fig. 2 we show the dependence of T_C of (GaMn)As on continuous variation of the electron number [2]. The presence of the holes plays crucial role in the formation of the effective ferromagnetic interatomic exchange interactions. With decreasing number of holes the Curie

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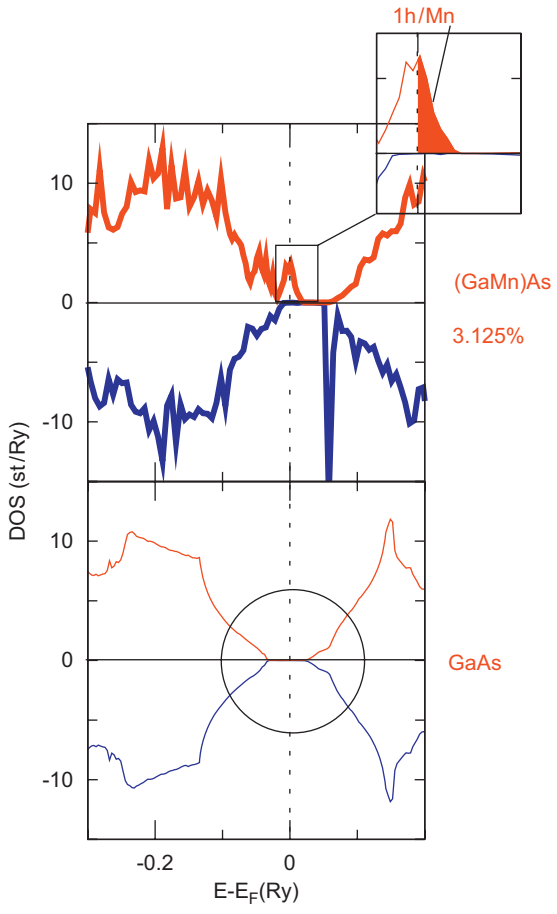

Fig. 1. (Color online) Lower panel: The density of states of semiconductor GaAs. Upper panel: The density of states of the diluted magnetic semiconductor (GaMn)As. The calculation is performed for the ferromagnetic ordering of the Mn moments. The substitution of 3% of Ga atoms by Mn atoms results in a half-metallic state with semiconducting spin-down channel and with exactly one hole per Mn atom in the spin-up channel.

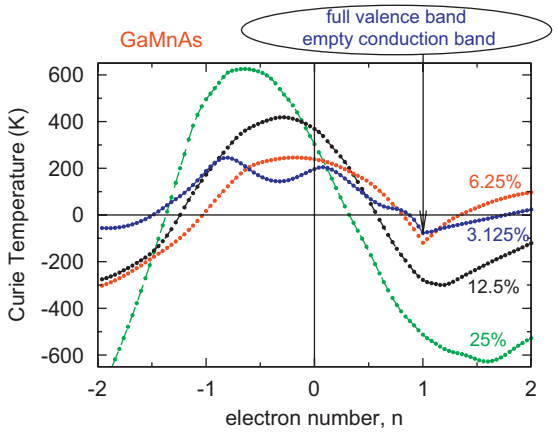

Fig. 2. (Color online) The dependence of the Curie temperature on the electron number. The mean-field value of T_C is proportional to the sum of the interatomic exchange parameters. The negative value of T_C means prevailing antiferromagnetic exchange interactions and the instability of the ferromagnetic structure. $n=0$ corresponds to the nominal number of electrons giving 1 hole per Mn atom. For low Mn concentrations of 3% and 6% $n=1$ corresponds to the completely filled valence band and completely empty conduction band. For larger concentrations there is an overlap between the valence and conduction bands.

temperature decreases. For completely filled valence band and empty conduction band ($n=1$ in the figure) the leading interatomic exchange interactions are antiferromagnetic.

Two features of the holes are crucial for mediating the exchange interaction between Mn atoms: the exchange interaction with magnetic impurity and the delocalization from the impurity. Both components are necessary since neither a hole localized on the impurity atom nor the holes that do not interact with impurities can mediate the interaction between impurities [3]. These two properties of the holes are competitive with each other since increasing delocalization of the holes from the impurity leads to decreasing exchange interaction with the

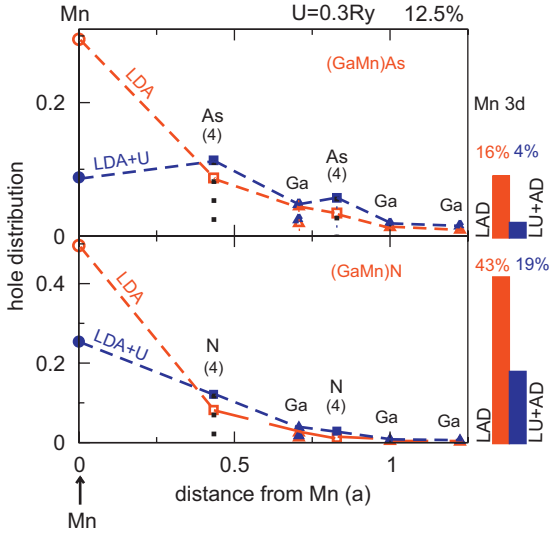

Fig. 3. The hole distribution in (GaMn)As and (GaMn)N with 12.5% of Mn. The calculations are performed within local density approximation (LDA) and LDA+U approaches. The LDA+U scheme assumes stronger on-site Coulomb correlations of the Mn 3d electrons. In LDA+U, the part of the hole localized on Mn atoms decreases strongly compared to LDA that corresponds to increased delocalization of the hole from the impurity. On the other hand, the decreased contribution of the Mn 3d states to the hole (histograms in the right part of the figure) can be treated as decreasing exchange interaction between impurity and hole.

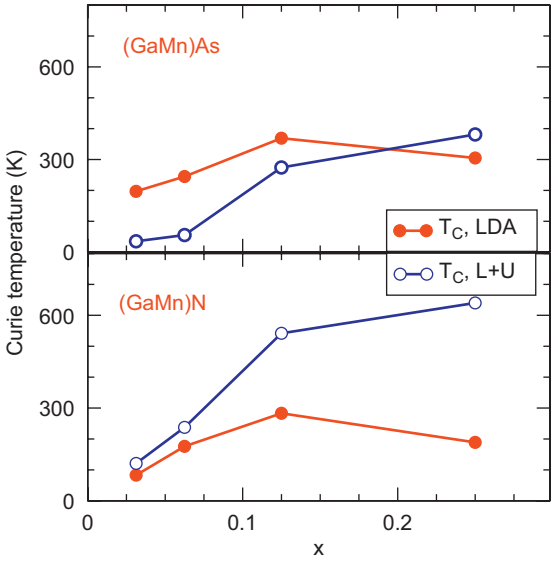

Fig. 4. The dependence of the calculated Curie temperature of (GaMn)As and (GaMn)N on the Mn concentration calculated within LDA and LDA+U (denoted with L+U) approaches. Since the compromise between the delocalization of the hole from impurity and the exchange interaction with impurity is different for the two systems the dependence of T_C on U is also different.

impurity (Fig. 3). The Curie temperature appears as a compromise between two properties (Fig. 4).

In the low Mn-concentration region of (GaMn)As the LDA+U leads to very weak exchange interaction hole-impurity resulting in very small effective interatomic exchange interaction. On the other hand, in high-concentration region the changes in the properties of the holes called by U compensate each other and the values of T_C calculated with both approaches are similar. In (GaMn)N the situation is different. The values of T_C are similar at low concentrations. At high concentrations the stronger delocalization of the holes in LDA+U calculation becomes more important that leads to substantially higher T_C. This shows that controlled 'engineering of hole properties' is a possible way to higher T_C.

3. Heusler alloys

A number of the Heusler alloys have half-metallic ground state. The hypothetic nonmagnetic Heusler alloys are metals with high density of states at the Fermi level in both spin channels. The gap in one of the spin-subsystems of ferromagnetic Heusler alloys is a result of the spin-polarization in the material. Taking NiMnSb as an example (Fig. 5) the strong spin-polarization results in the spin splitting of the Mn 3d states. The different positions of the Mn 3d states in two spin channels lead to different conditions of the interatomic hybridization in the channels and finally to the hybridizational gap in the spin-down subsystem.

Some of the half-metallic Heusler compounds have high Curie temperature. It is however not clear if the high Curie temperature should be attributed to the half-metallicity. The effective interatomic exchange interactions are determined by the properties of the electron structure of the system. This relation is, however, by no means simple. The model-Hamiltonian studies introduce various exchange mechanisms, e.g., RKKY, double exchange and super exchange. Within the DFT calculations different exchange mechanisms are present simultaneously and influence each other. On a qualitative level some features of these individual exchange mechanisms can be distinguished in the properties of calculated exchange parameters and related to the half-metallicity. This is helpful for deeper understanding of the magnetism of the systems and predictions for new systems.

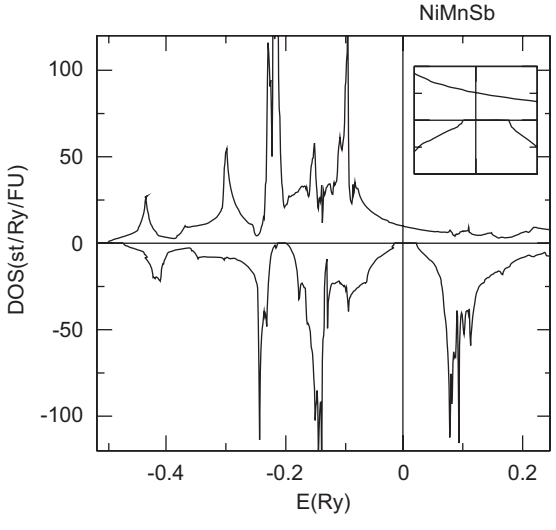

Fig. 5. The density of states of the half-metallic NiMnSb. The inset zooms in the energy region around the Fermi level.

For example, within a RKKY picture the half-metallic gap is expected to lead to an exponential decay of the interatomic exchange interaction with interatomic distance that correlates with properties of the calculated parameters in half-metals. Another example: The properties of many Heusler alloys can be interpreted in terms of the competition between RKKY and super-exchange mechanisms where the first can be related to the spin-polarization of the sp electrons whereas the strength of the second depends on the electronic structure of the empty states close to the Fermi level [4].

The aspect that has not yet received sufficient attention is the role of the longitudinal fluctuations in the finite-temperature properties of half-metallic systems. In the mapping of an itinerant-electron system on the Heisenberg Hamiltonian the longitudinal fluctuations of the magnetic moments are neglected. However, a consequent picture of an itinerant-electron magnet supposes that the local magnetization can fluctuate not only in direction but also in length [5–7].

Here we consider the thermal behavior of the Ni sublattice in NiMnSb. In the ground state, the Mn atoms possess the spin moment 3.85 μ_B, the Ni atoms are characterized by the induced moment $m_0 = 0.20\,\mu_B$. A number of experiments report on the anomalies in the properties of NiMnSb at the temperature of about 90 K. These anomalies have been attributed to the transition from the half-metallic to a normal metallic state caused by the thermal processes in the Ni sublattice.

The thermal properties of physical systems depend on the energetics and the statistical weight of the excited states. The tool for the study of the excited magnetic states within DFT is the constrained density functional theory calculations. In the frozen-magnon calculations aimed to the mapping of the itinerant-electron system on the Heisenberg Hamiltonian only the directions of the moments are constrained. The energies of the longitudinal fluctuations of the atomic moments are calculated by the imposing an effective magnetic field collinear to the constrained moment.

There is an important specific feature of the longitudinal fluctuations in the case of half-metallic systems. The semiconducting gap in one of the spin channels results in the integer numbers of the majority and minority electrons per unit cell. Therefore the moment per unit cell is an integer. As long as the half-metallic state is preserved the magnetic moment of the system remains constant and the change of one of the atomic moments must be compensated by an opposite change of other moments (Fig. 6). This violates an intuitive relation between induced and inducing moments since the increase of the inducing moment leads to the decrease of the induced moment. Extending the calculations of longitudinal fluctuations to noncollinear configurations we formulate the model describing the energetics of the transversal and longitudinal fluctuations of the Ni moments. Since here we are interested in temperatures that are much lower than the Curie temperature of NiMnSb the disordering of the Mn sublattice is neglected.

The energy of the excited states of Ni moment is given by

$$E(\theta, m) = a(1 - \cos 2\theta) + b(m - m_0)^2$$

where θ is the angle between Ni moment and z-axis and the value of the Ni moment. Parameters a and b are given by $a = 0.8$ mRy, $b = 58.6$ mRy. The average value of a quantity $f(\theta,m)$ is

$$\frac{1}{Z}\int_0^{\pi/2} d\theta \sin\theta \int_{-\infty}^{\infty} dm\, m^2 f(\theta, m) \exp(-E(\theta, m)/k_B T).$$

The partition sum Z is given by the same integrals for the case of $f(\theta, m) = 1$.

The model that consequently treats the Ni moments as fluctuating three-dimensional atomic magnetization leads to the

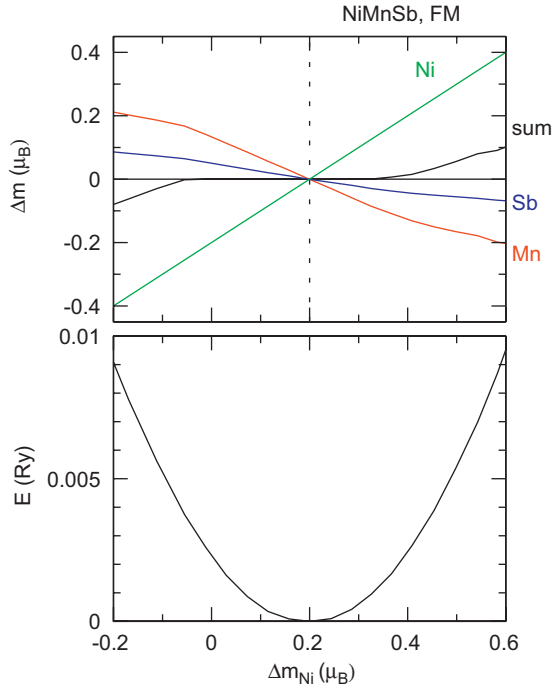

Fig. 6. (Color online) The longitudinal fluctuations in half-metallic NiMnSb. The calculations are performed for the ground-state ferromagnetic structure. The longitudinal constraining field is applied to the Ni atom. The bottom panel gives the energy of the system per formula unit as a function of the constrained Ni moment. The minimum of the energy corresponds to the ground state value of the Ni moment. The upper panel gives the deviations of the atomic moments and of the moment per formula unit from the ground state value. Because of the half-metallicity the total moment remains constant in a broad interval of the variation of the Ni moment. The increase (decrease) of the Ni moment leads to the decrease (increase) of the Mn moment.

result that the net magnetization of the Ni sublattice remains almost unchanged with increasing temperature (Fig. 7). If Jacobian m^2 responsible for larger statistical weight of the states with larger m is omitted a strong decrease of the Ni magnetization is obtained. This decrease is even stronger if the longitudinal fluctuations are neglected completely.

These results show that the spin-fluctuations of the induced Ni moments in half-metallic NiMnSb increase much faster with increasing temperature than the fluctuations in the Mn sublattice. However, the average Ni magnetization depends very weakly on temperature that is the result of the compensation of effect of the transversal fluctuations leading to the decrease of the magnetization by the longitudinal fluctuations. Since the experimental

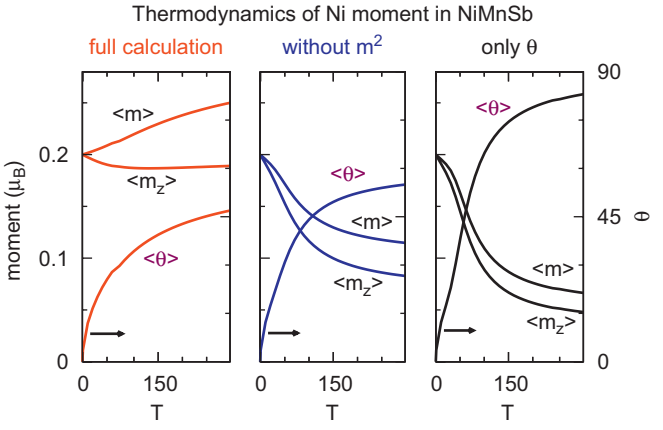

Fig. 7. (Color online) The temperature dependence of the average values of the Ni magnetization m_z, the local atomic moment m, and angle θ of the deviation of the Ni moment from the z-axis. The calculations are performed within three different schemes.

magnetization does not reveal any specific features in the low-temperature region we conclude that the description with the account for the longitudinal Ni fluctuations gives the correct picture of the magnetic fluctuations in the system.

4. Conclusion

The origin of the half-metallicity is different in diluted magnetic semiconductors and Heusler alloys. In DMS the properties of the hole states at the top of the valence band play a crucial role in the formation of the thermal properties. In Heusler alloys the factors determining the thermal behavior are distinct. Here the relation between half-metallicity and the longitudinal fluctuations of atomic moments is considered. The temperature dependence of the Ni magnetization in NiMnSb is studied.

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