Magnetic properties of Mn-doped Bi$_2$Se$_3$ topological insulators: ab initio calculations

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Doping Bi$_2$Se$_3$ by magnetic ions represents an interesting problem since it may break the time reversal symmetry needed to maintain the topological insulator character. Mn dopants in Bi$_2$Se$_3$ represent one of the most studied examples here. However, there is a lot of open questions regarding their magnetic ordering. In the experimental literature different Curie temperatures or no ferromagnetic order at all are reported for comparable Mn concentrations. This suggests that magnetic ordering phenomena are complex and highly susceptible to different growth parameters, which are known to affect material defect concentrations. So far theory focused on Mn dopants in one possible position, and neglected relaxation effects as well as native defects. We have used ab initio methods to calculate the Bi$_2$Se$_3$ electronic structure influenced by magnetic Mn dopants, and exchange interactions between them. We have considered two possible Mn positions, the substitutional and interstitial one, and also native defects. We have found a sizable relaxation of atoms around Mn, which affects significantly magnetic interactions. Surprisingly, very strong interactions correspond to a specific position of Mn atoms separated by van der Waals gap. Based on the calculated data we performed spin dynamics simulations to examine systematically the resulting magnetic order for various defect contents. We have found under which conditions the experimentally measured Curie temperatures $T_C$ can be reproduced, noticing that interstitial Mn atoms appear to be important here. Our theory predicts the change of $T_C$ with a shift of Fermi level, which opens the way to tune the system magnetic properties by selective doping.

I. INTRODUCTION

Bi-chalcogenides Bi$_{1-x}$Sb$_x$, Bi$_2$Te$_3$, and Bi$_2$Se$_3$ have drawn attention of large groups of researchers not only because of their interesting topological properties, but also due to their unique thermolectric properties. The surface of 3D topological insulators (TIs) hosts Dirac electrons with linear dispersion relation. Due to the strong spin-orbit coupling the direction of electron movement is coupled to its spin in the vicinity of the Dirac point. When magnetic order is introduced into bulk TI, the time reversal symmetry is broken. Consequently, an energy gap at the Dirac point might be opened, which enhances electron scattering and reduces the surface conductivity. This mechanism might provide a unique way of surface electronic transport manipulation in future cutting-edge spintronics applications.

In an analogy to diluted magnetic semiconductors, magnetic order can be formed in the bulk of a 3D topological insulator by adding a small amount of magnetic dopants. Formation of long-range ferromagnetic order has been demonstrated experimentally in 3D TIs Bi$_2$Se$_3$ and Bi$_2$Te$_3$ doped by a few percent of transition metals (Fe, Cr, Mn) with Curie temperature being in the order of few Kelvins. In different experimental and theoretical works, however, the research leads to different conclusions. The critical temperature measurements for Mn-doped bulk Bi$_2$Se$_3$ with few at% of Mn ions ranges from $T_C \approx 5$ K up to 20 K. Moreover, in some cases the ferromagnetic state in Mn-doped Bi$_2$Se$_3$ has not been found at all. A spin glass state has also been reported. The reason of the discrepancies may stem from nontrivial interactions between magnetic atoms inside the bulk of 3D TIs and their environment which might host number of additional defects on different lattice positions.

Despite the expected opening of the TI surface state gap in the presence of ferromagnetic order, finite density of states has been observed near the Dirac point in a number of studies. This has been explained by the presence of in-gap states, based on scanning tunneling spectroscopy (STS) measurements and a phenomenological model. The in-gap states are formed due to the hybridization of the magnetic impurity with bulk states rather than with the surface state itself. Therefore, a lot information can be learned from bulk Bi$_2$Se$_3$, and the bulk form is chosen to be the focus of this paper.

In an ideal case, Bi$_2$Se$_3$ has a layered structure consisting of Bi and Se hexagonal layers gathered into quintuple layers (QLs). Atomic layers inside QLs are ordered as Se(I)–Bi–Se(II)–Bi–Se(I); see Fig. 1. Bi layers inside QLs are equivalent, as well as the outer Se(I) layers. However, the central Se(II) layer has apparently a different sur-
FIG. 1. Hexagonal cell of the Bi$_2$Se$_3$ structure. Possible Mn dopant positions, namely the substitutional one (Mn$_i$), and the interstitial one in the van der Waals gap (Mn$_i$) are shown.

rounding than the outer ones. Different quintuple layers are separated by van der Waals (vdW) gaps in the crystal lattice along the c-axes (perpendicular to the layers) and held together by relatively weak vdW forces. Magnetic Mn dopants can reside at different position in the crystal lattice (Fig. 1). Mn atoms in Bi$_2$Se$_3$ or Bi$_2$Te$_3$ crystal lattice prefer to occupy substitutional positions (Mn$_i$) where Mn atoms replace Bi atoms. In this case Mn atoms act as electron acceptors, which would induce hole-like bulk conductivity. However, experimental studies have shown an electron bulk conductivity in Bi$_2$Se$_3$, which supports the assumption there must be also other doping-induced or native defects. Doping-induced defects may include Mn in interstitial positions (Mn$_i$), reported in several experiments. This problem has already been thoroughly studied in Bi$_2$Te$_3$, where interstitials appear to play a significant role. Interstitial sites in the Van der Waals gap between the quintuple layers represent the most favorable position for Mn$_i$ interstitials. In contrast to the substitutional Mn defects, interstitial Mn atoms are electron donors. For Bi$_2$Te$_3$ our previous study shows that the presence of Mn$_i$ atoms shifts the Fermi level into the Mn-impurity peak in the majority spin channel located inside the gap, while Mn$_i$ atoms shift the Fermi level into the conduction band. Thus Mn atoms in different positions modify the bulk conductivity and, as we shall show, also exchange interactions, in significantly different ways.

Another modification of the ideal Bi$_2$Se$_3$ structure can be caused by native defects, which occur regardless of the Mn-doping, and their formation depends on the growth conditions. Experimentally studied samples were usually n-type, even in the presence of Mn$_i$ acceptors. Samples with p-type conductivity have also been found, namely in Ca-counterdoped samples and in some of the Mn-doped samples. There is a general agreement that the most probable defect responsible for increasing the Fermi level are V$_{Se}$, Se vacancies. This is supported by ab initio calculations of defect formation energies. According to calculations based on the tight-binding model, vacancies are also expected to affect the TI surface state in the vicinity of the Dirac point, despite being deep below the surface. Other typical native defects in Bi$_2$Se$_3$ are antisites, substitutions of Se-atom in the lattice by Bi (Bi$_{Se}$) or vice versa (Se$_{Bi}$), which lead to Bi-rich and Se-rich Bi$_2$Se$_3$ samples, respectively. In the former case, the excess Bi atoms act as electron acceptors. In the latter condition, where Se atoms dominate the sample, Se$_{Bi}$ act as electron donors.

Importantly, all the defects mentioned above influence the bulk conductivity in the system and thus modify the indirect exchange interactions between the magnetic moments of the Mn-dopants. The authors of previous theoretical studies limited their research to magnetism in binary chalcogenides due to magnetic dopants on substitutional positions without considering possible co-existing interstitial magnetic moments or native defects. The goal of this paper is to provide a thorough picture of complex interplay between magnetic dopants in Bi$_2$Se$_3$ on different positions and native defect in the structure. This effort aims towards answering a question how the magnetic ground state in Mn-doped Bi$_2$Se$_3$ is influenced by the mentioned factors and how to reach the long-range ferromagnetic ordering of Mn magnetic moments at higher temperatures. We should note that most of the experimental analysis came to conclusion that in Mn-doped chalcogenides one does not usually observe any clustering of Mn atoms, therefore random dopant distribution can be assumed.

Because of small amounts of magnetic atoms in the samples, the dominant exchange mechanisms between the magnetic moments are indirect RKKY interaction and super-exchange. Especially the first one is strongly influenced by the number of carriers in the system. Thus it depends on the ratio of substitutional and interstitial Mn atoms as well as on the concentration of antisite defects and vacancies. By means of ab initio methods we calculated exchange interactions between magnetic moments of Mn atoms. In particular we studied how the interaction changes due to increasing number of Mn$_i$ dopants. The influence of native defects has also been taken into account. Finally, we have used the ab initio results as an input for atomistic Monte Carlo (MC) simulations to calculate Curie temperatures as a function of Mn concentration.

The paper is organized as follows. In Section II we describe the ab initio and MC calculations. In Sec. III we introduce and analyze our results. Finally, we sum up the results and draw conclusions of our research in Sec. IV.

II. FORMALISM AND COMPUTATIONAL DETAILS

A. Ab initio calculations

Our density functional theory (DFT) calculations were based on Green function tight-binding linear muffin-tin orbital method making use of atomic–sphere approximation (TB-LMTO-ASA). To treat disorder in solid crystals we have employed the coherent potential approx-
The importance of spin-orbit interaction in con- 
figurations. The geometries were relaxed with a residual force criterion of 
2.5 meV/Å. For the self-consistency cycle, we have employed an energy criterion of 10⁻³ eV. A k-point mesh of 
10x10x2 is used to sample the Brillouin zone. The dis- 
tortion of the structure caused by Mn dopants could be re- 
lected in the TB-LMTO-CPA approach by a modific- 
ation of Wigner-Seitz radii, namely global radii 
wQ associated to the volume of the unit cell, and local radii wQi associated to the atomic specie Qi. The con- 
tentional choice is wQ = wQ all for all species occupying one 
place. We have modified this choice locally for Q=Mn, 
Bi in such a way that the volume of the Bi-sublattice, 
(1 − x)(wBi)³ + x(wMn)³, is preserved, while wMn reflects the relaxed atomic surrounding obtained from VASP cal- 
culations. According to the transformation properties of the LMTO structure constants, this leads to a cor- 
responding modification of hopping integrals, and during the selfconsistent loop also to the change of potential parameters. The use of CPA without disorder-induced local relaxations has also been found to introduce significant errors in calculations of other materials, for example TiAlN alloys. In this system the effect of relaxation was succesfully incorporated by a different approach, the independent sublattice model, leading again to an agree- 
mement with supercell calculations. Small total volume changes due to Mn-doping and native defects were ne- 
glected. BiSe and SeBi antises as well as VSe vacancies were also treated within CPA, with the same concentra- 
tions on each sublattice.

In order to map the problem of magnetic ordering into the classical effective Heisenberg Hamiltonian as de- 
scribed below in Sec. 11 10 we calculate exchange interac- 
tions between magnetic dopants D, D' occupying sites 
R and R' from first principles employing the Liechten- 
stein formula. Note that because of the vertex cancellation 
theorem the formula can be constructed for disor- 
dered systems in an analogous way to the ordered system by considering conditionally averaged Green functions within the CPA method:
sites \( R \) (see\textsuperscript{[66,67]}, for a more accurate definition). \( G_{\sigma RR'}^{DD'} \)
are site off-diagonal blocks of the conditionally averaged Green function, the average of the spin-dependent Green
function with spin \( \sigma \in \{ \uparrow, \downarrow \} \) over all configurations with
atoms of the types \( D, D' \) fixed at sites \( R \) and \( R' \), respectively.

Due to the translational invariance of the effective system its exchange interactions \( J_{RR'}^{DD'} \) are fully described by \( J_{RR}^{DD'}(R - R') = J_{RR}^{DD'}(\Delta R) \). Note, that within basic assumptions of CPA these quantities are independent of
particular configuration, and can thus be calculated only once for each defect concentration. They of course depend on defect concentration, especially in systems where a small concentration change affects significantly states at the Fermi level.

\section*{B. Atomistic simulations}

In the second stage we employed atomistic simulations\textsuperscript{[68-71]} to calculate the Curie temperatures of given samples. This method allows us to study basic ther-modynamic properties of a material on the scale of distances between the atoms. At this point, we define a 3-
dimensional supercell of Mn atoms of size \( L \times L \times L \), where
\( L \) is number of elementary unit cells repeating along one direction. In the supercell, we randomly generated substi-tutional \( \text{Mn}_{\text{Bi}} \) atoms with equal concentration, \( x \), on both Bi sublattices, and \( \text{Mn}_{\text{B}} \) atoms with concentration \( x_{\text{int}} \). In our notation each magnetic dopant indexed by \( i \) is thus of type \( D_i \in \{ s_A, s_B, 1 \} \), denoting the substitutional \( \text{Mn}_{\text{Bi}} \) on the A or B sublattice, or \( \text{Mn}_{\text{B}} \) interstials in the VdW gap. It is assigned a position \( \mathbf{R}_i \)
from the set of its parent sublattice points within the supercell. Since the sublattices are equivalent, it is sufficient to define \( J_{\text{ss}}(\mathbf{R}) = J_{\text{AAsB}}(\mathbf{R}) = J_{\text{BAsB}}(\mathbf{R}) \) and \( J_{\text{bb}}(\mathbf{R}) = J_{\text{AsA}}(\mathbf{R}) = J_{\text{BAsB}}(\mathbf{R}) \). Each particular configura-tion with \( N \) magnetic dopants is thus described by a set of \( D_i \) and \( \mathbf{R}_i \) for \( i = 1 \ldots N \). The total exchange energy of the supercell is then given by Hamiltonian of
the Heisenberg type

\begin{equation}
H_{\text{xc}} = - \sum_{i,j} J_{DD'}(\mathbf{R}_i - \mathbf{R}_j) \hat{e}_i(\mathbf{R}_i) \cdot \hat{e}_j(\mathbf{R}_j),
\end{equation}

where \( \hat{e}_i(\mathbf{R}_i) \) and \( \hat{e}_j(\mathbf{R}_j) \) are unit vectors with the direc-tions of \( i \)-th and \( j \)-th magnetic moments, respectively, at sites occupied by Mn dopants (in the calculated particular configura-tion). Note, in the atomistic simulations we did not consider any other atoms than Mn atoms, their effects is included via their influence on the exchange constants \( J_{ij} \).

To estimate the critical temperature we used the Up-psala Atomistic Spin Dynamics (UppASD) code\textsuperscript{[72-75]}. We made use of the classical MC method implemented in the UppASD package utilizing Metropolis algorithm. The magnetic ground state was obtained by making use of the simulated annealing technique, in which the sim-u-lation is started at temperature much higher than the transition temperature and then is slowly cooled down towards \( T = 0 \). At each temperature step we performed from \( 10^5 \) up to \( 5 \times 10^5 \) MC steps. For each examined dopant concentration associated to a unique set of ex-change interactions we generated 10 different random Mn dopant configurations according to the given concentrations. To improve the statistics we performed in parallel 5 simulations for each such configuration, and averaged the contributions of all of them.

At each temperature step we evaluated heat capacity, \( C \), magnetic susceptibility, \( \chi \), and Binder cumulant, \( U \), defined as

\begin{equation}
U \equiv U(L, T) = 1 - \frac{\langle M^4 \rangle}{3 \langle M^2 \rangle^2},
\end{equation}

where \( M \) is total magnetization of the supercell, and \( \langle \ldots \rangle \) stands for averaging over MC steps at a constant tem-perature. The Binder cumulant\textsuperscript{[76]} allows us to reduce the finite size effect in the estimation of Curie temper-ature in ferromagnetic systems, which are prevalent in other methods, such as via the estimation of susceptibility and/or specific heat peaks. The basic properties of Binder cumulant\textsuperscript{[74]} are: (i) When \( T \to 0 \), \( U(L, T) \to 2/3 \), (ii) when \( T \to \infty \), we obtain \( U(L, T) \to 1/3 \), and (iii) when \( T \to T_C \), the Binder cumulant \( U(L, T) \to U^* \), which is an invariant with respect to the supercell size, \( L \). Thus curves \( U(L, T) \) calculated for different sizes \( L \) intersect in the same point, where \( T = T_C \).

\section*{III. RESULTS AND DISCUSSION}

\subsection*{A. Electronic structure}

Here we present the calculated densities of states (DOS’s) for systems with the considered Mn dopants of two different characters, Mn\( \text{Bi} \) and Mn\( \text{B} \) (assuming always the same concentration of Mn per formula unit i.e. \( x = 0.05 \)), \( \text{V}_{\text{Se}} \) defects, and their combinations.

Let us start with the results for the pure Bi\(_2\)Se\(_3\) compo-nent without any native defect. The DOS (Fig.\textsuperscript{[2]} (a)) shows that it is an insulator with the band gap of 0.39 eV, a large value compared to other bismuth-chalcogenides\textsuperscript{[12]}. The obtained gap size is in good agreement with the experimentally determined one (0.33 eV)\textsuperscript{[22]}. In the valence band the Se-4p electrons prevail, whereas Bi-6p states dominate in the conduction band, as has already been shown\textsuperscript{[20,27]}. In the next step we consider \( \text{V}_{\text{Se}} \) native defects with concentration \( x = 0.075 \) per formula unit. These defects act as electron donors, shifting the Fermi level upwards. Furthermore, it introduces mid-gap states inside the whole gap (Fig.\textsuperscript{[2]} (b)). That behavior is different from the most common defects in Bi\(_2\)Te\(_3\) systems, Bi and Te antisites.
1. Mn dopants in the substitutional position (Mn\textsubscript{Bi})

Our VASP based simulations reveal lattice relaxation around Mn dopants similarly to the case of Bi\textsubscript{2}Te\textsubscript{3}.\textsuperscript{18} Within LDA and GGA-PBE approaches we obtained for 4% of Mn\textsubscript{Bi} the following relaxation of inter-atomic distances between Mn atoms and Bi, Se atoms. The Mn-Se distance shrinks from the initial 2.97 Å to 2.60 Å and the Mn-Bi distance 4.14 Å is unchanged. In the TB-LMTO method the optimal choice to incorporate this relaxation was to assign the specie-dependent Wigner-Seitz radius \(w_{\text{Mn}}\) the Mn bulk native value (2.80 a.u.) instead of the Bi sublattice value, see also the Supplementary information of Ref.\textsuperscript{18} for more details.

Mn\textsubscript{Bi} acceptors shift the Fermi level to the valence band, where it crosses a small majority spin Mn impurity peak, acting as a virtual bound state. The size of this peak and its position w.r.t. valence band edge is highly sensitive to the amount of relaxation, as shown in Fig. 3(a) for several different radii \(w_{\text{Mn}}\). The local Mn\textsubscript{Bi} DOS is overall significantly modified by relaxation. Only very little minority states are present at the Fermi energy. The band gap survives with its size reduced, contrary to the case of Mn-doped Bi\textsubscript{2}Te\textsubscript{3}.\textsuperscript{18} The local Mn\textsubscript{Bi} DOS contains also a minority peak slightly above the former conduction band edge, in agreement with the
calculation based on the Korringa-Kohn-Rostoker Green function method and the Dyson equation\textsuperscript{28}. We find that the unrelaxed DOS differs from the relaxed one, as well as the magnetic moment and other properties.

The presence of V\textsubscript{Se} again induces mid-gap states. \(E_F\) is moved upwards and, interestingly, it can be fixed on the shallow mid-gap states inside the former gap. A low conductivity can be expected in this situation.

2. \textit{Mn dopants in the interstitial position (Mn\textsubscript{i})}

Only small lattice relaxations were observed in the supercell based VASP calculations for Mn\textsubscript{i} atoms placed in the VdW gap, therefore no special treatment within LMTO approach was used for this case. States of interstitial Mn atoms fill the minority band gap. Mn\textsubscript{i} behaves as electron donor, oppositely to the effect of Mn\textsubscript{Bi}. \(E_F\) now crosses the minority Mn electron peak, strongly hybridized with Se and Bi atoms, as shown in Fig. 4. For majority states a gap remains open, and only electron states are present at the shifted \(E_F\). This is basically independent of the Mn\textsubscript{i} concentration in the studied concentration range (1-10\%). Mn\textsubscript{i} concentration increase leads only to an enhancement of virtual bound states.

V\textsubscript{Se} defects do not cause a significant change of \(E_F\) position. The induced mid-gap states again remove the remaining gap in the majority channel.

B. Magnetic moments

The values of magnetic moments for the Mn\textsubscript{Bi} and Mn\textsubscript{i} atoms obtained from first principle calculations are significantly different (Tab. I) and depend rather weakly on concentrations of Mn atoms and native defects studied in this paper. The magnetic moment of Mn\textsubscript{Bi} atoms slowly shrinks with the increasing concentration of Mn\textsubscript{Bi} atoms, from the zero concentration limit value of 4.18 \(\mu_B\) (where \(\mu_B\) denotes the Bohr magneton). This magnetic moment slightly increases with an addition of Mn\textsubscript{i} or V\textsubscript{Se}. An inverse effect was observed in the presence of Bi\textsubscript{Se}, which suppresses Mn\textsubscript{Bi} magnetic moments, especially for low Mn\textsubscript{Bi} concentration. Similarly to what we have found for DOSes, Mn magnetic moment would be significantly modified if the relaxation was not taken into account.

Magnetic moment magnitudes of Mn\textsubscript{i} atoms fit in the range 3.21 - 3.15 \(\mu_B\) for Mn\textsubscript{i} concentrations between 1\% and 10\%. All the investigated native defects enhance magnetic moments of Mn\textsubscript{i} atoms, this effect is most pronounced for the presence of Bi\textsubscript{Se}, where the obtained moment values are close to 3.50 \(\mu_B\), depending on the

| Mn\textsubscript{Bi} conc. (\(\times 10^{-2}\) per f.u.) | Mn\textsubscript{i} | Bi\textsubscript{Se} | V\textsubscript{Se} | \(\mu\text{MnBi}\) (\(\mu_B\)) | \(\mu\text{Mn}_i\) (\(\mu_B\)) |
|-------------------|--------|--------|--------|----------------|----------------|
| 5                 | -      | -      | -      | 4.03           | 4.59           |
| 5*                | -      | -      | -      | 4.59           | 3.16           |
| 5                 | - 5    | - 7.5  | -      | 3.91           | 3.49           |
| 5                 | - 5    | - 7.5  | -      | 3.49           | 3.24           |
| 5                 | -      | - 7.5  | -      | 3.25           | 3.17           |
| 2                 | 4      | -      | -      | 3.25           | 4.16           |
| 2                 | 2      | -      | -      | 3.54           | 4.16           |

TABLE I. Selected values of calculated manganese magnetic moments \(\mu\text{MnBi}\) and \(\mu\text{Mn}_i\) for different concentrations of magnetic Mn\textsubscript{Bi} and Mn\textsubscript{i} together with a specified presence of native defects (Bi\textsubscript{Se}, V\textsubscript{Se}). In the special case denoted by (*) no relaxation around Mn\textsubscript{Bi} was allowed.
concentration.

The low variation of moment magnitude enables us to approximate the value of magnetic moment by a fixed value, achieving a deviation less than two percent from the calculated value in the considered region of the concentrations. Thus in our spin dynamics simulations we have always used magnetic moments $4.00 \mu_B$ for Mn$_{Bi}$ and $3.50 \mu_B$ for Mn$_i$ atoms.

C. Exchange interactions

Calculated exchange interactions between Mn$_{Bi}$ atoms are shown in Fig. 5 as a function of their distance $|\Delta R|$. These are split into interactions between Mn moments on the same (a,b) and different (c,d) Bi sublattices, and also into interactions between Mn located inside one QL (a,c) and at different QLs (b,d). The interactions are plotted for Mn atoms in Bi$_2$Se$_3$ without any native defects, as well as Bi$_2$Se$_3$ with Bi$_{Se}$. Moreover, for the Bi-rich form of Bi$_2$Se$_3$ we assumed different concentrations of Mn$_i$ atoms in the vdW gap.

First of all let us note that in the same Mn sublattice (Fig. 5a) the strongest interaction between the closest possible Mn atoms is always negative (antiferromagnetic). This interaction also varies with the presence of native defects and magnetic impurities. Although this interaction is the strongest one, in dilute systems one generally needs to consider a larger amount of neighbors and the importance of the interaction to the nearest neighbor is limited due to the magnetic percolation effect. The other values of $J_{ss}$ are positive. The other positive interactions may overcome that of the negative first interaction, and we show that this indeed happens for selected cases. In the case of no interstitial Mn atoms, the presence of Bi$_{Se}$ defects shifts the values of $J_{ss}$ in the positive direction. In turn the effect of Mn$_i$ atoms seems to be opposite. With increasing $x_{int}$, the values of $J_{ss}$ are lowered. Similar trends can be observed for the values of $J_{ds}$ acting between different QLs, shown on Fig. 5b).
is only one negative interaction, which is, however, very small. The strongest interactions are positive.

Let us now concentrate on the interactions between substitutional Mn atoms belonging to different magnetic sublattices. Similarly to $J^{ss}$, also the first value of $J^{ds}$ is negative (Fig. 5(c)). In most of the studied cases, the strongest $J^{ds}$ interaction inside QL is the second one, which is positive just in the case of small concentrations of Mn$_{Bi}$ atoms ($x_{int} = 0$ or 0.02). Generally, $J^{ds}$ values inside QL decay relatively quickly with distance, with values approaching zero already for distances above 2.5. When the interstitial Mn$_i$ atom concentration exceeds certain critical value ($x_{int} = 0.04$), all the significant $J^{ds}$ interactions turn to be negative and decrease almost exponentially towards zero with only little deviations.

Most interesting results concern $J^{ds}$ interactions acting between Mn atoms located in different QLs (Fig. 5(d)). Almost all of these interactions are positive. The by far largest value of $J^{ds}$ is obtained for the distance $d \approx 2.23 \, a$, and it is actually the largest from all the calculated interaction values. In order to understand this anomaly, positions of possible magnetic sites (Bi sublattice) of one lattice layer are depicted in the inset of Fig. 5(d) together with the $J^{ds}$ interaction intensity. Depicted exchange interactions fulfill the three-fold symmetry as expected. Mn$_{Bi}$-Mn$_{Bi}$ connections with the maximum interaction value actually pass very close to Se atoms located in the layers between them. Along the Mn$_{Bi}$-Se-Se-Mn$_{Bi}$ chain, both Mn$_{Bi}$-Se distances are only $0.7 \, a$, and Se-Se distance is $0.85 \, a$ (across the vdW gap). Se presence it thus sufficient to enhance the interaction even above the value corresponding to the closest Mn$_{Bi}$-Mn$_{Bi}$ distance $a$. For the unrelaxed Mn$_{Bi}$ we obtain significantly different exchange interactions than for the relaxed ones. This is probably the root cause for the difference from the results of a previous calculation$^{11}$, where relaxations were neglected.

Fig. 6 describes the exchange coupling involving Mn$_i$ atoms located in the vdW gaps. Figs. 6(a) and (b) plot the interactions between Mn$_i$ type magnetic moments. Inside one vdW gap one can notice a dominance of negative $J^{i}$ values. The largest interaction, which is most sensitive to concentration of Mn$_i$ atoms, is the nearest neighbor contribution. The absolute value of this interaction decreases with increasing $x_{int}$. The coupling strength between Mn$_i$ atoms belonging to neighboring vdW gaps, shown in Fig. 6(b), features both positive and negative values of $J^{i}$. The interactions between magnetic
FIG. 7. (Color online) Lines: Exchange interactions between different magnetic dopants as a function of the Fermi level position relative to the Fermi level of pure Bi$_2$Se$_3$, summed over all considered shells. Points: exchange interactions between different magnetic dopants calculated for a specific combination of dopants (see text), depicted at the energy corresponding to its own Fermi level (summed over all considered shells). Subscripts of dopants’ labels specify dopant concentration in percents per f.u.

moments of Mn$_i$ and Mn$_{Bi}$, $J^{is}$, atoms are plotted on Figs. 6(c) and (d). The overwhelming majority of them are again negative. Especially noticeable are the relatively strong coupling strengths between close Mn$_i$ and Mn$_{Bi}$ moments.

Already from these figures one can see that the dependence of exchange interactions on the presence of various defects/dopants is strong and complex. Considering the vast number of possible defect combinations here it would appear as difficult to map the possible behavior of exchange interactions in this configuration space. However, a significant contribution to exchange could be due to conduction electrons, which would depend mostly on the position of the Fermi level. Therefore we have decided to examine exchange interactions as a function of the Fermi level, described by its shift $\delta E$ from its value for the unperturbed system. The corresponding calculations of exchange interactions for a number of possible Fermi level values were performed for the reference system with just two magnetic dopants in the unperturbed Bi$_2$Se$_3$, which formally corresponds to the limit of zero concentration of magnetic dopants treated in the framework of the CPA. These can also be calculated from the Lichtenstein formula (Eq. 1). We show here only sums of exchange interaction over all the considered neighbors, $J_0^{DD'} = \sum_{\Delta R} J^{DD'}(\Delta R)$, instead of interactions for specific distances. This is the most relevant quantity in a dilute medium, and its use makes the whole comparison feasible. In Fig. 7 the sums are plotted for the reference system with zero defect concentration and just a shifted Fermi level, together with sums calculated for systems with specific combinations of defects. The Fermi level shift on the $x$ axis represents an input parameter for the first type of calculation, while for the latter it is determined from the self-consistent cycle. The agreement appears to be rather good, especially the shapes of dependencies are similar for both types of calculations. Few smaller discrepancies arise, mainly overall weaker exchange interactions were obtained for truly disordered systems than for the reference system. This reduction can be due to increased electron scattering. The correspondence with Fermi level shifted systems indicates the importance of RKKY interaction relying on conduction electrons.

We can now obtain some insight into the overall evolution of magnetic interactions with doping. Most important here is the increase of interactions between Mn$_{Bi}$ atoms for $p$-doped samples with $E_F$ in the range of Fermi level shift $\delta E < -10$ mRy, where positive exchange interactions appear, suggesting a possibility of a more stable FM order there. This situation is expected in the case of pure Mn$_{Bi}$ doping and also Bi$_{Sc}$ antisites. The tendency to order might however be reduced by the presence of Mn$_i$ and V$_{Se}$ dopants, which both shift the Fermi level upwards. Furthermore, Mn$_i$ moments provide a strong negative coupling to Mn$_{Bi}$ moments.
D. Curie temperatures

Let us now study the finite temperature magnetism in Mn-doped Bi$_2$Se$_3$ using MC simulations with exchange coupling strengths introduced in the previous subsection. Fig. 8(a) shows an example of averaged physical quantities calculated using atomistic MC simulations for a Bi-rich Mn-doped Bi$_2$Se$_3$ with $x_{\text{int}} = 0.00$ and $x = 0.10$: (a) magnetization $m$, and magnetic susceptibility $\chi$ in the inset, (b) Binder cumulants $U$ for different sizes of simulated supercell: $L = 20, 30, \text{and } 40$.

FIG. 8. (Color online) Example of temperature dependence of quantities calculated using atomistic MC simulations for a Bi-rich Mn-doped Bi$_2$Se$_3$ with $x_{\text{int}} = 0.00$ and $x = 0.10$: (a) magnetization $m$, and magnetic susceptibility $\chi$ in the inset, (b) Binder cumulants $U$ for different sizes of simulated supercell: $L = 20, 30, \text{and } 40$.

function of substitutional Mn$_{Bi}$ atoms concentrations, $x$. At first sight, one can notice the linear dependence of $T_C$ on $x$ for all the studied cases. In simulations it was impossible to obtain magnetic ordering for concentrations of Mn$_{Bi}$ atoms less than $x = 0.04$. It is caused not only by the decreasing intensity of exchange interactions $J_{ij}$ (Fig. 7), but probably also by the vicinity of the percolation limit.

Inclusion of Bi$_{Se}$ native defects causes a remarkable increase of $T_C$ (Fig. 9). The temperatures are shifted to higher values and the slope of the linear dependence becomes steeper. Further increase of Mn$_i$ concentration reduces the critical temperature as well as the slope, similarly to the presence of V$_{Se}$ defects. This behavior correlates with our findings based on studying the interaction sums $J_{ij}$. The few existing experimentally measured values of $T_C$ (shown in Fig. 9) appear to agree with our predictions if the presence of a sufficient amount of undetermined defects (Mn$_i$ and V$_{Se}$) is assumed. Notably, in one case ferromagnetic order has been observed only after doping has changed the sample conductivity from n-type to p-type, in agreement with our predictions about Fermi level dependence.

IV. CONCLUSIONS

We have calculated the electronic structure and exchange interactions in Mn-doped Bi$_2$Se$_3$ employing first-principles methods. Apart from the mostly expected Mn position substituting Bi atoms we also considered interstitial Mn, and find that in this position it has strikingly different effect. Our calculations predict a signifi-
significant relaxation of atoms surrounding substitutional Mn. Magnetism-related properties are sensitive to it, and its neglect would lead to a significantly different prediction of exchange interactions or magnetic moment.

Interestingly, although the nearest neighbor interaction is always negative in the studied systems, in some cases interactions to more distant neighbors overcome this contribution and the system then prefers ferromagnetic ordering. We have found that in the studied cases the strongest interaction corresponds to a specific pair of Mn atoms with the distance 2.23 higher than that of nearest neighbors. This quite unusual behavior is a consequence of the lattice structure and cannot be expected for example in the commonly studied cubic (Ga,Mn)As dilute magnetic semiconductors. This also means that the interaction range cannot be limited to just few nearest neighbors here, we recommend to include shells up to the distance 3a. For this reason we also do not expect any 2D magnetic arrangement along layers, as already noticed in a recent experiment.79

Magnetic ordering as a function of temperature was investigated. Our spin dynamics simulations predict the existence of a phase transition to FM order for a wide range of Mn-doping concentrations. In the interesting concentration range \( x = 0.05 - 0.1 \) a linear increase of \( T_C \) with the concentration of substitutional Mn is obtained, in agreement with the preceding works.32 Furthermore, we find that an increase of interstitial Mn has the opposite effect and decreases the Curie temperature. A plausible scenario for the experimentally observed weak dependence of \( T_C \) on Mn concentration could thus be based on a simultaneous increase of both MnBi and MnI. Another explanation may be due to the influence of Mn doping on native defects, which has already been suggested.15,23,80 Therefore we also performed calculations of the system in the presence of the most probable native impurities. We find that the presence of Se vacancies decreases \( T_C \), while Bi antisites increase it. A sufficient concentration of these extra defects can also prevent formation of FM order at all. The order of magnitude of variations of \( T_C \) for constant Mn concentrations is consistent with the experimentally reported ones and underline of the importance of coexistence of different defect types.

The total variation of exchange interactions and the resulting evolution of \( T_C \) when varying dopant concentrations can be largely explained as the consequence of the shift of the Fermi level in this system. For small Fermi level shifts due to dopants the sums over exchange parameters show an overall increase with decreasing Fermi level, hence we expect a more stable FM order and a higher \( T_C \) for p-type samples. Notably, the most common defects here, Se vacancies, shift the Fermi level to higher energies. Therefore counterdoping is needed to obtain p-type samples, and its proper application can lead to an increase of \( T_C \).

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