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Magnetic interactions in $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ monolayers: *ab initio* study

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Abstract

Magnetic anisotropy in low dimensional semiconductors can lead to long-range ferromagnetic order. This feature is useful for various applications such as spintronic and sensoric. The exchange interaction integrals have been observed through magnetic, structural and electronic properties of $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ first-principles simulation in the VASP software package and Heisenberg model approach. The structural parameters for the bulk layered $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ were determined and in good agreement with the experiment. Calculations have established that the number of layers does not affect the magnetic properties and entire magnetic moment is localized on Cr atoms. Exchange interaction integrals between the first, second and third neighbors have been calculated for monolayers. The dependence of the exchange interaction integral on the Hubbard coefficient has been established. The exchange integral with the first neighbors J_1 was -2.34 ($Cr_2Ge_2Te_6$) and -1.61 ($Cr_2Si_2Te_6$) meV at the Hubbard coefficient of 3 eV. Thus, strong ferromagnetic order exists in plane of monolayers of $Cr_2Ge_2Te_6$, $Cr_2Si_2Te_6$ and magnetic anisotropy leads to long-range ferromagnetism.

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1. Introduction

Magnetic materials are widely used in devices of nanoelectronics. Scaling of devices leads to the need to use quasi-two-dimensional (2D) structures. However, Mermin – Wagner theorem asserts that at finite temperatures, the quantum spin Heisenberg model with isotropic and finite-range exchange interactions on two-dimensional lattices can be neither ferro- nor antiferromagnetic [1]. Despite this, some semiconductor single-layer MAX_3 (M = Mn, Ni, V, Cr, Fe, A = Si, Ge, X = Se, Te) materials were studied from the first principles. Calculations from the first principles showed that this class of materials includes wide-band, narrow-band semiconductors, as well as metals

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and semimetals. Most of the studied structures are magnetic materials. The ferromagnetic order was observed in $MSiSe_3$ (M = Mn, Ni), $MSiTe_3$ (M = V, Ni), $MnGeSe_3$, $MGeTe_3$ (M = Cr, Mn, Ni), $FeSnS_3$ and $MSnTe_3$ (M = V, Mn, Fe). Previously, the DFT study proposed several potential magnetic single-layer Van der Waals structures such as VX_2 (X = S, Se), $FeBr_3$, $CrSiTe_3$, $CrGeTe_3$ and $MnPX_3$ [2].

Ferromagnetism in few layers of $Cr_2Ge_2Te_6$ has been observed experimentally using a highly sensitive microscopic technique [3]. The authors showed that the $Cr_2Ge_2Te_6$ compound has a ferromagnetic order with spins ordered along the *c* direction, up to 65 K. The Cr local magnetic moment m (Cr^{3+}) was 2.8 μ_B at 5 K.

The explanation of the observed properties in 2D structures is the fact that the mathematical derivation of the Mermin – Wagner theorem does not take into account the magnetic anisotropy. All of the above allows asserting that the search of realistic low-dimensional ferromagnetic semiconductors is an actual task. In contrast to diluted magnetic semiconductors, the $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ exhibits intrinsic ferromagnetism, that provides a stable long-range order.

The bulk crystals of $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ are layered structures with weak interplanar Van der Waals bonds and strong bonds in the plane [4]. This makes it possible to synthesize quasi-two-dimensional geometric structures. The possibility of controlled synthesis of structural modifications is an important advantage [5]. Magnetism in 2D and 3D structural modifications of $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ can be described by the Heisenberg model [6] Theoretical predictions have shown that the direct exchange interaction leads to antiferromagnetic order while the superexchange interaction leads to ferromagnetic order and is realized through Cr-Te-Cr ions at angle close to 90%. The temperature of the phase transition from paramagnetic to ferromagnetic is 66.6 K for $Cr_2Ge_2Te_6$ [2]. However, there are no 2D materials that would exhibit ferromagnetism at room temperature up to now. The Curie temperature can be substantially increased by structural deformation or change in the composition (doping).

In this paper we present results of the study of intrinsic ferromagnetism in the two-dimensional structures of $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$. Using these compounds as example, the mechanisms of the long-range ferromagnetic order formation in similar systems can be studied with the aim of increase Curie temperature in 2D semiconductors.

1.1. Exchange interaction in classical Heisenberg model

Exchange interaction plays a key role in the establishment of a magnetic order. Determination of mechanism and type of microscopic exchange interactions is necessary for describing magnetic properties, such as magnetic order, exchange interaction constant, magnetic anisotropy energy, etc. Calculations of these properties make it possible to identify the features of the material for spintronic and sensoric applications.

The determination of the mechanisms through which the spin, charge, orbital and elastic subsystems of matter reach an ordered or disordered state at low temperatures is based on the modeling of the ground quantum states. Thus, the main goal of magnetic order modeling is to find the ground state of structure at absolute zero temperature, where the main external parameters are the ratio of exchange interactions in the system. There are various magnetic models: Heisenberg, Ising, Stoner, and others [7, 8] through which exchange interaction can be calculated.

The energy parameters of the system can be easily obtained using computational methods within the framework of first-principles calculations. Further, the values of the exchange integral are extracted using the model Hamiltonian and the total energy of the system without involving experimental methods. The simplest and most common model of magnetism in solid states is the Heisenberg [9] model in which magnetic interaction maps through localized spin moments. The resulting classical Hamiltonian

$$\hat{H} = \hat{H}_0 + \sum J_{ij} S_i S_j \,, \tag{1}$$

where J_{ij} is exchange integral between sites i and j and $S_{i(j)}$ is the spin operator on site i(j).

The energy differences approach has been used in order to obtain the Heisenberg exchange parameters J_{ij}. Its essence is to calculate the difference in total energy between different magnetic configurations. In this approach the total energies of the $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ in the ferromagnetic (FM) and three configurations of antiferromagnetic (AFM) states are calculated on the basis of an *ab initio* density functional theory method.

2. Results

2.1. Methodology

The basic approach for modeling the exchange interaction is the use of the local force theorem. Calculations of the electronic structure ground state were carried out using the methods of density functional theory. The results obtained by such calculations will include all types of exchange interaction mechanisms, as well as allowance for the dependence of the exchange integrals on the distance and angle between the ions.

We used the supercell method to apply the energy differences approach when studying the exchange interaction of a structure. To begin with, we accepted the assumption that the magnetic interaction is realized only between the Cr atoms by various mechanisms (direct exchange, superexchange).

Further, we decided to calculate the integral of the exchange interaction between the first, second and third nearest neighbors. In this way, four types of magnetic order configuration were used (FM, AFM1, AFM2 and AFM3). Fig. 1 demonstrate part of $Cr_2Ge_2Te_6$ crystal structure with Cr magnetic atoms. The arrows indicate the direction (sign) of the total spin. Accordingly, magnetic order configurations were created by established of local effective magnetic moment for each Cr atom. The chromium magnetic moment sign corresponds to the direction of magnetization, which made it possible to create structures with a ferromagnetic order and several antiferromagnetic configurations. Each supercell is formed by double multiples of the primitive lattice vectors *a, b.* Thus, supercells have been contained 2×2×1 $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ unit cells.

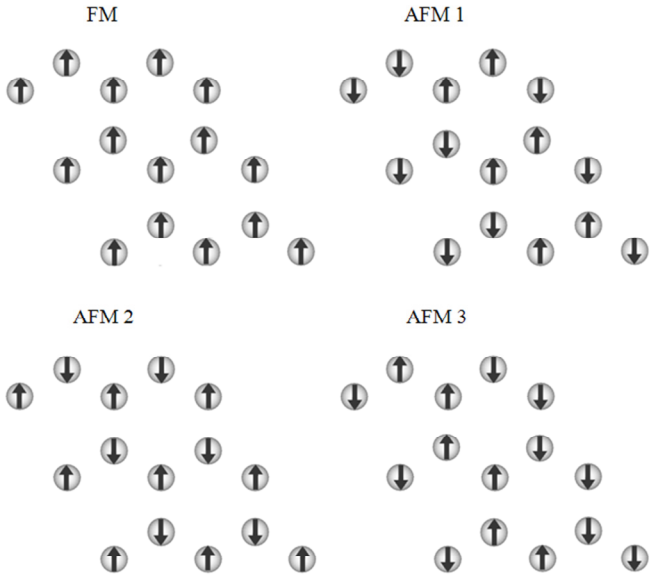

Fig. 1. Magnetic order configurations of Cr atoms in $Cr_2Ge_2Te_6$ monolayers

The corresponding total energies of the ferromagnetic and antiferromagnetic states of supercells under study in frame of Heisenberg model are

$$E_{AFM1} = E_0 + S^2\left(-j_1 - j_2 + j_3\right), \quad (2)$$
$$E_{AFM2} = E_0 + S^2\left(-3j_1 + 3j_2 - j_3\right), \quad (3)$$
$$E_{AFM3} = E_0 + S^2\left(j_1 - j_2 - j_3\right), \quad (4)$$
$$E_{FM} = E_0 + S^2\left(3j_1 + 3j_2 + j_3\right), \quad (5)$$

where S=3 for Cr atoms.

In that case the exchange integrals determinate via energy difference of different magnetic order configurations are:

$$J_1 = \left(-E_{AFM2} + E_{AFM3} + E_{FM} - E_{AFM1}\right)/288 \quad (6)$$
$$J_2 = \left(E_{AFM2} - E_{AFM3}\right)/288 + J_1/2 \quad (7)$$
$$J_3 = \left(E_{AFM3} - E_{AFM1}\right)/216 - J_1/3 \quad (8)$$

where J_1 is characterize exchange interaction between nearest neighbors, J_2 and J_3 between second and third neighbor atoms respectively.

2.2. Computational details

All of calculations have been carried out using VASP (Vienna *Ab-initio* Simulation Package) [10]. VASP computer program for the simulation of the atomic scale materials, e.g. electronic structure calculations and quantum-mechanical molecular dynamics, using projector-augmented-wave method and a plane wave basis set. The basic methodology is density functional theory (DFT).

The projector-augmented wave (PAW) potentials and Perdew–Burke–Ernzerhof (PBE) functional [11] have been used. A vacuum layer of 15 Å along *z* direction was constructed to eliminate the interaction with spurious replica images. The atomic structures were relaxed until the forces on all unconstrained atoms were smaller than 0.01 eV/Å. Cutoff energy of 440 eV and a 4×4×1 *k*-points grids determined by a fine grid of gamma-centered method in the Brillouin zone have been used. The valence electron configurations for Cr, Ge, Si and Te were $[Ar]3d^5 4s^1$, $[Ar]3d^{10}4s^2 4p^2$, $[Ne]3s^2 3p^2$ and $[Kr]4d^{10}5s^2 5p^4$, respectively.

Structure and electronic properties of $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ bulk systems were obtained by quantum mechanical simulation. We used the DFT-D3 functional which implemented in VASP because our previous calculation of layered $Cr_2Ge_2Te_6$ established better results with functional where the van der Waals forces taking into account.

2.3. Structure and electronic properties

First of all calculations of energy minimization were performed. The structural properties of the unit cell have been determined (Table 1). Our results are in good agreement with the literary sources [12].

Table 1. Parameters of $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$

		a, Å	c, Å	V, nm^3	d, Å	m_{Cr}, μ_B
$Cr_2Ge_2Te_6$	Calc.	6.89	19.96	0.82	3.26	3.14
	Ref. [12]	6.82	20.56	0.83	-	2.80
$Cr_2Si_2Te_6$	Calc.	6.81	20.01	0.80	3.26	3.14
	Ref. [12]	6.90	20.28	0.83	3.77	3.77

On the second stage the simulations of electronic ground states and band structures were performed. In accordance with the calculations, $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ are semiconductors with 0.7 eV and 0.6 eV band gap respectively. These results were obtained for the value of the Hubbard coefficient of 3 eV for *d* chromium electrons. Also, the bandgap was calculated without applying Hubbard correction, but the value of the bandgap was too low. This is due to the well-known problem of the DFT method, which underestimates the exchange-correlation energy.

2.4. Exchange interaction calculation

After obtained adequate fundamental characteristics and parameters of the $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$, we proceeded to the next stage. The influence of the layers number on the material magnetic properties was studied.

The distance between chromium atoms in two adjacent layers is approximately equal to 6.62 Å. The exchange interaction via the direct exchange mechanism does not occur at such distance between atoms, but a superexchange via the chalcogen orbitals is possible. Moreover distance between chromium atoms in neighbor layers is approximately the same as between the second nearest neighbors in the plane of the layer. Thus, the study of the magnetic properties dependence on the number of layers is necessary for determining the dimensionality of the magnetic structure in a bulk semiconductor.

Calculations to determine the dependence of the magnetic and electronic properties on the number of layers (for structures from 1 layer to 4 layers) were carried out. It was found that the effective magnetic moment has not changed. These results confirm the absence of exchange interaction between the layers of the structures. Further simulations were carried out only for structures with one layer.

Total energy of the systems has been calculated. Since, it is the sum of E_0 and the energy contributions of all types the exchange interactions in the supercell for each configuration, in accordance with the Heisenberg model, the values of exchange integrals between chromium atoms (the interaction between the first, second and third neighbors) for different values of the Hubbard coefficient have been established (Table 2).

Table 2. Exchange integrals for different value of Hubbard coefficient

	U, eV	J_1	J_2	J_3
$Cr_2Ge_2Te_6$	0	−1.84	0.07	0.20
	3	−2.34	$-2.89 \cdot 10^{-6}$	0.14
	5	-1.73	0.23	-0.26
$Cr_2Si_2Te_6$	0	-1.30	0.04	0.03
	3	-1.61	0.01	-0.20
	5	-1.62	0.01	-0.21

4. Conclusion

Exchange interaction integrals between the first, second and third neighbors have been calculated for monolayers of $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$ by quantum mechanical simulation and Heisenberg model approach. The dependence of the exchange interaction integral on the Hubbard coefficient has been established. The exchange interaction between the nearest neighbors is dominant and there is -2.34 meV and -1.61 meV for $Cr_2Ge_2Te_6$ and $Cr_2Si_2Te_6$. Thus, a strong ferromagnetic order exists in the monolayers.

The effective magnetic moment of Cr atoms is 3.14 μ_B. The ferromagnetic order prevails in the structuresunder study. Strong hybridization of the p states of the chalcogen and *d* states of the transition metal has been observed, which indicates a magnetic interaction via the superexchange mechanism.

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