Magnetic anisotropy energy in disordered Ge\(_{1-x}\)Mn\(_x\)Te

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Abstract

We theoretically analyze the influence of chemical disorder on magnetic anisotropy in Ge\(_{1-x}\)Mn\(_x\)Te semiconductor layers known to exhibit carrier-induced ferromagnetism and ferroelectric distortion of rhombohedral crystal lattice. Using DFT method we determine the local changes in the crystal structure due to Mn ions substitution for Ge and due to the presence in Ge\(_{1-x}\)Mn\(_x\)Te of very high concentration of cation vacancies. We calculate the effect of this structural and chemical disorder on single ion magnetic anisotropy mechanism and show that its contribution is order of magnitude smaller as compared to magnetic anisotropy mechanism originating from the spin polarization induced by Mn ions into neighboring Te and Ge ions. We also discuss magnetic anisotropy effects due to pairs of Mn ions differently allocated in the lattice. The spatial averaging over chemical disorder strongly reduces the strength of this magnetic anisotropy mechanism and restores the global rhombohedral symmetry of magnetic system.

Keywords: ferromagnetic semiconductors, magnetic anisotropy

1. Introduction

GeTe belongs to the IV-VI family of narrow gap semiconductors. At temperatures below \(T_0 = 670\) K its crystal structure has rhombohedral symmetry \(C_{3v}\) which can be characterized by three parameters: the lattice constant \(a_0 \approx 6\) Å, the rhombohedral angle \(\alpha \approx 88.3^\circ\) and the relative displacement of Te and Ge sublattices along [111] crystallographic direction. This displacement which is equal to \(a_0\sqrt{3}\tau\), where \(\tau \approx 0.03\), causes GeTe to be ferroelectric.

Manganese ions Mn\(^{2+}\) introduce in Ge\(_{1-x}\)Mn\(_x\)Te local magnetic moments and this IV-VI diluted magnetic (semimagnetic) semiconductor (DMS) exhibits ferromagnetic transition with the Curie temperature \(T_C(x)\) up to 190 K \(^1\)\(^2\). Due to simultaneous ferroelectric and ferromagnetic ordering Ge\(_{1-x}\)Mn\(_x\)Te belongs to the class of multiferroic materials, which may become very interesting for possible future applications.

Our previous theoretical analysis of the physical mechanisms of magnetic anisotropy in Ge\(_{1-x}\)Mn\(_x\)Te \(^3\), hereafter referred as paper I, was inspired by recent, unexpected results of magnetization and ferromagnetic resonance experiments which clearly showed that the easy axis of magnetization in thin layers of Ge\(_{1-x}\)Mn\(_x\)Te, for the manganese content of about 10 at. %, is perpendicular to the layer \(^4\)\(^5\)\(^6\)\(^7\)\(^8\). In ferromagnetic thin layers the shape anisotropy usually dominates with easy magnetization axis located in the layer plane. This is indeed observed in Ge\(_{1-x}\)Mn\(_x\)Te layers for higher content of manganese, above 20 at. %. For these layers the X-ray diffraction analysis (XRD) shows that the increase of Mn content results in transition from rhombohedral to cubic (rock-salt) crystal structure.

In the paper I we performed extensive \textit{ab initio} density functional theory (DFT) calculations of magnetic anisotropy energy (MAE) in Ge\(_{1-x}\)Mn\(_x\)Te. The aim was to elucidate microscopic mechanisms responsible for the magnetic anisotropy. We concluded that the main contribution to MAE is given by the spin polarization induced in Te and Ge neighbors of Mn, and not by the Mn ions themselves. The Mn spin polarizes its neighborhood, the spins of Ge ions are approx-
imately parallel and the spins of Te ions approximately antiparallel to the direction of the Mn spin. The degree and the spatial range of spin polarization is relatively small in insulating crystal but it strongly grows with the increasing concentration of holes. Because of spin-orbit (S-O) interaction, the directions of Te and Ge spins forced by the direction of Mn spin do not, in general, correspond to minimum of the total energy of the system. This forcing of Ge and Te polarizations by the Mn spin is the principal reason why variations of the directions of Mn spins result in changes of the total energy.

Among the local configurations of Mn.

Apart from the identification of the main physical mechanism responsible for magnetic anisotropy we also showed that MAE is determined by the hole concentration, macroscopic crystal structure, and the local configuration of Mn.

The paper I was devoted almost exclusively to the situations where there was only one Mn ion in $2 \times 2 \times 2$ rhombohedral supercell containing 64 atoms. In all cases, the angular dependence of MAE on the Mn spin direction characterized by the angle $\theta$ was well approximated by the formula

$$E_A(\theta) = a_2c (\cos 2\theta - 1).$$ (1)

Here $\theta$ is the angle measured in the (-110) plane from the [111] direction. Thus, for $\theta = 0$ and $\theta = 90^\circ$, the Mn spin is parallel to [111] and to the [11-2] crystallographic directions, respectively. The same definition of $\theta$ is used in the present paper.

One should keep in mind that a supercell containing one Mn ion simulates perfect, translationally invariant crystal with rhombohedral symmetry. In actual random substitutional alloys, this symmetry is locally destroyed.

Although macroscopic structural, mechanical, electrical or magnetic properties can have the global rhombohedral symmetry as confirmed by XRD, at the unit cell scale this symmetry is destroyed. This is due to the randomness of the occupancies of lattice sites in the chemically mixed cation sublattice (which is sometimes called chemical disorder), and to the presence of native defects, in our case the cation vacancies. The random positions of manganese ions together with different ionic radii of Ge and Mn lead to local deformation of the lattice. The local deformations are also caused by the germanium vacancies. Each cation vacancy, like in other IV-VI semiconductors, delivers two holes, thus in real sample with the hole concentration of the order $10^{21}$ cm$^{-3}$ we expect $5 \times 10^{20}$ cm$^{-3}$ of vacancies.

For comparison, the Mn concentration $x = 0.01$ corresponds to about $1.9 \times 10^{20}$ of Mn ions per cubic centimeter.

The influence of the chemical disorder on the magnetic anisotropy in Ge$_{1-x}$Mn$_x$Te is the topic of the present paper. The paper is organized as follows.

In Section 2 we analyze the single ion magnetic anisotropy (SIMA) in Ge$_{1-x}$Mn$_x$Te. In the paper I we explicitly showed that SIMA in the conducting Ge$_{1-x}$Mn$_x$Te, is of minor importance compared to the anisotropy caused by spin polarized free carriers. However, the calculations were performed for systems with manganese ion’s neighbourhood of perfect rhombohedral symmetry. On the other hand it is well known from numerous electron paramagnetic resonance experiments (EPR) that the ground state splittings and consequently magnetic anisotropy properties of Mn$^{2+}$ ion strongly depend on the symmetry of its surrounding. Previous calculations performed for Pb$_{1-x}$Mn$_x$Te and Sn$_{1-x}$Pb$_x$Mn$_x$Te show that the ground state splitting of Mn$^{2+}$ ion in disordered environment may be of the order of 1 Kelvin. Because the difference in ionic radii of Ge and Mn is much smaller than that of Pb and Mn, the local lattice distortions (which strongly influence the magnetic properties of Mn) are also smaller. Thus, we do not expect that SIMA driven by the microscopic lattice distortions are dominant in Ge$_{1-x}$Mn$_x$Te. On the other hand, the band structure of GeTe is significantly different from those of other IV-VI semiconductors due to ferroelectric properties of the crystal. That is why direct calculations of SIMA in Ge$_{1-x}$Mn$_x$Te are necessary.

In Section 2 we briefly describe mechanism responsible for SIMA and the method of calculations. The obtained results confirm that even in the presence of disorder, in conducting Ge$_{1-x}$Mn$_x$Te SIMA is of secondary importance.

Section 3 presents results of ab initio calculations of MAE of pairs of Mn ions in Ge$_{1-x}$Mn$_x$Te. All nonequivalent positions of two Mn in the $2 \times 2 \times 2$ supercell are taken into account. We also show a few results for three Mn ions in the supercell. In the calculations the spins of Mn ions are always parallel. This is justified, because according to the results of Section II the energies connected with local magnetic anisotropy easy axes are small, and in the first approximation the possible noncollinearity of Mn spins can be neglected. We explicitly show that the direction of easy axis of magnetiza-
tion strongly depends on the relative position of Mn ions, and MAE is not described by Eq. (1). For chosen two configurations of two manganese ions we analyze contributions of kinetic, electrostatic and exchange-correlation energies to MAE. It is shown that the Mn ions introduced to GeTe causes significant perturbation in spatial distribution of electron charge and, consequently, significant change of electrostatic potential which, via the S-O interaction, influences MAE.

In Section 2 we summarize the main conclusions of the paper.

2. Single ion magnetic anisotropy

2.1. Theory

According to the Hund’s rule, the ground state of Mn$^{2+}$ ion is $^6S$, with the orbital momentum $L = 0$ and spin $S = 5/2$. As the orbital singlet, it does not interact with the crystal environment, and its ground state without external magnetic field is six-fold degenerate. This model of Mn$^{2+}$ ion explains a number of phenomena, e.g., the results of magnetization measurements in diluted magnetic semiconductors. However, if we consider problems in which very small excitation energies are of importance, this model is no longer valid. An example of such a problem is the splitting of the ground state of Mn ion in a crystal field measured in EPR experiments. In the theoretical analysis for zero magnetic field, the Mn$^{2+}$ ion is described by a $6 \times 6$ matrix, $H_{\text{MM}}$, which plays a role of effective spin Hamiltonian [9]. The subscripts $-5/2 \leq M, M' \leq 5/2$ denote the projections of Mn spin on the quantization axis. For example, for a perfect cubic symmetry of Mn surrounding

$$H = \frac{a}{6}(S_x^2 + S_y^2 + S_z^2).$$

(2)

The lowest excitation energies of the ion (i.e., the eigenvalues of $H_{\text{MM}}$) strongly depend on the symmetry of its neighborhood, and are in the range $10^{-4} - 10^{-1}$ K. If the Hamiltonian $H_{\text{MM}}$ is not diagonal, it leads not only to the ground state splitting but also to the magnetic anisotropy of the ion [10].

Density functional theory, which is one of the basic theoretical methods used to study condensed matter properties, is not suitable for this problem because DFT calculations determine the electron density in the ground state, and provide no direct information about the excited states of the system, particularly in situations where the energies of the excited states are very small. In this case one should use methods based on perturbation theory.

There are two mechanisms known in the literature which lead to the ground state splitting: interaction with excited states of $3d^5$ configuration, and hybridization between $3d$ and orbitals of the surrounding ions. In the first mechanism [11] the internal manganese S-O interaction couples $^6S$ with the excited $^4P$ states, due to which the ground state of Mn is no longer a pure $S$ state with total angular momentum $L = 0$. Consequently, the interaction with the crystal environment becomes possible. As a result, ground state splitting and nondiagonal effective Hamiltonian $H_{\text{MM}}$ are finite.

In DMS, the second mechanism, i.e., the hybridization between $3d$(Mn) orbitals and the orbitals of the neighboring ions, plays a more important role. In this case, a system consisting of $3d$(Mn) electrons and valence band carriers is considered. In the ground state of this system, which is six-fold degenerate due to manganese spin $S = 5/2$, there are five electrons on the $3d$ shell and the host bands are filled up to the Fermi energy. In the excited state, one electron is transferred from the host band to the $3d$ shell (or from the $3d$ shell to the band) resulting in one additional hole (or electron) in the host bands, respectively. Such virtual transfers of electron were used earlier in theories of $sp - d$ exchange interaction in semiconductors [12, 13, 14]. As a consequence of this $3d$ shell - band states hybridization, the ground state of the system is no longer six fold degenerate, and the resulting low energy excitation spectrum and the anisotropic properties of the ion take place, in accord with experimental observations. This mechanism was described in Ref. [15] and successfully applied to EPR results for PbTe:Mn layers grown on BaF$_2$ and KCl substrates [15], to the single ion anisotropy in Sn$_{1-x-y}$Pb$_x$Mn$_y$Te mixed crystals [16] and to the analysis of magnetic specific heat in Pb$_{1-x}$Mn$_x$Te [17]. This method is also used in the present paper for calculations of effective spin Hamiltonian. Here, we do not repeat detailed description of the method and formulas contained in Ref. [15] but sketch only the main idea of calculations.

We consider GeTe crystal at the temperature $T = 0$ with one germanium atom replaced by manganese atom. It is assumed that this replacement does not change appreciably neither the band structure nor the spatial electron distribution. The only difference comparing to the pure GeTe is the pres-
ence of additional 3d shell on one of the cation places with five electrons on it. If we neglect hybridization between 3d orbitals and the orbitals of the neighbouring atoms, in the ground state of such a system there are five electrons on 3d shell, and free electrons fill the band states up to the Fermi energy. This ground state is sixfold degenerate due to the total spin $S = 5/2$ of the 3d shell. In the excited states of the system one electron is transferred from 3d shell to an unoccupied band state, or one electron from the band is transferred to the 3d shell. Such transfers require excitation energy denoted by $\epsilon_0$, which will be the only fitting parameter for comparison of MAE given by the effective Hamiltonian with the DFT results.

In the excited states there are four or six electrons on the 3d shell, and according to the Hund’s rule their total angular momentum $L = 2$ and the total spin $S = 2$. Due to nonzero total angular momentum, in the excited states the internal Mn spin-orbit coupling $\sim \mathbf{L} \cdot \mathbf{S}$ should be taken into account. The inclusion of the internal S-O coupling is crucial for the splitting of the ground state and magnetic anisotropy properties of the ion, otherwise the ground state is not split, independently whether the band spin-orbit coupling is present or not.

In the Hamiltonian of the system the ground and excited states are connected by hybridization between 3d(Mn) orbitals and orbitals of neighbouring Te ions. The effective spin Hamiltonian for the ground state is calculated within the framework of the second order perturbation theory for degenerate spectra with respect to hybridization.

The main differences between the present calculations and those presented in Ref. [15] for Pb$_{1-x}$Mn$_x$Te are related to the tight binding model of the band structure and to the hybridization parameters between 3d states of Mn ion and the orbitals of neighboring Te ions used in calculations. In Ref. [15] we considered Mn ion in PbTe using the tight binding model that takes into account nearest cation - anion neighbors and nearest and next nearest cation - cation and anion - anion neighbors. The model was parametrized according to Ref. [15]. The integrals describing hybridization Mn 3d - Te orbitals were taken from Ref. [19]. Here, the tight binding model takes into account integrals up to the third neighbour, and their values were taken from DFT calculations for GeTe as the matrix elements of Kohn – Sham Hamiltonian between pseudoatomic orbitals of Ge and Te. Using \textit{ab initio} OpenMX package [20] we performed calculations for both fully relativistic and scalar relativistic pseudopotentials. Thus, we can compare effective spin Hamiltonian obtained for situations with and without the band spin-orbit interaction.

From DFT calculations performed for $2 \times 2 \times 2$ supercell containing 64 atoms with one Ge replaced by Mn atom we obtain hybridization parameters between 3d(Mn) states and s and p orbitals of the nearest Te ions.

In calculations, like in the paper I, the crystal structure parameters were assumed $a_0 = 5.98$ Å, $\alpha = 88^\circ$ and $\tau = 0.03$.

Having the effective spin Hamiltonian we obtain $E_A(\theta, \varphi)$, i.e., the dependence of single ion anisotropy energy on the direction of Mn spin defined by the angles $\theta$ and $\varphi$. To this aim we introduce a matrix $D(\theta, \varphi)$

$$D(\theta, \varphi) = D_z(\varphi)D_y(\theta),$$

where $D_z$ and $D_y$ are rotation matrices for spin $S = 5/2$ around the $z$ and the $y$ axis, respectively.

Now, we denote by $|a>$ a state of the Mn spin for which the projection on the quantization axis $z$ is $S_z = 5/2$, i.e., in this state the Mn spin points in the $z$ direction. Then $|a' > = D(\theta, \varphi)|a>$ denotes the state in which the spin points in the $z'$ direction defined by the angles $\theta$ and $\varphi$. We define

$$E_A(\theta, \varphi) = < a|H|a'>$$

as the angular dependence of the single ion anisotropy energy on the spin’s direction. For example, for the Mn ion in perfect cubic environment the effective spin Hamiltonian, Eq. (2), leads to

$$E_A(\theta, \varphi) = \frac{5}{4}a \left[ (\cos \theta)^4 + (\sin \theta)^4 \right]$$

which is identical to that obtained by Yosida and Tachiki using a different approach [15].

2.2. Determination of transfer energy $\epsilon_0$

To determine the energy $\epsilon_0$, i.e. the energy necessary to transfer an electron between the 3d shell and the top of the valence band, we performed scalar relativistic calculations for GeTe. Next, using the tight binding parameters from the obtained Kohn - Sham Hamiltonian we calculated the effective spin Hamiltonian and the angular dependence of MAE, $E_A(\theta, \varphi)$, for for hole concentrations $p = 0$ and $p = 10^{21}$ cm$^{-3}$ for different values of $\epsilon_0$. The
results were compared to MAE obtained from DFT calculations for 64-atom supercell containing one Mn ion for vanishing S-O coupling for Ge and Te atoms. Such a comparison makes sense only when the band spin-orbit interaction is neglected because, as we know from paper I, only in such a case MAE is due to Mn ion and does not depend on the direction of spin polarization of Ge and Te ions. From DFT calculations we obtain \( a_{2c} = -0.053 \) K and \( a_{2c} = 0.101 \) K for insulating and conducting cases, respectively. To obtain these values by the effective Hamiltonian method we must assume \( \epsilon_0=2.92 \) eV for the insulating, and \( \epsilon_0=2.58 \) eV for the conducting cases, respectively. To obtain these values by the effective Hamiltonian method we must assume \( \epsilon_0=2.92 \) eV for the insulating, and \( \epsilon_0=2.58 \) eV for the conducting cases, respectively. To obtain these values by the effective Hamiltonian method we must assume \( \epsilon_0=2.92 \) eV for the insulating, and \( \epsilon_0=2.58 \) eV for the conducting cases, respectively. To obtain these values by the effective Hamiltonian method we must assume \( \epsilon_0=2.92 \) eV for the insulating, and \( \epsilon_0=2.58 \) eV for the conducting cases, respectively.

2.3. Dependence of magnetization easy axis direction on disorder

To simulate microscopic disorder in Ge\(_{1-x}\)Mn\(_x\)Te we start from the perfect GeTe lattice characterized by \( a_0 = 5.98 \) Å, \( \alpha = 88^\circ \), \( \tau = 0.03 \) with one Ge replaced by Mn. The directions and lengths of six bonds connecting Mn with its nearest Te neighbours are specified by \( (\theta_i^0, \varphi_i^0, d_i^0) \), \( i = 1, \ldots, 6 \). We assume that the microscopic disorder leads to small changes in \( (\theta_i, \varphi_i, d_i) \),

\[
\begin{align*}
\theta_i &= \theta_i^0 + r_i^\theta \delta \theta \\
\varphi_i &= \varphi_i^0 + r_i^\varphi \delta \varphi \\
d_i &= d_i^0 + r_i^d \delta d
\end{align*}
\]

where \( r_i^\theta, r_i^\varphi, r_i^d \) are homogeneously distributed random numbers from the interval \((-0.5, 0.5)\). In calculations it is assumed that Mn-Te hybridization parameters change with the bond’s length as \( d^{-7/2} \).

For a given configuration of Mn surrounding we calculate effective spin Hamiltonian, and using Eq. (4) we find \( E_A(\theta, \varphi) \). Having this functional dependence we obtain direction of the easy axis of magnetization and \( \Delta E_A \), the difference between maximal and minimal values of \( E_A(\theta, \varphi) \). In Fig. 2 we present normalized to unity histograms (probability densities) of directions of the easy axis of magnetization with respect to [111] crystallographic direction, Fig. 2a, and of \( \Delta E_A \), Fig. 2b. These histograms result from \( 4 \times 10^5 \) random configurations.

To obtain typical deflections of directions and lengths of Mn-Te bonds from those for the ideal lattice we performed, using OpenMX package [21], geometry optimization for the \( 2 \times 2 \times 2 \) 64-atom supercell. We repeated the optimization for three different cases: 1) with one Mn ion, 2) with two Mn ions placed at nearest neighbours positions and 3) with two Mn ions placed at the two diagonal vertices of the elementary cell and with one Ge vacancy on the face of the elementary cell.

Comparing the directions and lengths of Mn-Te

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Figure 1: Angular dependence of MAE for \( p = 0 \) (a) and \( p = 10^{22} \) cm\(^{-3} \) (b). Continuous lines correspond to DFT calculations. Dotted and broken lines are single ion anisotropies for two values of transfer energy \( \epsilon_0 \).

Figure 2: Probability density for the angle between easy axis and [111] direction (a) and for anisotropy energies (b) for different levels of disorder quantified by the spreads of the angles \( \delta \theta, \delta \varphi \) and bond length \( \delta d \).
bonds between cases 2) and 3) with those in 1) we find
that the the deflections are very small. The highest
deflections are of the order of $1^\circ$ and changes of
bond lengths are of the order of 0.01 Å. We see
that even for very small deflections of di-
rections and lengths of bonds from the ideal val-
cues, the influence on the distribution of the di-
rections of the easy axes is quite substantial. However, the
probability distribution for $\Delta E_A$ for such small $\delta \theta$,
$\delta \varphi$ and $\delta d$ remains well centered around the mean
value, which is of the order of 0.5 K with the vari-
ance less than 0.1 K.

We have also calculated the averaged over dis-
order the magnetic field dependent magnetizations
of Mn ion with magnetic field along [111] and per-
pendicular to [111] direction in different tempera-
tures. The differences are noticeable, however in
very small magnetic fields and extremely low tem-
peratures only. The differences which might be
compared to those experimentally observed are only
for unphysically high level of disorder, see Fig. 2.

We conclude therefore that the single ion
anisotropy does not play a decisive role in magnetic
anisotropy energy in Ge$_2$Mn$_4$Te. The present
calculations further confirm the conclusion of the
paper I that MAE in Ge$_2$Mn$_4$Te is mainly due
to polarization of valence band carriers.

3. Supercells containing more than one Mn ion

In the present Section we analyze magnetic
anisotropy for all possible configurations of two Mn
ions in the $2 \times 2 \times 2$ supercell, for the case of
three Mn ions we show only results for a few ran-
domly chosen configurations. Technical details of
calculations were presented in the paper I. We used
OpenMX package [21]. In all calculations of MAE
the number of integration points in the Brillouin
zone were 512 and 2744 for insulating and conduct-
ing cases, respectively. As was shown in the paper
I such numbers give convergent results. In the con-
ducting case, the calculations were performed for
hole concentration $p = 10^{21}$ cm$^{-3}$, which is typical
for samples studied experimentally. For geometry
optimization, the number of integration points in
the Brillouin zone reduced to 64 give convergent
results. The force criterion for geometry optimization
was equal to $5 \times 10^{-3}$ Hartree/Bohr.

In order to describe possible configurations, first,
we introduce notation describing positions of Mn
ions in the supercell.

Let us consider three vectors $c_1$, $c_2$ and $c_3$, parallel
to the [100], [010] and [001] crystallographic direc-
tions, respectively. The lengths of the vectors are
the same, $a_0/2$. The symbol $\{(ijk) \}$ describes the po-
sition of an atom in the supercell $r = ic_1 + jc_2 + kc_3$
where $i$, $j$, $k$ are integer numbers.

The first Mn atom is always placed at $\{000\}$. The
$2 \times 2 \times 2$ supercell contain 32 different cation po-
sitions, thus the second Mn atom may be placed
at 31 remaining positions. However, some of the
resulting 31 configurations are equivalent because
of the periodic boundary conditions; for example
configurations $\{110\}$ and $\{330\}$ are equivalent.
Actually, there are 21 nonequivalent configurations.
We stress that due to nonzero Mn spin this num-
ber is larger then the number resulting from purely
genomical symmetry considerations for a rhombo-
dedral lattice. Consider, for example, three nearest
neighbor pair configurations for which the second
Mn atom is placed at $\{110\}$, $\{011\}$ and $\{101\}$, re-
spectively. For vanishing spin, those three configu-
rances are equivalent from the purely geometrical
point of view, being related by the rotation along
[111] axis by the angle $\pm 120^\circ$. However, for finite
$S$, they are nonequivalent if we consider magnetic
properties of the crystal, what is explicitly shown
in the following in Fig. 3.

In the calculations, the Mn spin vectors are
placed in the (-110) plane. Due to reflection sym-
metry with respect to this plane, the configurations
$\{011\}$ and $\{101\}$ give identical results for the angular
dependence of $E(\theta)$, thus it is enough to perform
calculations for one of them, but for arbitrary direc-
tion of manganese spins it is necessary to calculate
MAE for both.

In Figs. 3 and 4 we present the results for the cho-
sen example configurations for insulating and con-
ducting cases, respectively. Also we show arithme-
tical averages over all nonequivalent configurations.
Let us notice, however, that the results presented
in the paper I indicate that even in the insulating
case the pair of Mn ions in the $2 \times 2 \times 2$ supercell
cannot be treated as isolated. Thus, strictly speak-
ing, these arithmetical averages cannot be treated
as the averages over the quenched disorder. Never-
theless, they give some information about behavior
of MAE in macroscopic crystal where the magnetic
ions are placed randomly.

In Figs. 3 and 4 we compare also MAE for nonre-
Figure 3: Angular dependence of the energy of magnetic anisotropy for $2 \times 2 \times 2$ supercell containing two Mn ions for insulating case. Continuous lines - nonrelaxed lattice, broken lines - relaxed lattice.

Figure 4: Angular dependence of the energy of magnetic anisotropy for $2 \times 2 \times 2$ supercell containing two Mn ions for hole concentration $p = 10^{21}$ cm$^{-3}$. Continuous lines - nonrelaxed lattice, broken lines - relaxed lattice characterized by lattice parameters $a_0 = 5.98$ Å, $\alpha = 88^\circ$, $\tau = 0.03$. The dotted lines are for nonrelaxed lattice for other lattice parameters $a_0 = 5.98$ Å, $\alpha = 88.3^\circ$, $\tau = 0.025$.

Figure 5: Angular dependence of MAE for several configurations of three Mn ions in $2 \times 2 \times 2$ supercell for hole concentration $p = 10^{21}$ cm$^{-3}$.

Table 1: Values of coefficients $a_{2c}$ and $a_{2s}$, describing MAE for $2 \times 2 \times 2$ supercell containing two Mn ions for nonrelaxed and relaxed lattices and hole concentration $p = 0$.

| configuration | $f$ | $a_{2c}$ | $a_{2s}$ | $a_{2c}$ | $a_{2s}$ |
|---------------|-----|----------|----------|----------|----------|
| \{110\}      | 1   | 0.49     | 0.69     | 0.62     | 0.92     |
| \{011\}      | 2   | 0.48     | -0.34    | 0.20     | -0.47    |
| \{002\}      | 1   | -0.12    | -1.13    | -0.84    | -1.56    |
| \{112\}      | 1   | 0.24     | -0.01    | -0.11    | -0.10    |
| \{013\}      | 2   | -0.33    | -0.42    | -0.72    | -0.36    |
| \{020\}      | 2   | 0.31     | 0.57     | 0.42     | 0.80     |
| \{130\}      | 2   | 0.04     | 0.96     | 0.05     | 0.71     |
| \{121\}      | 2   | 0.22     | 0.01     | -0.05    | 0.06     |
| \{022\}      | 2   | 0.32     | -0.16    | -0.10    | -0.27    |
| \{132\}      | 2   | 0.36     | -0.22    | -0.05    | -0.21    |
| \{123\}      | 2   | 0.38     | 0.11     | 0.15     | 0.11     |
| \{220\}      | 1   | 0.26     | 0.29     | 0.15     | 0.50     |
| \{222\}      | 1   | 0.48     | -0.01    | 0.20     | 0.00     |
| average      |     | 0.23     | 0.04     | -0.01    | 0.02     |
Table 2: Values of coefficients $a_{2c}$ and $a_{2s}$ describing MAE for $2 \times 2 \times 2$ supercell containing two Mn ions for nonrelaxed and relaxed lattices and hole concentration $p = 10^{21}$ cm$^{-3}$.

| configuration | nonrelaxed | relaxed |
|---------------|------------|---------|
| $\{110\}$    | 1 -3.91    | 1.88    |
| $\{011\}$    | 2 -6.93    | -3.02   |
| $\{002\}$    | 1 -3.81    | -1.55   |
| $\{112\}$    | 1 -7.31    | -6.39   |
| $\{013\}$    | 2 -3.02    | -4.22   |
| $\{020\}$    | 2 -3.13    | 1.27    |
| $\{130\}$    | 2 -0.29    | -0.42   |
| $\{121\}$    | 2 -7.16    | 0.98    |
| $\{022\}$    | 2 -7.47    | -4.08   |
| $\{132\}$    | 2 -5.67    | -2.42   |
| $\{220\}$    | 1 -4.87    | 8.11    |
| $\{222\}$    | 1 -3.36    | -1.48   |
| average       | -4.93      | -3.03   |

laxed (continuous lines) and relaxed (broken lines) supercells. As in the case of single Mn ion in the supercell, the relaxation of the lattice leads to significant changes in MAE. For comparison, by the dotted lines we show MAE for nonrelaxed lattice with slightly different lattice parameters: $a_0 = 5.98$ Å, $\alpha = 88.3^\circ$, $\tau = 0.025$. Like in paper I, for single Mn ion in the supercell, such changes result in changes of MAE.

The results for all configurations are summarized in Tables 1 and 2. The first column of each table gives configurations, in the second column there are corresponding weight factors $f$. The factor $f = 1$ is for a configuration which remains the same when reflected in the (-110) plane, and $f = 2$ if there exist two nonequivalent configurations related by reflection in the (-110) plane. The coefficients $a_{2c}$ and $a_{2s}$ describe curves used to fitting the calculated points:

$$E_A(\theta) = a_{2c} \cos(2\theta) + a_{2s} \sin(2\theta)$$  \hspace{1cm} (7)

It turns out that inclusion of terms proportional to $\cos(4\theta)$ and $\sin(4\theta)$ to the fitting formula does not improve quality of the fit, because the coefficients describing these terms are more than order of magnitude smaller than $a_{2c}$ and $a_{2s}$.

From the presented results we draw two main conclusions. First, for a given pair configuration the direction of the easy axis of magnetization, in general, is very different from [111] crystallographic direction or the direction perpendicular to [111]. However, after the assumed averaging procedure the average of the $a_{2s}$ coefficient is very small, it means that the average MAE possesses rhombohedral symmetry of the macroscopic crystal. Similar behavior was previously observed in calculations of single ion magnetic anisotropy in Sn$_{1-x}$Mn$_x$Te [16] in which disorder effects were taken into account.

Second, in most of cases the values of $\sqrt{a_{2c}^2 + a_{2s}^2}$ for pair configurations are significantly larger than the average of coefficient $a_{2c}$. This fact is also connected with varying directions of the easy axes of magnetization for different pair configurations.

In Fig. 6 we show results for several randomly chosen configurations of three Mn ions in $2 \times 2 \times 2$ supercell. We are not able to perform calculations for all possible configurations because in this case the number of configurations is too large, however one may notice that the qualitative results are similar to the case of two Mn ions in the supercell.

Angular dependencies for the kinetic, electrostatic and exchange-correlation components of MAE are shown in Fig. 6. Their nonconstant angular dependencies prove that the spatial charge distribution varies with the Mn spin’s direction.

Two features may be noticed. First, the changes of kinetic, electrostatic and exchange-correlation energies with the direction of manganese spins are much larger than the changes of their sum, the magnetic anisotropy energy. However this is usual in DFT calculations - the dependence of components
of the total energy on external parameters is much stronger than the dependence of the total energy itself. The other feature is more interesting. Let us notice that the maxima and minima of components are placed in different positions than the maxima and minima of MAE. This effect results from the hypolarization induced by Mn ions into neighboring smaller than the contribution originating from spin the single ion contribution is order of magnitude anisotropy energy. Our calculation revealed that calculated the single ion contribution to magnetic in Ge method we determined the local crystal structure perpendicular magnetic anisotropy. Using DFT distortion of rhombohedral crystal lattice and exhibit ers known to undergo ferroelectric structural dis- in ferromagnetic Ge presence of chemical disorder on magnetic anisotropy 4. Conclusions In this work, we theoretically analyzed the influence of chemical disorder on magnetic anisotropy in ferromagnetic Ge$_{1-x}$Mn$_x$Te semiconductor layers known to undergo ferroelectric structural distortion of rhombohedral crystal lattice and exhibit perpendicular magnetic anisotropy. Using DFT method we determined the local crystal structure in Ge$_{1-x}$Mn$_x$Te substitutional solid solution and calculated the single ion contribution to magnetic anisotropy energy. Our calculation revealed that the single ion contribution is order of magnitude smaller than the contribution originating from spin polarization induced by Mn ions into neighboring Te and Ge ions. This effect results from the hybridization of magnetic 3d orbitals of Mn ions and valence band states of GeTe subject to spin-orbit interactions. [3]

We also discussed magnetic anisotropy effects due to pairs of Mn ions differently allocated in the supercell and showed that the spatial averaging over the chemical disorder strongly reduces the strength of this magnetic anisotropy mechanism and restores the global rhombohedral symmetry of magnetic system.

Finally, the calculations show also that although in principle ab initio numerical methods may be applied to the calculations of MAE, in order to take into account disorder and make a direct quantitative comparison with experiment, much larger systems must be considered.

Acknowledgement

The authors acknowledge the support from NCN (Poland) research project no. UMO-2011/01/B/ST3/02486. This research was supported in part by PL-Grid Infrastructure.

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