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Abstract

The possibility of half-metallic diluted antiferromagnetic semiconductors of II–VI compounds is investigated on the basis of first-principles electronic structure calculation. The electronic structures of ZnS, ZnSe, ZnO, CdS and CdSe doped with two kinds of 3d transition metal ions are calculated using the Korringa–Kohn–Rostoker (KKR) method and their magnetic transition temperatures are determined using a cluster-type approximation. It is predicted that II–VI compound semiconductors doped with two kinds of magnetic ions might be good candidates for half-metallic antiferromagnets.

1. Introduction

Numerous experimental and theoretical attempts have been made over the last decade to exploit electron spins in addition to charges as a new degree of freedom carrying information. Such technology, called spin-electronics (spintronics for short) or magnetoelectronics, is among the most challenging targets in electronic device development. One of the key issues in spin-electronics is half-metallicity, i.e. metallic in one spin direction of electrons but insulating in the other. Materials having such a property are important candidates for spin-electronics materials. Many kinds of ferromagnetic half-metals have been investigated. For example, some of the Heusler alloys, which are well known as half-metals, have been investigated intensively [1]. The half-metallicity of zincblende type CrAs was first predicted theoretically and then verified experimentally [2]. In addition to these examples, a considerable number of transition metal oxides and diluted magnetic semiconductors are known to be half-metals.

Though most investigations of half-metallicity have targeted ferromagnets, this property is not specific to ferromagnets. Half-metallic antiferromagnets were proposed many years ago by van Leuken and de Groot [3]. They pointed out that, as a special case of ferrimagnetism,
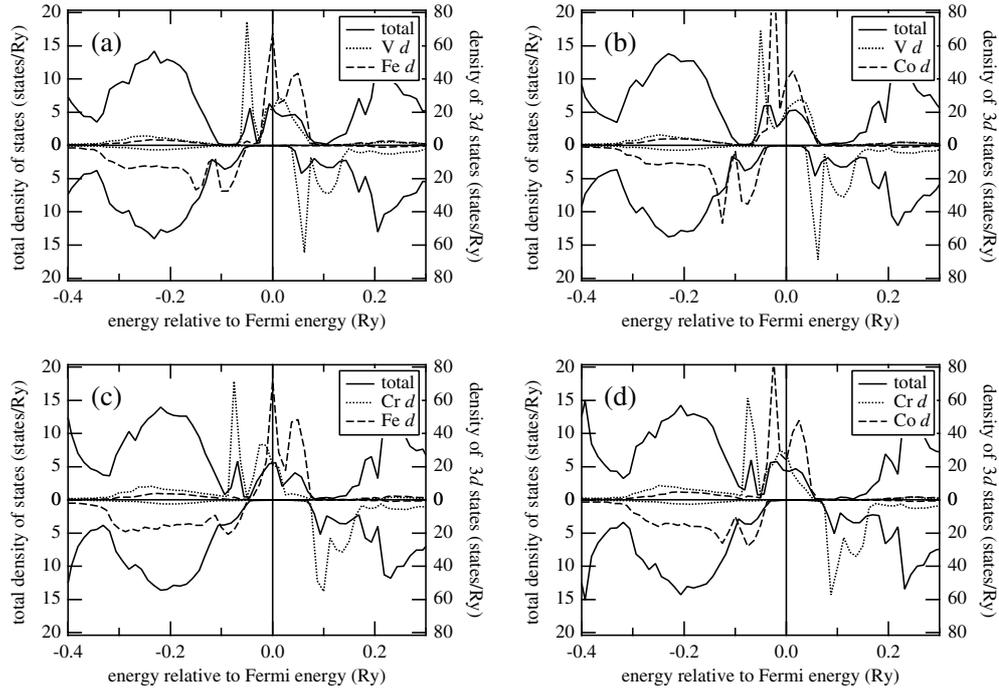
Figure 1. Total density of states and partial 3d density of states of the magnetic ion sites of $Zn_{0.9}A_{0.05}B_{0.05}S$ in the antiferromagnetic states: (a) V–Fe, (b) V–Co, (c) Cr–Fe and (d) Cr–Co.

Table 1. Total and local magnetic moments of II–VI half-metallic antiferromagnetic semiconductors. The impurity concentration for each ion is 5%.

	Magnetic ions	Total moment (μ_B)	Local moment (μ_B)
ZnS	V–Fe	−0.05	+2.17(V), −3.02(Fe)
	V–Co	0.00	+2.09(V), −2.02(Co)
	Cr–Fe	0.00	+3.28(Cr), −3.17(Fe)
	Cr–Co	+0.05	+3.21(Cr), −2.15(Co)
ZnSe	V–Fe	−0.05	+2.29(V), −3.07(Fe)
	V–Co	0.00	+2.22(V), −2.03(Co)
	Cr–Fe	0.00	+3.43(Cr), −3.20(Fe)
	Cr–Co	+0.05	+3.36(Cr), −2.15(Co)
ZnO	V–Fe	−0.10	+1.60(V), −3.28(Fe)
	V–Co	−0.04	+1.54(V), −2.27(Co)
	Cr–Fe	−0.04	+2.68(Cr), −3.36(Fe)
	Cr–Co	+0.03	+2.66(Cr), −2.30(Co)
CdS	V–Fe	−0.06	+2.23(V), −3.42(Fe)
	V–Co	0.00	+2.18(V), −2.35(Co)
	Cr–Fe	0.00	+3.37(Cr), −3.51(Fe)
	Cr–Co	+0.05	+3.31(Cr), −2.46(Co)
CdSe	V–Fe	−0.05	+2.52(V), −3.43(Fe)
	V–Co	0.00	+2.45(V), −2.35(Co)
	Cr–Fe	0.00	+3.68(Cr), −3.53(Fe)
	Cr–Co	+0.05	+3.62(Cr), −2.45(Co)
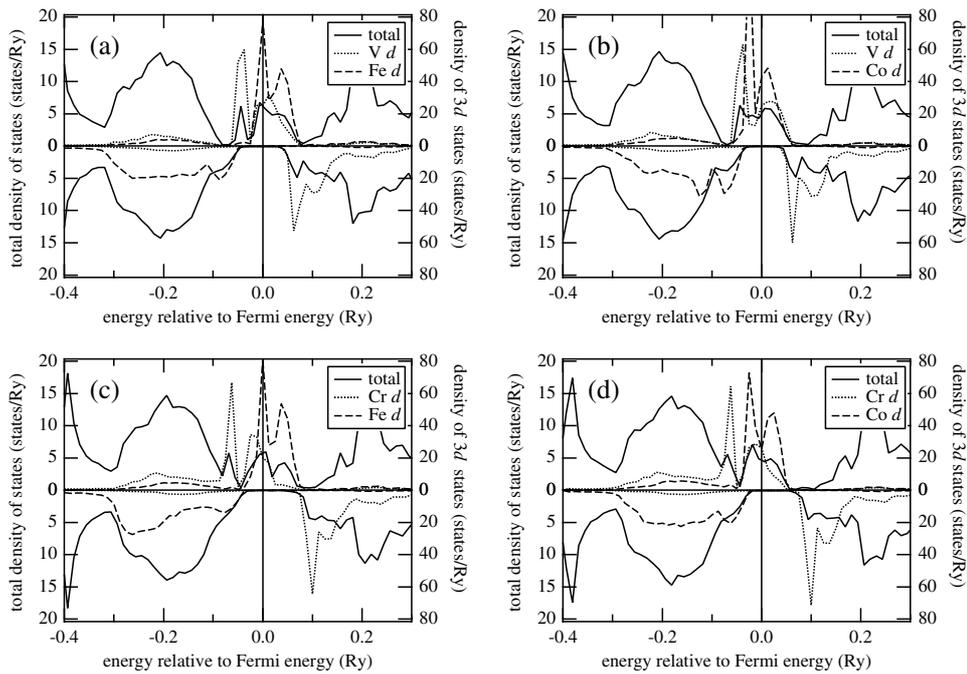
Figure 2. Density of states of $Zn_{0.9}A_{0.05}B_{0.05}S$ e in the antiferromagnetic states: (a) V–Fe, (b) V–Co, (c) Cr–Fe and (d) Cr–Co.
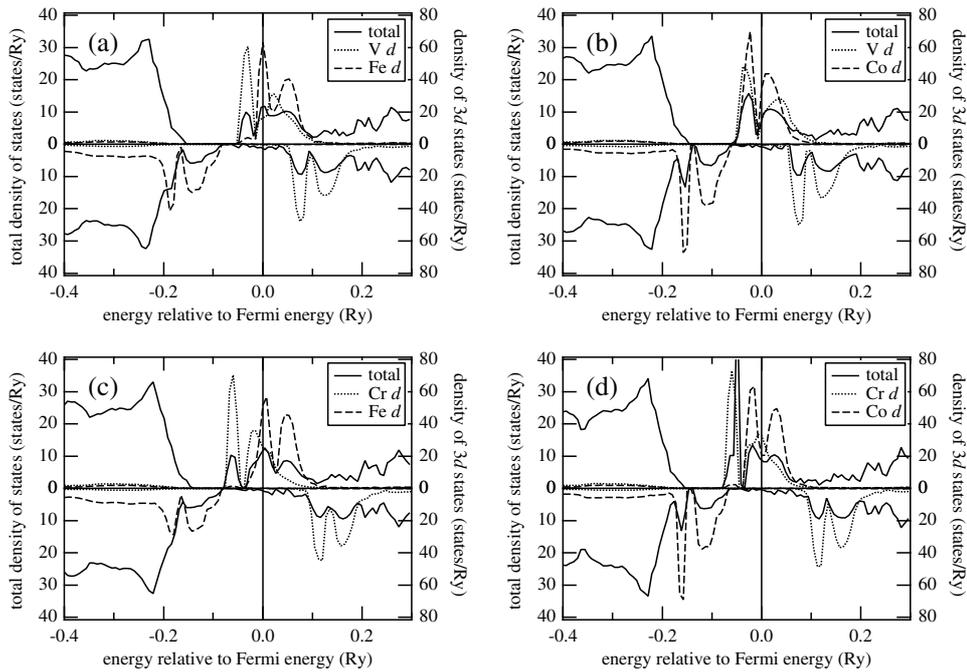
Figure 3. Density of states of $Zn_{0.9}A_{0.05}B_{0.05}O$ in the antiferromagnetic states: (a) V–Fe, (b) V–Co, (c) Cr–Fe and (d) Cr–Co.
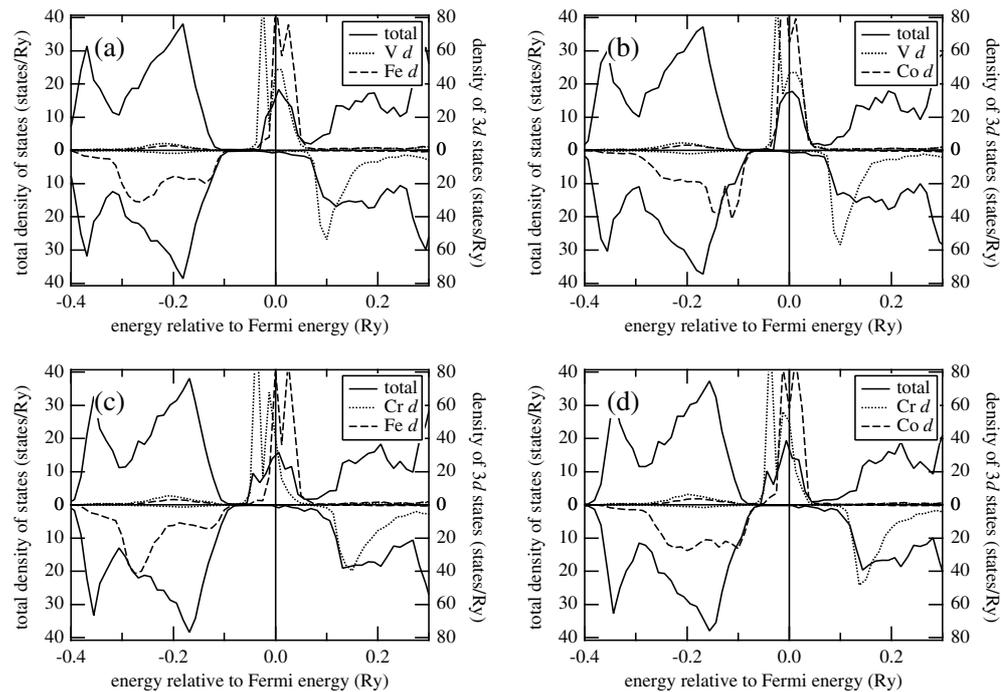
Figure 4. Density of states of $Cd_{0.9}A_{0.05}B_{0.05}S$ in the antiferromagnetic states: (a) V–Fe, (b) V–Co, (c) Cr–Fe and (d) Cr–Co.

it might be possible that the system becomes half-metallic and yet carries no magnetization. This is impossible for normal antiferromagnets because of the spin-rotational (or time-reversal) symmetry, but it is not necessarily true for ferrimagnets with a compensated magnetic moment. Thus, there could be a half-metal composed of two kinds of magnetic ions: one with an up magnetic moment and the other with a down magnetic moment. In such a system, the total magnetic moment could be compensated without destroying the half-metallicity.

Half-metallic antiferromagnets could be even more useful than half-metallic ferromagnets for the following reasons: (1) they usually have a high magnetic transition temperature due to strong magnetic couplings; (2) they are insensitive to external fields; (3) they do not produce stray fields; (4) it is expected that it will be easy to inject spins because of their small shape magnetic anisotropy. As candidates for half-metallic antiferromagnets, double perovskite transition metal oxides have been proposed [4, 5]. However, no experimental evidence for the existence of half-metallic antiferromagnets has been reported. This may indicate that it is difficult to realize half-metallic antiferromagnetism using intermetallic compounds and transition metal oxides.

Seeking different types of systems as possible candidates for half-metallic antiferromagnets, we have proposed half-metallic diluted antiferromagnetic semiconductors [6]. The basic idea of using diluted magnetic semiconductors (DMSs) to realize antiferromagnetic half-metals is described in our previous paper [6]. In the present paper, we give the results of first-principles electronic structure calculations of II–VI compound semiconductor based half-metallic diluted antiferromagnetic semiconductors, ZnS, ZnSe, ZnO, CdS and CdSe, and discuss their electronic and magnetic properties.
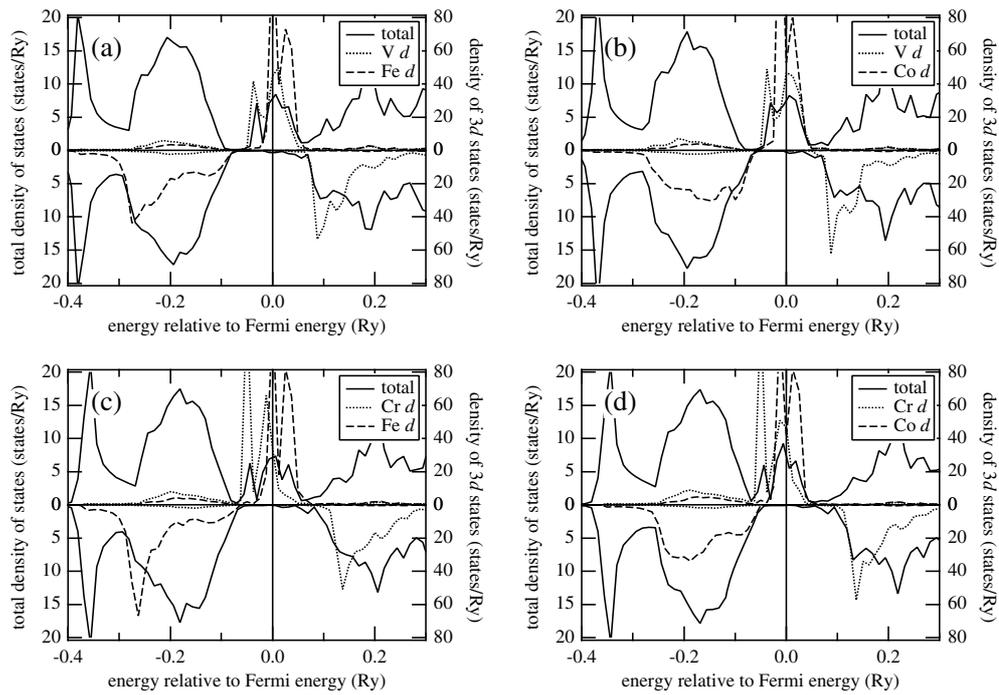
Figure 5. Density of states of $Cd_{0.9}A_{0.05}B_{0.05}Se$ in the antiferromagnetic states: (a) V–Fe, (b) V–Co, (c) Cr–Fe and (d) Cr–Co.

2. Calculation

We have performed first-principles electronic structure calculation using the Korringa–Kohn–Rostoker (KKR) Green's function method with the coherent potential approximation (CPA) and the local density approximation (LDA) of the density functional method. The details of the calculation are mostly the same as used in our previous paper [6] and used by other authors in similar calculations on the ferromagnetic DMSs [7, 8]. We assumed the zincblende structure for ZnS, ZnSe and CdSe, and the wurtzite structure for ZnO and CdS. In order to obtain the antiferromagnetism, we introduced two kinds of transition metal ions into the systems. In the present study, we adopted the combinations of V–Fe, V–Co, Cr–Fe and Cr–Co. The magnetic ions are supposed to substitute randomly for part of the Zn and Cd sites.

The magnetic transition temperatures (Néel temperatures, T_N) were calculated using the effective exchange coupling constants J_{ij} [9] obtained by the KKR–CPA–LDA method. Thus the obtained J_{ij} are used to construct the Heisenberg Hamiltonian, assuming that a classical spin exists on each magnetic ion. We applied the cluster approximation (CA) proposed by Mano [11, 12] to this model. Though the mean field approximation (MFA) is used frequently to estimate the magnetic transition temperature, it is known to greatly overestimate the transition temperature for diluted spin systems [10, 8]. In order to overcome this difficulty without relying on Monte Carlo simulations on diluted spin systems, we use the above CA scheme. In the present study, the one-site approximation of CA was used and three kinds of neighbours that have large J_{ij} components were taken into account. We assumed classical spins, while the original CA assumed Ising spins.
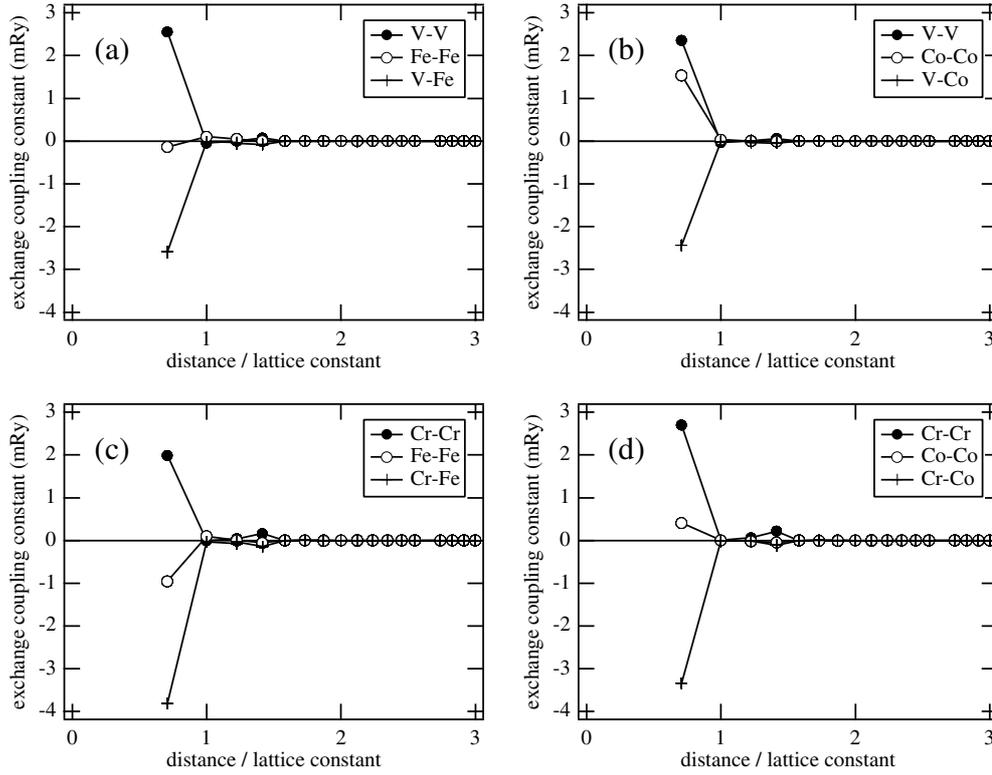
Figure 6. Exchange coupling constants of $Zn_{0.84}A_{0.08}B_{0.08}S$: (a) V–Fe, (b) V–Co, (c) Cr–Fe and (d) Cr–Co.

3. Results and discussions

Figure 1 shows the calculated density of states of $Zn_{0.9}A_{0.05}B_{0.05}S$ (A = V, Cr, B = Fe, Co) in the antiferromagnetic states. The upper half shows the spin-up states and the lower half shows the spin-down states. It is clear that the antiferromagnetic state realizes a half-metallic electronic structure: the spin-up states are metallic and the spin-down states are insulating. The calculated magnetizations and local magnetic moments are summarized in table 1. From the values in table 1, we see that in many cases the magnetizations are completely cancelled while the local magnetic moment of each magnetic ion keeps a large value. Note that the magnetization is not the sum of the local magnetic moment, since the latter is merely the integrated magnetic moment within each muffin-tin sphere.

For other compounds, the results are summarized in figures 2–5. Also, in these systems, the antiferromagnetic state realizes a half-metallic electronic structure. The total magnetic moment per impurity is integer, as is characteristic for half-metallic systems. Only ZnO-based systems and (CdVFe)S do not show such a tendency, and it is probable that it originates from the small but non-zero density of states in the spin-down states near the Fermi energy. In addition to the above examples, we found that similar properties are observed for various combinations of host semiconductors and magnetic ions: e.g. (ZnVNi)S, (ZnMnFe)S, (ZnCrMn)Se, (ZnMnFe)Se, (CdVNi)S, (CdVCo)Te and (CdCrFe)Te.

Figure 6 shows the exchange coupling constants J_{ij} of $Zn_{0.84}A_{0.08}B_{0.08}S$. We see that the coupling constants between the same elements are mostly positive, while those between the dif-
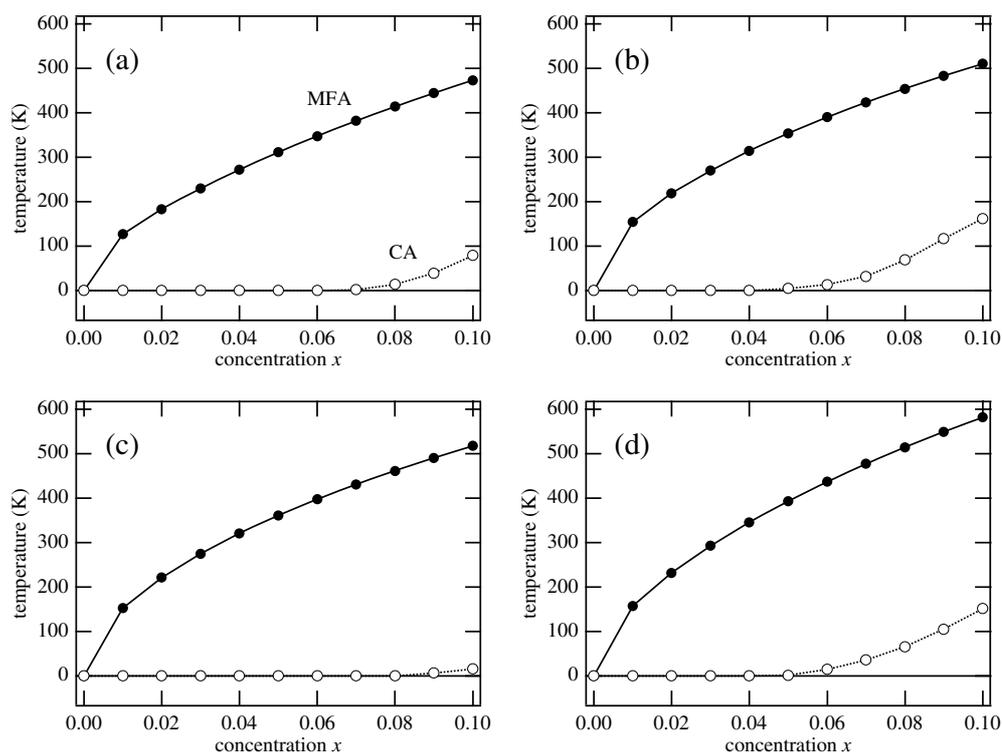
Figure 7. Néel temperature of $Zn_{1-2x}A_xB_xS$: (a) V–Fe, (b) V–Co, (c) Cr–Fe and (d) Cr–Co.

ferent elements are large negative values. The negative coupling constants reflect the fact that the antiferromagnetic coupling between an ion with less-than-half valence d electrons and one with more-than-half valence d electrons is more stable than the ferromagnetic coupling. The exception is the coupling between Fe atoms: these are mostly negative, in spite of the coupling between the same elements. This is a case where the antiferromagnetic superexchange is stronger that the ferromagnetic double-exchange coupling due to their nearly half-filled d orbitals.

The Néel temperatures of $Zn_{1-2x}A_xB_xS$ calculated with the exchange coupling constants in figure 6 are shown in figure 7 as a function of the impurity concentration. The behaviour of the Néel temperatures calculated with MFA have a shape of $\sqrt{x}$ near $x \sim 0$, indicating that the double exchange plays a role in determining the magnetic coupling [6]. It is found that CA shows a lower Néel temperature than MFA and also gives rise to a critical concentration that is missing in MFA. Because the exchange coupling is rather short ranged, as is shown in figure 6, the impurity concentration should not be too low to realize the half-metallic antiferromagnetic property. However, the required concentration is not extremely high for II–VI-type semiconductors.

Although the MFA gives similar Néel temperatures for all combinations of the magnetic ions, the Néel temperatures of $Zn_{1-2x}Cr_xFe_xS$ calculated by CA is much lower than those of $Zn_{1-2x}V_xCo_xS$ and $Zn_{1-2x}Cr_xCo_xS$. This is due to the negative coupling constants between Fe ions pointed out above. In the present case of the zincblende structure, the negative magnetic coupling produces frustration. The Néel temperatures of $Zn_{1-2x}V_xFe_xS$ lies in between those of $Zn_{1-2x}Cr_xFe_xS$ and those of $Zn_{1-2x}V_xCo_xS$ and $Zn_{1-2x}Cr_xCo_xS$, which is due to the fact that the coupling constant between two Fe atoms is nearly zero in this case.

Other II–VI compounds show similar behaviours to ZnS cases, though we omit detailed discussions for them. The transition temperatures of these systems are more or less the same as those of ZnS.

In summary, we have proposed a new magnetic system composed of II–IV-based compound semiconductors doped with two types of magnetic ions. We predict that some of those systems will show a half-metallic antiferromagnet (or the special case of ferrimagnetism with compensated magnetic moments). Since the systems have 100% spin-polarized Fermi surfaces like usual ferromagnetic DMSs, they can be used as spin-electronics materials.

Acknowledgments

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