New Ferromagnetics Based on Manganese-Alloyed Chalcopyrites $A^{II}B^{IV}C^{V}_2$

V. M. Novotortsev$^a$, A. V. Kochura$^{a,b,c}$, and S. F. Marenkin$^a$

$^a$ Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia
$^b$ Kursk State Technical University, Kursk, Russia
$^c$ Wihuri Physical Laboratory, University of Turku, Finland

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Abstract—This review describes the principles of semiconductor spintronics, represents the physicochemical properties of materials based on manganese-alloyed $A^{II}B^{IV}C^{V}_2$ compounds, considers the results from theoretical simulation of magnetic properties of $A^{II}B^{IV}C^{V}_2$ alloyed with 3d metals, summarizes the basic approaches to explanation of ferromagnetism with Curie points above room temperature arising in $A^{II}B^{IV}C^{V}_2$:Mn, and indicates promising ways to synthesize and study magnetic semiconductors based on chalcopyrites $A^{II}B^{IV}C^{V}_2$ in order to produce a suitable material for spintronic devices.

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INTRODUCTION

Modern electronics is based on the use of two major electron characteristics: charge and spin. However, their fields of application are different. Charge is used at all stages of data processing, including transfer, transformation, and storage, while electron spin and its resulting collective magnetic phenomena are applicable only in the writing—storage—reading process. The term spintronics, which is widely used nowadays, underlines the importance and prospects of combining charge and spin effects in electronic devices, which can upgrade electronics to a qualitatively new level. Spin control means control of spin orientation for individual charge carriers (electrons or holes) or additional control of spin value for an ensemble of particles. The goal of spintronics is to identify the features of interaction between a particle’s spin and environment in solids and to understand how they can be used to create and retain for a given time the fixed spin polarization of an ensemble of particles, as well as to detect its current spin state.

Creation of spin polarization or generation of a nonequilibrium spin ensemble can be achieved in several ways. The traditional way uses optical methods, where polarized photons interact and polarize the charge carriers in a solid. However, such a method is inapplicable to mass production of spintronic devices owing to problems of integration and miniaturization of optical components. A very promising method for creating nonequilibrium spin polarization, which needs no magnetic or optical effect to be applied to the media, is based application of the Hall spin effect [1]. With respect to practical realization, the most developed method uses injection of spin-polarized charge carriers from a magnetic electrode, where a nonequilibrium spin ensemble is created in the specimen. The elimination rate of this ensemble is determined by the spin relaxation time $\tau$, which is usually $10^{-12}$ s but can achieve the level of about $10^{-6}$ s [2]. Silicon devices at a temperature of 60 K achieved values of $\tau \approx 5 \times 10^{-7}$ s and transfer of spin-polarized electrons to a distance of up to 0.35 mm [3].

An essential advantage of spintronic devices is the high rate of change in the spin state of the system ($10^{-10}$ s and lower). This is similar to switching the information signal from the state of logical zero to the state of logical one, which is applied in traditional computer systems. In combination with very low energy losses for spin changes and capacity to remember and store the preceding logical state without additional energy consumption, there arises an opportunity to create components of miniature computer devices with very low energy consumption. They include magnetoresistive memory cells, spin diodes, spin field transistors, galvanic insulators, magnetic field sensors, spin gates, logical nanoelements, magnetic neurons, and spin microprocessors [5].

The range of promising materials to be applied in spintronic devices is very broad [4], from multilayer metal films with giant magnetoresistance (GMR),
which are successfully used in data storage systems [5], to organic semiconductors. Such semiconductors are characterized by weak spin–orbit interaction, various chemical properties, and low production cost.

One of the major hindrances that prevent use of spin components in data processing devices is the absence of a spin-polarized electron injecting material able to function in the same temperature modes as usual electronic devices. Use of Fe, Co, and Ni metals with insufficient structural and electronic compatibility with semiconductors would not achieve the required spin injection levels. Creation of a substance having both semiconductor and ferromagnetic properties and being structurally compatible with the traditional electronic engineering materials is now one of the major problems of spintronics.

The properties of such a material should satisfy the following requirements [6]. (1) Ferromagnetic properties depending on the concentration of charge carriers. This results in their potential control, for example, by doping in production or by means of electric fields in the case of spin diodes. (2) The Curie point ($T_C$) should be at least 400 K in order to use the material without any problem of stabilizing the device temperature. (3) Insensitivity of magnetic properties to potential deviations from a uniform distribution of magnetic ions in a semiconductor. Satisfaction of this provision enables development of the technology to obtain materials with reproducible properties. (4) The exchange field of free charge carriers should be sufficient for origination of GMR and effect of tunnel magnetoresistance. (5) Appearance of significant magneto-optical effect making it possible to realize optical reading of data written by means of a magnetic field. (6) Sufficient lifetime of magnetic quasiparticles to control spin orientation of individual particles or their ensembles by optical or electric signals. This results in the possibility of controlling magnetization of a substance.

The most popular ferromagnetic semiconductors capable of having the aforesaid properties are manganese-alloyed $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ compounds. The highest Curie point ($T_C = 185$ K) was recorded for (Ga,Mn)As films containing 12.5 wt % Mn and grown by means of molecular beam epitaxy (MBE) [7].

Higher solubility of d-elements is shown by complex binary semiconductors $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ as the nearest structural and chemical analogs of $\text{A}^{\text{II}}\text{B}^{\text{IV}}\gamma$ semiconductors. $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ compounds are characterized by high compatibility with Si, Ge, and $\text{A}^{\text{II}}\text{B}^{\text{IV}}\gamma$ semiconductors. This compatibility appears not only in their similar crystal structure but also in such properties of these materials as band structure, primarily covalent nature of chemical bonds, effective mass of free charge carriers, and scattering mechanisms of charge carriers. For Mn-alloyed $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ compounds, the highest $T_C \sim 367$ K was observed in the case of Mn-alloyed polycrystalline ZnGeAs$_2$ [8], giving the precondition for further development of ferromagnetic heterostructures [9] and related spintronic devices.

This review made an attempt to analyze the present methods for production of ferromagnetic semiconductors based on $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ and experimental results from studies of their properties.

**PROPERTIES OF $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ COMPOUNDS**

The $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ group includes 64 compounds if we take into account all the possible combinations of elements $\text{A}^{\text{II}}(\text{Be},\text{Mg},\text{Zn},\text{Cd})\text{B}^{\text{IV}}(\text{C},\text{Si},\text{GeSn})\text{C}_2^\gamma(\text{N},\text{P},\text{As},\text{Sb})$. The enthalpy of formation of 16 of these compounds (primarily containing carbon) is positive; i.e., they are unstable and, therefore, only 48 compounds of this group are suitable objects for synthesis and study. The theoretical estimates of magnetic order arising in Mn-alloyed $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ compounds showed that, with higher Mn content, only 19 of them can become semimetals retaining ferromagnetic properties [10]. Mn is a transitive 3d metal having an uncompensated magnetic moment and the ability to have a different oxidation state than the group number. Its oxidation state is 2+ in Mn$^{2+}$–$\text{A}^{\text{II}}\text{B}^{\text{IV}}\gamma$ solid solutions and 3+ in Mn$^{3+}$–$\text{A}^{\text{II}}\text{B}^{\text{IV}}\gamma$ solid solutions. In total, Mn may take 11 oxidation states from 3− to 7+, while 2+, 4+, and 7+ are the most common states. This makes it very interesting to use Mn as a doping element for production of ferromagnetics with high Curie points.

At present, high-temperature ferromagnetism has been experimentally found for eight Mn-alloyed $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ compounds. Figure 1 illustrates the crystal structure compatibility of the traditional electronic engineering materials and some $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$–Mn compounds.

A distinctive feature of $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ compounds is highly probable formation of defects in the crystal lattice, because the initial components (group II and V elements) are volatile and those of group IV are amphoteric. The deviations from stoichiometry in single crystal growth of these compounds promote formation of vacancies in cationic and anionic sublattices, and antistructural disorder is also highly probable, primarily in the cationic sublattice of $\text{A}^{\text{II}}\text{B}^{\text{IV}}\gamma$ compounds. The disordering defects in the cationic sublattice primarily determine the type of conductivity and significantly affect the electrophysical properties of these compounds. Defects of other types may also arise and act as donor or acceptor centers. This complicates the unambiguous understanding of the causes of ferromagnetism arising in Mn-alloyed $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^\gamma$ compounds and explains the fact that their properties are still calculated theoretically by computer methods or described only at the phenomenological level [8, 10–13].