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Antiferromagnetic half metallicity in codoped chalcopyrite semiconductors Cu($Al_{1-2x}A_xB_x$)Se_2 (A and B are 3d transition-metal atoms)

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ABSTRACT

Electronic structures and magnetic properties of group I–III–VI_2 chalcopyrite-type compounds Cu($Al_{1-2x}A_xB_x$)Se_2 are calculated using the Korringa–Kohn–Rostoker Green's function method, where A (Ti, V, Cr, Mn) and B (Fe, Co, Ni) are 3d transition metal atoms, and x is atomic concentration. We found that codoping of Cr–Co and V–Ni pairs at Al site of host $CuAlSe_2$ exhibit antiferromagnetic (AF) half metallicity with low Curie temperature (T_C). The AF half metallic property is supported by nullified net magnetic moment and compensated density of states in the minority spin direction. On the other hand, codoping of Cr–Ni, Mn–Co, V–Co, and Ti–Co pairs at Al site of host $CuAlSe_2$ manifest ferrimagnetic half metallicity with a small net magnetization and keeping antiparallel local spin moments. In Mn–Co case T_C is close to room temperature. Besides, Cr–Fe, V–Fe, and Ti–Ni codoping cases lead to an instable magnetic ordering and therefore obtain a disordered local moment (spin-glass like) state.

1. Introduction

Antiferromagnetic half metals (AFHM) have drawn much attention for stable magnetic state with full spin polarization in spintronic applications. The existence of AFHM was first introduced by van Leuken and de Groot [1] for the half Heusler type intermetallic compound, $V_7MnFe_8Sb_7In$, on the basis of electronic structure calculations. Subsequently, Pickett proposed that some double perovskites materials might be possible candidates for half metallic antiferromagnets [2]. Later on, Long et al. [3] pointed out the possibility of half metallic antiferromagnet on the transition metal (TM) pnictides. Before that, Bergqvist and Dederichs [4], Akai and Ogura [5] explained the stability mechanism of the half metallic diluted antiferromagnetic semiconductors. In AFHM the electrons, which are responsible for the metallic behavior share the same spin while the electrons with the opposite spin are insulating. In particular, they possess no macroscopic magnetization, though their carriers are fully spin polarized. This happens as a special case of ferrimagnetism where the materials become half metallic and yet carries no net magnetization at the Fermi level.

In a usual antiferromagnetic (AF) material the net magnetic moment is compensated by the reversal of a spin-density wave, where the electronic structures of the up spin and down spin electrons are identical. These effects cause no spin polarization of the conduction electrons at the Fermi level [1]. On the contrary, in AFHM, the vanishing effect of local spin moments (sum to zero net magnetic moment) is yielded by the requirement of the integral net magnetic moment of the codoping atoms. Dual doping of a suitable 3d TM pair with total sixteen valence electrons at III site of a limited group of I–III–VI_2 chalcopyrite semiconductor predicts a zero net magnetic moment [4,5]. As a result, a full spin polarization of the conduction electrons is obtained at the Fermi level, where the host semiconductor is doped by at least two types of magnetic atoms of equal concentration. The AFHM may be useful for the following reasons: (i) they usually exhibit higher magnetic transition temperature than room temperature [4], (ii) they are insensitive to external fields for null net magnetic moment, (iii) injection of spins is rather easy because of magnetic anisotropy [3]. These are significant features of the AFHM for spintronic applications.

Numerous experimental and theoretical [2–15] attempts have been exploited to obtain room temperature diluted magnetic states (DMS) based on groups III–V, II–VI, II–IV–V_2 and I–III–VI_2 compound semiconductors. The mineral of chalcopyrite crystal $CuFeS_2$ is an antiferromagnetic material with Néel temperature of

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$T_N \sim 850$ K and reduced magnetic moment of 3.85 μ_B per Fe, which has been explained in terms of the energy band scheme of this material. Cu($Al_{1-x}Fe_x$)S_2 alloys are therefore investigated to understand the electronic states of Fe 3*d* orbitals from its band structure [12]. Although enough literatures are available on DMS, half metallic ferromagnets and AF [5,6,13–19], still the quest for AFHM is at the preliminary stage. We are motivated to design rather new sorts of AFHM by calculating electronic structures, magnetic properties and the stability of magnetic states of Cu ($Al_{1-2x}A_xB_x$)Se_2, where *A* (Ti, V, Cr, Mn) and *B* (Fe, Co, Ni) are 3*d* TM atoms, and *x* is atomic concentration. Recently, investigations on AFHM were reported by some research groups [3–5]. Those materials contain at least two types of magnetic atoms with local spin moments aligned antiparallel to each other, contrary to ferromagnetic half metals [13] which can be manifested with one type of magnetic atom. From a technological point of view, materials having such properties can be used for spin injection devices, vertical recording, high density information storage, and so on.

In this paper, we compare the calculated total energy per primitive unit cell of ferrimagnetic (FiM) state and the corresponding disordered local moment (DLM) state, which simulates a spin-glass state. Relatively lower energy state of various spin orientations is taken as the stable magnetic phase. Those stable FiM states exhibit zero or negligibly small net magnetic moment and half metallicity as well are considered as AFHM. The stability of FiM and dominating DLM states can be described by some magnetic coupling mechanisms, namely double-exchange and super-exchange, respectively. The magnetic phases are treated by the single site coherent potential approximation (CPA). The AFHM having zero net magnetic moment is applicable in (i) the zero spontaneous magnetization, i.e., the vanishing effect of the external field, and (ii) obtaining spin-resolved information on a nano scale in SP-STM (spin-polarized scanning tunneling microscopy) as a tip (data reading) material [20,21].

The layout of this paper is as follows: Section 2 deals with the calculation outlines and chalcopyrite structure, numerical results for electronic states of codoped systems, magnetic properties, and Curie temperature are presented in Section 3, along with the discussion of underlying mechanisms. The results are summarized in Section 4.

2. Calculation method

We use KKR-Green's function method in combination with CPA and generalized gradient approximation (GGA) with the parametrization given by Perdew and Wang [22] of density functional theory (DFT) for electronic and magnetic structure calculations. CPA provides a rather accurate treatment of disordered systems within the single-site approximations [23]. The form of the potential was treated as muffin-tin (MT) type, where the system is considered to be filled with non-overlapping spheres of spherical potentials, centered on the atomic positions. Angular momentum of scattering is used up to $\ell = 2$. The relativistic effects are considered within the scalar relativistic approximation. In the unit cell, eight extra empty MT potentials with zero atomic charge filling up the open space of the chalcopyrite structure are used in addition to those eight atomic sites to perform an accurate calculation. Magnetic structures and related properties are computed using the KKR-CPA program package “Machikaniyama” coded by Akai [24].

The primitive unit cell of chalcopyrite structure contains eight atoms, two kinds of cations and one kind of anion. The crystal structure is a body centered tetragonal (BCT). The space group is $I\bar{4}2d$ and the symmetry is tetragonal. Anions are coordinated tetrahedrally with cations with the inner parameter of 0.26. The lattice parameters (measure the size of the unit cell) including the inner parameter are taken up from Ref. [25]. Simultaneously, two TM atoms doped ferromagnetic, AF and DLM states unit cells are constructed in the constraint of host BCT structure. The host system and the impurity doped magnetic states are treated with the CPA using the concept of *t*-matrices [26].

3. Results and discussion

3.1. Underlying mechanism

The stability of antiferromagnetic (AF) and ferromagnetic (FM) states can be depicted by coupling mechanisms between the magnetic states. The mechanism behind the occurrence of the half metallic AF in general in DMS with 3*d* TM atom is explained in Ref. [5]. The mechanisms of double-exchange and super-exchange in DMS are described in Ref. [6]. We explain the AF stability mechanism in chalcopyrite semiconductor $CuAlSe_2$ codoped with two kinds of 3*d* TM atoms. Typically we consider two magnetic atoms, say Cr and Ni having valence *d* electrons less and more than half filled, respectively. Although the number of *d* electrons vary from system to system, we assume that when Cr and Ni randomly mixed at Al^{3+} site, the available valence *d* electrons of Cr^{3+} and Ni^{3+} are d^3 and d^7, respectively. The magnetic couplings are shown schematically in Fig. 1. When two ions (i) and (ii) couple ferromagnetically to form a joint band (iv), electrons can hop between the states of different energies of occupied and empty states reducing their kinetic energies (transfer integral). This is nothing but the super-exchange interaction [3–6,27]. On the contrary, for AF coupling of those two ions (ii) and (iii) to produce the joint band (v), electrons of one of the spin states (say, up) can hop between the states of the same energy (degenerate states) reducing more kinetic energy. This correspond to the double-exchange interaction [3–6,28]. In terms of energy gain, double-exchange interaction is stronger than super-exchange interaction and hence AF state is more stable than FM state [5]. The FM coupling produces metallic bands in both spin directions at the Fermi level, whereas the AF coupling realizes a half metallic band. Obviously, the gain in band energy in AF coupling is higher than FM coupling, which indicates the stability of AF state.

3.2. Electronic structures

To understand the AF half metallicity, we introduce two types of magnetic ions at Al site of the host $CuAlSe_2$ with 3% concentration of each impurity ion. Electronic structures of such multi-component and partially disordered compounds are calculated in the following cases and their total energies per primitive unit cell are compared to seek a stable magnetic phase: (i) two types of magnetic ions couple ferromagnetically (FM state), (ii) those couple antiferromagnetically (AF state), and (iii) those couple such that the local spin moments arrange randomly (DLM state). Electronic structures *viz*. local and net density of states (DOS) for doping of total 6% concentrations of impurities are shown in Figs. 2–4.

Fig. 2 (a) shows the FM metallic state of a typical dual doped compound which is taken as Cu($Al_{0.94}Cr^{u}_{0.03}Co^{u}_{0.03}$)$Se_2$, where u signifies the up spin (parallel) configuration of the TM pair. The local spin moments inside the MT at Cr and Co sites are 2.99 μ_B/atom and 2.03 μ_B/atom, respectively, whereas saturate magnetic moment is 0.36 μ_B/cell. In addition, small local moments are induced at the neighboring non-magnetic host sites. An exemplary DLM state of the corresponding FM state is shown in Fig. 2(b), where the randomly oriented local spin moments nullify the net magnetic moment. In the present report, DLM state is