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LETTER TO THE EDITOR

Density functional theory of high- T_C ferromagnetism of (ZnCr)Te

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Abstract

We report the parameter-free, density-functional theory calculations of the electronic structure, interatomic exchange interaction and magnetic critical temperature of $\text{Zn}_{0.75}\text{Cr}_{0.25}\text{Te}$. This system has recently gained exceptional importance as the first diluted magnetic semiconductor (DMS), where the intrinsic ferromagnetism with Curie temperature higher than room temperature is confirmed by magnetic circular dichroism measurements. We obtain a value for the Curie temperature that is in good agreement with experiment. The role of the holes in the valence band in mediating the ferromagnetic exchange interactions is demonstrated. The application of the same calculational scheme to $\text{Zn}_{0.75}\text{Mn}_{0.25}\text{Te}$ shows that, in good correlation with experimental data, this system does not possess charge carriers and is characterized by strong antiferromagnetic exchange interactions. Comparing (ZnCr)Te with III–V DMS, we note the role of a large semiconducting gap for preserving high spin polarization of the states at the Fermi level at finite temperatures.

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

Recently the magnetism of diluted magnetic semiconductors has received tremendous attention. This attention was born from the widespread vision of semiconductor spintronic devices that promise to revolutionize modern electronics [1]. The interest in the diluted magnetic semiconductor (DMS) was strongly motivated by the discovery of ferromagnetism in $\text{Ga}_{0.947}\text{Mn}_{0.053}\text{As}$ with Curie temperature (T_C) as high as 110 K [2]. The ferromagnetism with a lower T_C (e.g., about 35 K for Mn concentration of 7% [3]) has also been observed in (InMn)As. Much effort has been devoted to studying the nature of the ferromagnetism in (GaMn)As and (InMn)As with the aim of designing ferromagnetic DMS materials with the Curie temperature exceeding the room temperature.

The theoretical prediction by Dietl *et al* [4] of the high- T_C ferromagnetism in (GaMn)N played an important role in the formulation of the direction of the search for new ferromagnetic DMS materials. A number of experimental studies indeed detected the ferromagnetism of (GaMn)N samples with Curie temperature higher than room temperature [5–7]. However, the

experimental data on the magnetic state of (GaMn)N is strongly scattered and ranges from a paramagnetic ground state to the ferromagnetic state with a very high Curie temperature of 940 K.

New proof of the complexity of the magnetism of DMS was given by the recent magnetic circular dichroism (MCD) measurements by Ando [8]. The measurements were performed on a high- T_C (GaMn)N sample and led Ando to the conclusion that the (GaMn)N phase in this sample is paramagnetic. The ferromagnetism of the sample was found to come from an unidentified phase. This work demonstrated the importance of MCD studies for the reliable establishment of the magnetic state of DMS.

At present, the list of DMS systems with the ferromagnetism confirmed by MCD measurements is very short: apart from the prototype DMS ferromagnets (GaMn)As [9] and (InMn)As [10] of the III–V type, it contains only one system (ZnCr)Te that belongs to the II–VI type of DMS. Very recently a (ZnCr)Te sample with high Cr concentration of 20% has been grown [11]. This concentration is substantially larger than the Mn-concentration reached in (GaMn)As and (InMn)As. The Curie temperature of $Zn_{0.8}Cr_{0.2}Te$ was found to be 300 K [11]. Note that (ZnCr)Te is the first II–VI DMS where high- T_C ferromagnetism is reliably detected. (For recent reviews on magnetic properties of II–VI DMS see [12, 13].) The current uniqueness of (ZnCr)Te makes it a system of exceptional importance for both basic and applied researches in the field of spin-electronics.

Up to now the main body of theoretical studies of the magnetism in II–VI DMS has been performed within the framework of a model-Hamiltonian approach, with the parameters of the Hamiltonian determined on the basis of available experimental data [12, 13]. Modern developments in the computational methods of the density functional theory (DFT) now allow for parameter-free investigation of the properties of complex DMS systems. For instance, many DFT calculations for the III–V DMS have been performed (see, e.g., [14–19] for an incomplete list of recent publications).

In this letter we report a DFT study of the exchange interactions and Curie temperature in (ZnCr)Te. The local density approximation (LDA) is used. The only DFT calculation of (ZnCr)Te known to us is the coherent-potential-approximation (CPA) study by Sato and Katayama-Yoshida [20], who compared the energies of the ferromagnetic state and the state of complete magnetic disorder. The ferromagnetic state appeared to be lower in energy, which reveals the trend to ferromagnetism in agreement with experiment. Since the CPA neglects the effects of the short-range order in the distribution of Cr atoms, it is important to perform the DFT study taking into account the relative coordination of Cr atoms. Such a technique is provided by the supercell approach.

In the calculations we use the scheme discussed in detail in [19, 21]. Here we give a short description only. In a cubic supercell of zinc-blende ZnTe containing four formula units, one of the Zn atoms is replaced by the Cr atom. The concentration of Cr is 25%, which is close to the experimental value of 20%.

To describe the exchange interactions in the system we use an effective Heisenberg Hamiltonian of classical spins

$$H_{\text{eff}} = - \sum_{i \neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j \quad (1)$$

where J_{ij} is an exchange interaction between two Cr sites (i, j) and \mathbf{e}_i is the unit vector pointing in the direction of the magnetic moments at site i .

We calculate the energy of the frozen magnon states $E(\mathbf{q})$ for a regular mesh of the wavevectors \mathbf{q} and use them to determine the Fourier transforms of the interatomic exchange parameters. Performing back Fourier transformation we obtain the J_{ij} parameters. The Curie

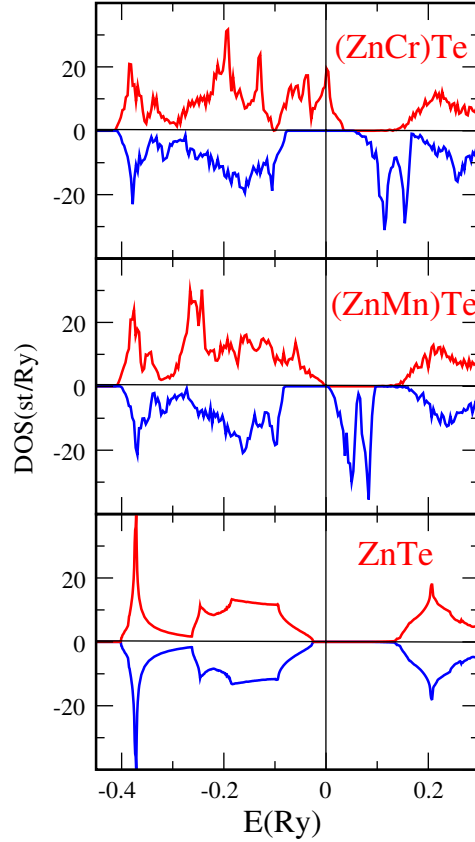


Figure 1. The calculated DOS. For each system the upper/lower curve shows spin-up/spin-down DOS. The concentration of Cr (upper panel) and Mn (middle panel) is 25%.

temperature is estimated in the mean-field (MF) approximation

$$k_B T_C^{\text{MF}} = \frac{2}{3} \sum_{j \neq 0} J_{0j}. \quad (2)$$

We use the rigid band approach to study the dependence of the exchange parameters and Curie temperature on the band occupation.

We begin the discussion of the calculational results with consideration of the density of states (DOS) (figure 1). Compared with semiconductor ZnTe the replacement of a Zn atom by a Cr atom adds to the valence band of the system five energy bands related to the Cr 3d states. Since there are five extra energy bands and only four extra electrons (the atomic configurations of Zn and Cr are $4s^2$ and $3d^5 4s^1$), the valence band is not filled and there appear unoccupied (hole) states at the top of the valence band. The integrated number of the hole states is exactly one hole per Cr atom (correspondingly, one hole per supercell).

There is an important difference between the DOS of (ZnCr)Te (figure 1) and the corresponding DOS of (GaCr)As, (GaMn)As or (GaFe)As (see [19]). In (ZnCr)Te the spin-up and spin-down impurity bands do not overlap. On the other hand, in all three III–V DMS, with a concentration of the 3d element of 25%, such an overlap takes place. The absence of the overlap in (ZnCr)Te leads to strongly expressed half-metallic behaviour with only spin-up states present at the Fermi level. There is a large energy distance between the Fermi level and the spin-down

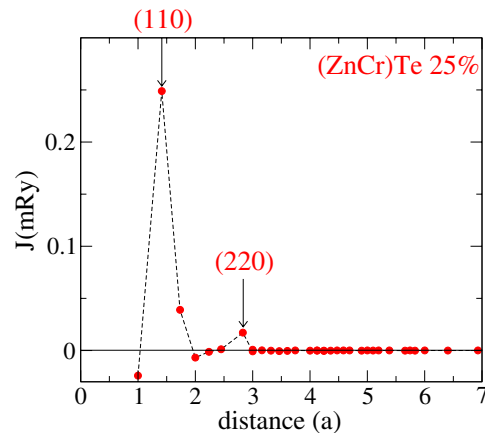


Figure 2. Heisenberg parameters of the exchange interaction between the Cr moments.

states, both occupied and unoccupied. The high spin polarization of the electron states at the Fermi level is an important condition of efficient spin-injection from ferromagnetic DMS into semiconductor. (As a reminder, spin-injection is a necessary component of spintronic devices.) The difference between (ZnCr)Te and the DMS on the GaAs can be related to a larger value of the semiconducting gap of ZnTe compared to GaAs. The impurity states lying in the gap hybridize less with the semiconductor states than the states lying within the valence or conduction bands. This leads to a smaller energy width of impurity bands in the case of (ZnCr)Te. Another important factor is larger interatomic distances in (ZnCr)Te. As a result, the spin-up and spin-down impurities do not overlap up to high impurity concentration.

The energy separation of the spin-up and spin-down electron states in (ZnCr)Te is an important property since it diminishes mixing between the majority and minority states with thermal disorder of the Cr moments, and correspondingly is favourable for the preservation of strong spin-polarization at finite temperatures.

The calculated magnetic moment of the Cr atom is $3.7 \mu_B$. The magnetic moment of the supercell is exactly $4 \mu_B$. An integer total moment is a consequence of the half-metallic character of the system.

Next we discuss the stability of the ferromagnetic state and the value of the magnetic transition temperature. The calculated interatomic exchange parameters are shown in figure 2. We see that there is strong ferromagnetic interaction between the Cr atoms separated by vector (110). There is an additional maximum of the interatomic exchange for atoms separated by vector (220). Note that the same crystallographic direction was found to be the direction of the exchange path for (GaCr)As and (GaMn)As [19]. Calculation of the Curie temperature using the exchange parameters depicted in figure 2 gives the value 346 K, which is in good agreement with experimental observation.

It is commonly accepted that the presence of holes is important for mediating ferromagnetic exchange interactions between the 3d magnetic impurities. To study the dependence of the interatomic exchange interactions on the number of holes we performed the calculation for different numbers of electrons. The calculation was performed in the rigid band approximation. A decrease in the number of holes leads to a fast decrease in the number of interatomic exchange interactions that change sign and become antiferromagnetic for a small number of holes. Correspondingly, the Curie temperature decreases quickly with decreasing hole number. The minimum of the exchange interaction is achieved for the case of the completely filled

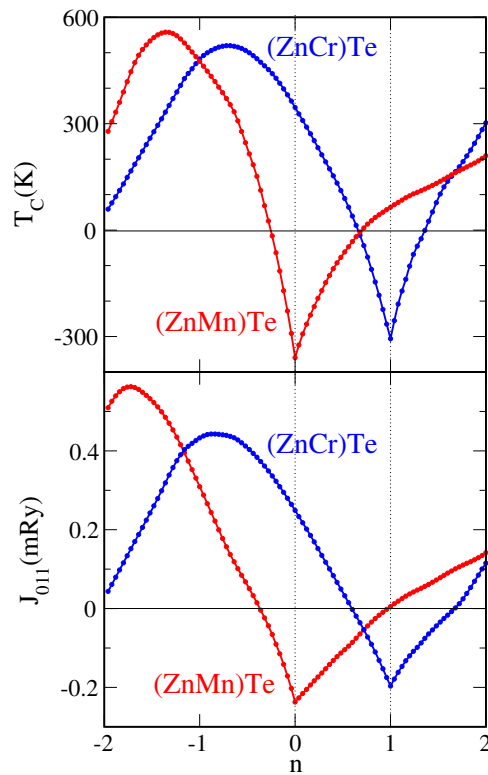


Figure 3. The MF value of the Curie temperature and the exchange parameter J_{110} as functions of the electron number. $n = 0$ corresponds to the nominal number of electrons.

valence band and empty conduction band. The presence of either holes in the valence band or electrons in the conduction band leads to increased ferromagnetic interactions. These results are in agreement with the physical picture of the antiferromagnetic superexchange mediated by the filled electron bands and the ferromagnetic kinetic exchange mediated by the charge carriers.

For comparison we performed the calculation for (ZnMn)Te with the same concentration of the 3d element of 25%. Similarly to the case of (ZnCr)Te, the replacement of a Zn atom by a Mn atom adds five spin-up energy bands to the valence band of ZnTe. Since Mn has one electron more than Cr, the number of valence electrons in (ZnMn)Te is also increased by five. The top of the spin-up valence band and the bottom of the spin-down impurity band in (ZnMn)Te almost coincide (figure 1). However, since there is no overlap of these bands the valence band is completely filled and the spin-down impurity band is empty. Therefore there are no charge carriers in the system. This results in antiferromagnetic interatomic exchange interactions (see values of J_{110} and T_C at $n = 0$ in figure 3). The deviation of n from the zero value adds either holes to the valence band ($n < 0$) or electrons to the conduction band ($n > 0$). Correspondingly the ferromagnetic interactions increase with n deviating from zero, resulting in the minimum of both T_C and J_{110} at $n = 0$. Remarkably, the form of the dependences $J_{110}(n)$ and $T_C(n)$ for (ZnMn)Te is qualitatively very similar to the form of the corresponding dependences for (ZnCr)Te with an obvious shift by -1 because of the difference in the number of electrons. This result proves the qualitative validity of the rigid band consideration used in the

calculations with varied electron number. Note that prevailing antiferromagnetic interactions in (ZnMn)Te are in agreement with experimental data [22].

We also performed the calculation for $\text{Zn}_{0.75}\text{Cr}_{0.25}\text{Se}$. The results obtained are qualitatively similar to those for $\text{Zn}_{0.75}\text{Cr}_{0.25}\text{Te}$. The calculated value of the Curie temperature of (ZnCr)Se is 267 K. Therefore a (ZnCr)Se sample similar to the sample of (ZnCr)Te should result in a high Curie temperature of the system. This Curie temperature is, however, noticeably lower than in the case of (ZnCr)Te.

Summarizing we have reported the LDA calculation of the electronic structure, interatomic exchange interactions and magnetic critical temperature of (ZnCr)Te. This system has recently gained exceptional importance for spintronic studies as the first DMS where the intrinsic ferromagnetism with Curie temperature higher than room temperature is confirmed by MCD measurements. We obtain a value for the Curie temperature which is in good agreement with experiment. The role of the holes in the valence band in mediating the ferromagnetic exchange interactions is demonstrated. It is shown that $\text{Zn}_{0.75}\text{Mn}_{0.25}\text{Te}$ does not possess charge carriers and is characterized by strong antiferromagnetic exchange interactions between the Mn moments. This result is in good correlation with experimental data. Comparing (ZnCr)Te with III–V DMS, we note the role of a large semiconducting gap for preserving high spin polarization of the states at the Fermi level at finite temperatures. It is desirable to extend the present study beyond the LDA. The possible approaches are the LDA + U [23] and the self-interaction correction (SIC) to the LDA [24].

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