Letter | Editors' Suggestion

Superexchange dominates in magnetic topological insulators

Cezary Śliwa,[1,*] Carmine Autieri,[2,3] Jacek A. Majewski,[4] and Tomasz Dietl[2,5,†]

[1]*Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46, PL-02668 Warsaw, Poland*

[2]*International Research Centre MagTop, Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46, PL-02668 Warsaw, Poland*

[3]*Consiglio Nazionale delle Ricerche CNR-SPIN, UOS Salerno, I-84084 Fisciano (Salerno), Italy*

[4]*Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, ulica Pasteura 5, PL-02093 Warsaw, Poland*

[5]*WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

(Received 30 July 2021; accepted 4 November 2021; published 6 December 2021)

It has been suggested that the enlarged spin susceptibility in topological insulators, described by interband Van Vleck's formalism, accounts for the ferromagnetism of bismuth-antimony topological chalcogenides doped with transition metal impurities. In contrast, earlier studies of HgTe and related topological systems pointed out that the interband analog of the Ruderman-Kittel-Kasuya-Yosida interaction (the Bloembergen-Rowland mechanism) leads to antiferromagnetic coupling between pairs of localized spins. Here, we critically revisit these two approaches, show their shortcomings, and elucidate why the magnitude of the interband contribution is small even in topological systems. From the proposed theoretical approach and our computational studies of magnetism in Mn-doped HgTe and CdTe, we conclude that in the absence of band carriers, the superexchange dominates and its sign depends on the coordination and charge state of magnetic impurities rather than on the topological class of the host material.

DOI: 10.1103/PhysRevB.104.L220404

Introduction. In the traditional approach to localized magnetism in solids, one considers pairwise exchange interactions between spins J_{ij} comprising the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling brought about by band carriers and the Anderson-Goodenough-Kanamori superexchange mediated mainly by anion orbitals [1]. However, it has been demonstrated that in the case of p-type dilute magnetic semiconductors (DMSs), the Zener model [2] is remarkably versatile, in which the local magnetization $\mathbf{M}(\mathbf{r})$ plays a role of a continuous order parameter. This approach has allowed understanding the physics of bound magnetic polarons [3,4] and ferromagnetism of p-type DMSs [5], and subsequently describing quantitatively a wealth of micromagnetic properties and spintronic functionalities of (Ga,Mn)As and related ferromagnets [6,7]. Notably, the equivalence between the RKKY and Zener models was established within the mean-field approximation (MFA) [8].

Ferromagnetic topological insulators [9,10], such as $(Bi,Sb,Cr)_2Te_3$, have made possible the experimental realization of the quantum anomalous Hall effect [11], the axion insulator [12], efficient magnetization reversal by spin currents [13], and the much disputed chiral Majorana fermions [14,15]. Interestingly, the appearance of ferromagnetism in these systems is also attributed to their topological character, as the inverted band structure enhances the interband spin susceptibility leading to carrier-independent spin-spin coupling [16], referred to as the Van Vleck magnetism [9,10,16]. That appears surprising, however, as early studies of spin-spin coupling mediated by an interband analog of the RKKY interaction (the Bloembergen-Rowland (BR) mechanism [17]) found predominately *antiferromagnetism* in topological Mn-doped zero-gap HgTe [18–20].

In this Letter, we resolve this puzzle by demonstrating that the mean-field Zener–Van Vleck model fails in the case of magnetism associated with interband bulk excitations in insulators. Furthermore, by making use of the recent progress in the theory of the indirect exchange interaction [21] and in the quantitative description of exchange splitting of bands in the whole Brillouin zone (BZ) [22], we determine various contributions to spin-spin coupling in nontopological CdTe and topological HgTe doped with Mn ions. We find that the superexchange dominates not only in (Cd,Mn)Te [23,24], but also in topological (Hg,Mn)Te. We also show that the conclusion about the predominant role of the superexchange substantiates the experimental results on (Cd,Hg,Mn)Te [25,26] and explains hitherto challenging chemical trends in the magnetic properties of V, Cr, Mn, and Fe-doped tetradymite topological insulators observed experimentally [9,10,27] and found in *ab initio* studies [28–30].

RKKY-BR vs Zener–Van Vleck models. For concreteness, we consider xN randomly distributed Mn spins $S = 5/2$ in zero-gap $Hg_{1-x}Mn_xTe$ in which both the conduction and valence bands are of Γ_8 symmetry at the BZ center. In the high-temperature expansion of the partition function for the pairwise interactions [25], the contribution of the RKKY-BR term to the Curie-Weiss temperature (equal to spin ordering temperature T_c within MFA) assumes the form [18,20,31]

$$\Theta_{\mathrm{CW}} = \frac{xS(S+1)}{3N\mathcal{V}} \sum_{i\neq j,\mathbf{q}} \exp[i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)] \times \sum_{\mathbf{k},n,n',\sigma,\sigma'} \frac{2|\langle u_{n,\mathbf{k},\sigma}|\beta s_z|u_{n',\mathbf{k}+\mathbf{q},\sigma'}\rangle|^2}{\mathcal{V}(E_{n',\mathbf{k}+\mathbf{q}} - E_{n,\mathbf{k}})} f_{n,\mathbf{k}}(1 - f_{n',\mathbf{k}+\mathbf{q}}), \quad (1)$$

*sliwa@ifpan.edu.pl

†dietl@MagTop.ifpan.edu.pl

where the Boltzmann constant $k_B = 1$; $\mathcal{V}$ is the crystal volume, and $\mathbf{k}, \mathbf{k}+\mathbf{q} \in$ BZ. We see that if the *p-d* exchange integral β were $\mathbf{k}$ independent, the summation over $\mathbf{k}$ would provide the spin susceptibility $\tilde{\chi}(\mathbf{q})$ of the Γ_8 bands n and n', as defined in Refs. [32] and [33]. Furthermore, if the contribution of the self-interaction energy were small compared to interaction energies for $i \neq j$, the term $i = j$ could be included in Eq. (1), transferring the sum over the cation positions $\mathbf{R}_i$ and $\mathbf{R}_j$ into the structure factor that is nonzero for $\mathbf{q} = 0$ only. This is the case of the long-range RKKY coupling, for which the sum over i, j can be approximated by $N^2\beta^2\tilde{\chi}(0)$, as presumed within the Zener–Van Vleck model [16,32,33]. However, in the case of the BR mechanism, the decay of the interaction with the interspin distance is faster [17–20] and, therefore, $\tilde{\chi}(q)$ beyond $q = 0$ determines the sign and magnitude of Θ_{CW} and T_C. In conclusion, atomistic computations of pair exchange energies J_{ij} are necessary in order to meaningfully evaluate the role of the interband contribution [34].

Theoretical methodology. We consider exchange interactions between Anderson magnetic impurities occupying cation substitutional positions in considered semiconductor compounds, whose band structures are described within the empirical tight-binding approximation taking into account spin-orbit interactions. This approach [35–37] was successfully applied to elucidate the nature of ferromagnetism in (Ga,Mn)N [38,39] and has recently been generalized by us to simultaneously take into account various contributions to the spin pair exchange energy [21], including the BR interband term. Assuming time-reversal symmetry (no spontaneous magnetization) and within the fourth-order perturbation theory in the *p-d* hybridization energy V_{hyb} between band states $E_{\mathbf{k},n}$ and Mn *d* orbitals residing at $E_d = E(d^5) - E(d^4)$ and $E_d + U = E(d^6) - E(d^5)$, the spin Hamiltonian is

$$\hat{\mathcal{H}}^{(4)}_{\text{eff}} = -\sum_{i\neq j} J^{(4)}_{ij,\alpha\beta}\hat{S}_{i,\alpha}\hat{S}_{j,\beta}, \tag{2}$$

where the tensor of exchange integrals (parameters) for spins at sites (i, j) can be written as a double integral over the BZ $[k \equiv (\mathbf{k}, n)]$,

$$J^{(4)}_{ij,\alpha\beta} = -\frac{1}{2(2S)^2}\sum_{m,m'}\sum_{k,k'} A^{(4)}_{kk'} W_{i\alpha,k'k,m} W_{j\beta,kk',m'}, \tag{3}$$

where m labels the *d* orbitals and

$$W_{i\alpha,k'k,m} = \sum_{a,b=\uparrow,\downarrow} \langle k'|V^{\dagger}_{\text{hyb}}|d_i m a\rangle\langle a|\sigma_\alpha|b\rangle\langle d_i m b|V_{\text{hyb}}|k\rangle, \tag{4}$$

where a and b are spin directions and σ_α the Pauli matrices. For an insulator in a zero-temperature approximation and using the notation

$$w_k = \frac{1}{E_d + U - E_k}, \quad w'_k = \frac{1}{E_d - E_k}, \tag{5}$$

$$w_{k'} = \frac{1}{E_d + U - E_{k'}}, \quad w'_{k'} = \frac{1}{E_d - E_{k'}}, \tag{6}$$

one can write $A^{(4)}_{kk'}$ in terms of the Heaviside step function Θ as

$$\begin{aligned} A^{(4)}_{kk'} \approx{}& \Theta(E_F - E_k)\Theta(E_F - E_{k'})w_k w_{k'}(w_k + w_{k'}) + \Theta(E_F - E_k)\Theta(E_{k'} - E_F)\frac{(w_k - w'_{k'})^2}{E_k - E_{k'}} \\ &+ \Theta(E_k - E_F)\Theta(E_F - E_{k'})\frac{(w_{k'} - w'_k)^2}{E_{k'} - E_k} - \Theta(E_k - E_F)\Theta(E_{k'} - E_F)w'_k w'_{k'}(w'_k + w'_{k'}) \\ &+ \frac{2}{U}[\Theta(E_F - E_k)w_k + \Theta(E_k - E_F)w'_k][\Theta(E_F - E_{k'})w_{k'} + \Theta(E_{k'} - E_F)w'_{k'}], \end{aligned} \tag{7}$$

where we assume that the Fermi energy E_F lies in the range $E_d < E_F < E_d + U$. Average values of the exchange integrals and $\Theta_0 = \Theta_{CW}/x$ are obtained by tracing the tensors,

$$J^{(4)}_{ij} = \frac{1}{3}\sum_{\alpha} J^{(4)}_{ij,\alpha\alpha}, \quad \Theta_0 = \frac{2}{3}S(S+1)\sum_{i\geqslant 1} z_i J^{(4)}_{0i}, \tag{8}$$

where z_i is a number of cation sites in the consecutive coordination spheres $i \geqslant 1$.

We represent $A^{(4)}_{kk'}$ as a sum of three contributions [23,40]: the superexchange (or *hh*) term includes contributions proportional to $\Theta(E_F - E_k)\Theta(E_F - E_{k'})$, the two-electron (or *ee*) term includes those proportional to $\Theta(E_k - E_F)\Theta(E_{k'} - E_F)$, and the electron-hole (*he*) term includes those proportional to $\Theta(E_F - E_k)\Theta(E_{k'} - E_F)$ or $\Theta(E_k - E_F)\Theta(E_F - E_{k'})$. Such a decomposition leads to the analogous decomposition of $J^{(4)}_{ij}$ and $\Theta_0 = \Theta_{hh} + \Theta_{ee} + \Theta_{he}$.

We use a 16-orbital sp^3 tight-binding model of the band structure together with the parameter values obtained recently by us employing a modified generalized gradient approximation (GGA)+U *ab initio* approach with $U_{Mn} = 5$ eV. These parameters are presented in Tables II and III of Ref. [22]. In particular, E_d in our Eqs. (5)–(7) is a mean value of $E_{eg\uparrow}$ and $E_{t2g\uparrow}$, whereas $E_d + U$ is a mean value of $E_{eg\downarrow}$ and $E_{t2g\downarrow}$. Finally, matrix elements of V_{hyb} are spin-averaged values of $V_{sd}\sigma$, $V_{pd}\sigma$, and $V_{pd}\pi$ [22]. Extensive magneto-optical data collected for $Cd_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xTe$ at the Γ and L points of the BZ served to benchmark the model [22]. Importantly, our tight-binding model reconfirms, for these compounds, stronger hybridization of t_{2g} orbitals with the band states, compared to the e_g case, which is crucial for the sign and magnitude of the interaction between localized spins.

In topological materials, the most interesting is the *he* term. It appears whenever transitions between the fully occupied valence bands and the empty conduction bands are symmetry allowed (the BR mechanism) or when there is a nonzero density of states at the Fermi level (the RKKY mechanism). This term features an energetic denominator $E_k - E_{k'}$. In

insulators, the latter is guaranteed to be nonzero by the Heaviside-Θ prefactors (it is understood that each term vanishes whenever the zero Heaviside-Θ prefactor does, even despite singular denominators). However, in a semimetal, the denominator is singular at the Fermi level (i.e., when either $E_k \to E_F^+$ and $E_{k'} \to E_F^-$, or vice versa). In undoped (or isoelectronically doped) HgTe, this happens at the Γ point of the BZ. For this reason, it has been essential to elaborate a special integration method. The Supplemental Material [41] presents issues associated with k and k' integrations in simple models [18–20] and a comparison of the second-order perturbation theory in the *p-d* exchange integral compared to the fourth-order perturbation theory in the hybridization matrix element $V_{\rm hyb}$ employed here.

Brillouin-zone integration. Although our goal is to find the exchange integrals $J_{ij}^{(4)}$ in the limit of an infinitely large system, it is typical in numerical calculations to replace the BZ integration by a summation over a discrete set of $\mathbf{k}$ points in the BZ. As pointed out in Ref. [42], such discrete $\mathbf{k}$-point mesh may be defined through the introduction of the superlattice vectors $\{\mathbf{g}_i\}$, being the linear combinations of primitive crystal translations $\{\mathbf{a}_i\}$,

$$\mathbf{g}_i = \sum_{j=1}^{3} \mathbf{a}_j M_{ji}. \tag{9}$$

In cubic systems, the three $\mathbf{g}_i$ can be taken as vectors along the three Cartesian axes with length La. This defines the equidistant $\mathbf{k}$-point mesh $\kappa_{\{m\}} = \frac{2\pi}{La}(m_x, m_y, m_z)$ of L^3 grid points. In addition, the grid points can be shifted.

However, the expressions for the J_{ij} tensor components involve double integration over the BZ. Here, we present an efficient method to deal with the double BZ integration facilitated by the specifics of the integrand. In particular, this method allows for accurate treatment in the *he* contribution for J_{ij} in the case of zero-gap systems. Indeed, the product $W_{i\alpha,k'k,m}W_{j\beta,kk',m'}$ includes a phase factor $\exp[i(\kappa - \kappa')(R_i - R_j)]$, and the summation over the images of R_i, $R_i + La_{\rm lat}(n_x, n_y, n_z)$ yields (by the principle of the Poisson summation) a set of Dirac δ's at $\kappa - \kappa' = \frac{2\pi}{La_{\rm lat}}(m_x, m_y, m_z)$,

$$\sum_{n_x,n_y,n_z} \exp\{i(\kappa - \kappa')[R_i - R_j + La_{\rm lat}(n_x, n_y, n_z)]\}$$
$$= \left(\frac{2\pi}{La_{\rm lat}}\right)^3 \exp[i(\kappa - \kappa')(R_i - R_j)] \sum_{m_x,m_y,m_z} \delta\left[\kappa - \kappa' + \frac{2\pi}{La_{\rm lat}}(m_x, m_y, m_z)\right], \tag{10}$$

where the δ suppresses only one integration. To handle this issue, we first sum over a shifted grid of equidistantly spaced k points,

$$\kappa = \frac{2\pi}{La_{\rm lat}}\left(m_x + \frac{\vartheta_x}{2\pi}, m_y + \frac{\vartheta_y}{2\pi}, m_z + \frac{\vartheta_z}{2\pi}\right), \quad \kappa' = \frac{2\pi}{La_{\rm lat}}\left(m'_x + \frac{\vartheta_x}{2\pi}, m'_y + \frac{\vartheta_y}{2\pi}, m'_z + \frac{\vartheta_z}{2\pi}\right), \tag{11}$$

then integrate over the common shift $(\vartheta_x, \vartheta_y, \vartheta_z) \in [0, 2\pi)^3 \equiv T^3$ (T^3 stands for the three-dimensional torus).

In order to calculate $J_0 + \sum_{i\geqslant 1} z_i J_i$, we rewrite (10) with $L = 1$ as

$$\sum_j \exp[i(\kappa - \kappa')(R_i - R_j)] = \left(\frac{2\pi}{a_{\rm lat}}\right)^3 \sum_{m_x,m_y,m_z} \delta\left[\kappa - \kappa' + \frac{2\pi}{a_{\rm lat}}(m_x, m_y, m_z)\right]. \tag{12}$$

Since $2\pi/a_{\rm lat}$ is the lattice constant of the reciprocal lattice, only the term with $m_x = m_y = m_z = 0$ remains in the last sum, and the Dirac δ suppresses one integration. Therefore, $J_0 + \sum_{i\geqslant 1} z_i J_i$ and, thus, $\tilde{\chi}(0)$ can be computed as a single integral over the BZ.

In insulators, the integration over ϑ's is approximated by a sum over an equally spaced grid (the trapezoids method). The number of required ϑ points in each Cartesian direction gets smaller as the larger supercells are considered. Ultimately, just one ϑ point is sufficient; it can be chosen as, e.g., $\vartheta_x = \vartheta_y = \vartheta_z = 0$ or $\vartheta_x = \vartheta_y = \vartheta_z = \pi$, in correspondence with the boundary conditions imposed on the electronic wave functions. In contrast, in semimetals, if the boundary conditions dictate $\vartheta = 0$, finite summation is not appropriate because the denominator $E_k - E_{k'}$ in Eq. (7) renders the quantity undefined. Therefore, a special set of ϑ points has been chosen here, which is equivalent to the transformation $\vartheta'_i \mapsto \vartheta_i = \vartheta'_i - \sin\vartheta'_i$ under the BZ integral. This transformation, besides possessing analytic properties, preserves periodicity while $d\vartheta_i/d\vartheta'_i = 0$ at $\vartheta'_i = 0$. As a result, the divergence of the integral at the origin cancels with the zero of the Jacobian of the transformation and the integral can be computed with the trapezoids method. Indeed, the singularity of the integrand at $\vartheta = 0$ is integrable, as long as the dimensionality is sufficient and the band structure is well behaved (k-linear terms, k^3 terms, and the anisotropy may play a role here). The RKKY (i.e., intraband) term is omitted in this discussion, as the density of states vanishes if the Fermi energy $E_F \to 0$.

The computations have been performed with an efficient algorithm based on the fast Fourier transform on a $16 \times 16 \times 16$ supercell (16 384 cation lattice sites) that also determines the grid density of k and k' points employing periodic boundary conditions. For $Cd_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xTe$, the grids with up to two and eight different ϑ values have been employed, respectively. Figure 1 demonstrates that the magnitude of Θ_{he}

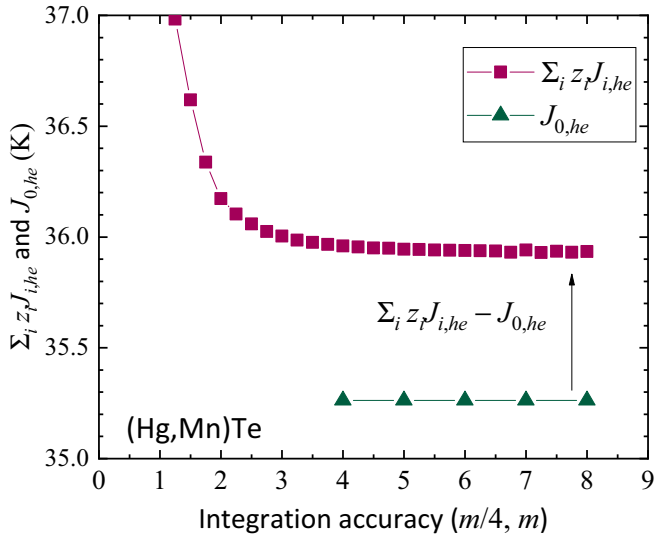

FIG. 1. Convergence of the interband *he* term for Mn pairs in HgTe with respect to the number m of ϑ points in each space direction in the trapezoids quadrature. Squares: the sum of exchange integrals including J_0 calculated for the $4 \times 4 \times 4$ supercell as a single BZ integral (abscissa provides $m/4$); triangles: the value of J_0 to be subtracted in order to obtain Θ_{CW} (abscissa provides m).

TABLE I. Consecutive nearest-neighbor exchange energies $-(J_i = J_{i,hh} + J_{i,ee} + J_{i,he})$, $i = 1, 2, 3, 4$ (from the fourth-order perturbation theory), and Curie-Weiss parameter $-\Theta_0$ in Kelvins compared to experimental results. Contributions from the superexchange (*hh*), electron-electron (*ee*), and interband (*he*) terms to Θ_0 are also shown.

	$Cd_{1-x}Mn_xTe$		$Hg_{1-x}Mn_xTe$		
	Theory	Expt.	Theory	Expt.	
$-J_1$	9.77	6.3 ± 0.3 [45] 6.15 ± 0.05 [47]	6.46	5.1 ± 0.5 [46] 4.3 ± 0.5 [48]	
$-J_2$	0.810	1.9 ± 1.1 [45] 1.80 ± 0.05 [47]	0.842		
$-J_3$	0.352	0.4 ± 0.3 [45] 1.39 ± 0.05 [47]	0.394		
$-J_4$	0.255	0.81 ± 0.05 [47]	0.467		
$-\Theta_0$	801	470 ± 34 [25]	666	500 ± 10 [25] 660 ± 88 [26]	
		Theory			
$-J_{1,he}$	−0.396	$-\Theta_{hh}$	772	−1.583	651
$-J_{2,he}$	0.421	$-\Theta_{ee}$	8.9	0.492	19.0
$-J_{3,he}$	0.131	$-\Theta_{he}$	20.0	0.112	−3.9
$-J_{4,he}$	0.061			0.154	

in $Hg_{1-x}Mn_xTe$ converges with the number of employed ϑ values. This means that in contrast to the static dielectric function [43,44], the spin susceptibility, though enhanced, is not singular at $q \to 0$ in the symmetry-induced zero-gap semiconductors. Aitken's δ-squared process served to accelerate the integration convergence. We have checked that Θ_0 calculated by the single integral, as outlined in a preceding paragraph, and after subtracting J_0, is in excellent numerical agreement (better than 1 K) with the value obtained by summing $z_i J_i$, $i \geqslant 1$, obtained by the double BZ integration. Actually, the coupling to the nearest neighbors (J_1) contributes over 50% to the value of Θ_0.

Discussion of theoretical results vis-à-vis experimental data. As expected theoretically for the random distribution of magnetic ions, experimental values of Θ_{CW} show a linear dependence on x in II-VI DMSs [25,51]. As shown in Table I, our theory, together with the employed tight-binding parametrization, explains the interaction sign but overestimates by 60% the absolute values of J_1 and Θ_0 in $Cd_{1-x}Mn_xTe$ and by 30% in the case of $Hg_{1-x}Mn_xTe$.

Extensive experimental studies of spin-glass freezing temperature T_f in wide-gap Mn- and Co-based DMSs, including $Cd_{1-x}Mn_xTe$, indicate that $\Theta_{\mathrm{CW}} \gg T_f \sim x^{\alpha}$, where $\alpha = 2.25 \pm 0.1$ [39,49,50,52]. A scaling argument [49,53] then implies $J_i \sim d_i^{-n}$, where d_i is the distance between spin pairs and $n = 3\alpha = 6.8 \pm 0.3$ [49]. Figure 2(a) demonstrates that the dependence of J_i on d_i obtained here for $Cd_{1-x}Mn_xTe$ is in agreement with the experimentally determined power law. However, an exponential decay would describe the computed data over a wider range of d_i.

Comparing $J_{i,he}$ values displayed in Figs. 2(c) and 2(d) to J_l data in Figs. 2(a) and 2(b), we find that the BR mechanism dominates at large d. It decays exponentially with d in the wide-gap $Cd_{1-x}Mn_xTe$, but for topological zero-gap $Hg_{1-x}Mn_xTe$, $J_{i,he}(d)$ shows a power-law dependence, also at large d. This behavior accounts for a relatively weak decay of T_f with decreasing x in $Hg_{1-x}Mn_xTe$ [54], leading to $n = 4.8$ [50]. As seen in Fig. 2(b), this value of n is consistent with our theoretical results, though we have to note that a considerable shift of bands with x is expected in topological materials, while our computations have been performed for Mn pairs in HgTe. As shown in Table I, the relevant ferromagnetic and antiferromagnetic contributions $J_{i,he}$, $i \geqslant 1$, actually cancel each other in Θ_{he}, making the contribution of the BR mechanism to Θ_0 negligible in both compounds. This explains why no effect of gap opening on Θ_{CW} was found in $Hg_{1-x-y}Cd_yMn_xTe$ [26]. At the same time, it is clear from Fig. 1 that the inclusion of the self-interaction term $J_{0,he}$ would drastically increase the magnitude of Θ_{he}.

Conclusions and outlook. Our results demonstrate that the interband BR term changes the sign from ferromagnetic to antiferromagnetic as a function of Mn pair distance, with the behavior contradicting the Van Vleck–like approach that predicts only the ferromagnetic coupling [16]. Such an alternating sign, reflecting the presence of both ferromagnetic and antiferromagnetic excitations in $\tilde{\chi}(q)$ [55], significantly reduces the role of the interband contribution making the superexchange to determine whether a spin glass or a ferromagnet becomes the magnetic ground state, i.e., the case of Mn^{2+} in II-VI compounds and Mn^{3+} in GaN, respectively.

There are persisting uncertainties concerning the distribution (random vs clustering [56]) and the location of transition metal (TM) impurities in the tetradymite lattice (substitutional vs interstitial positions in the van der Waals gap [57]). Nevertheless, a series of arguments allows extending the conclusion about the dominance of the superexchange to topological tetradymite chalcogenides doped by substitutional V, Cr, or Fe ions, whose magnetism has so far been merely attributed to

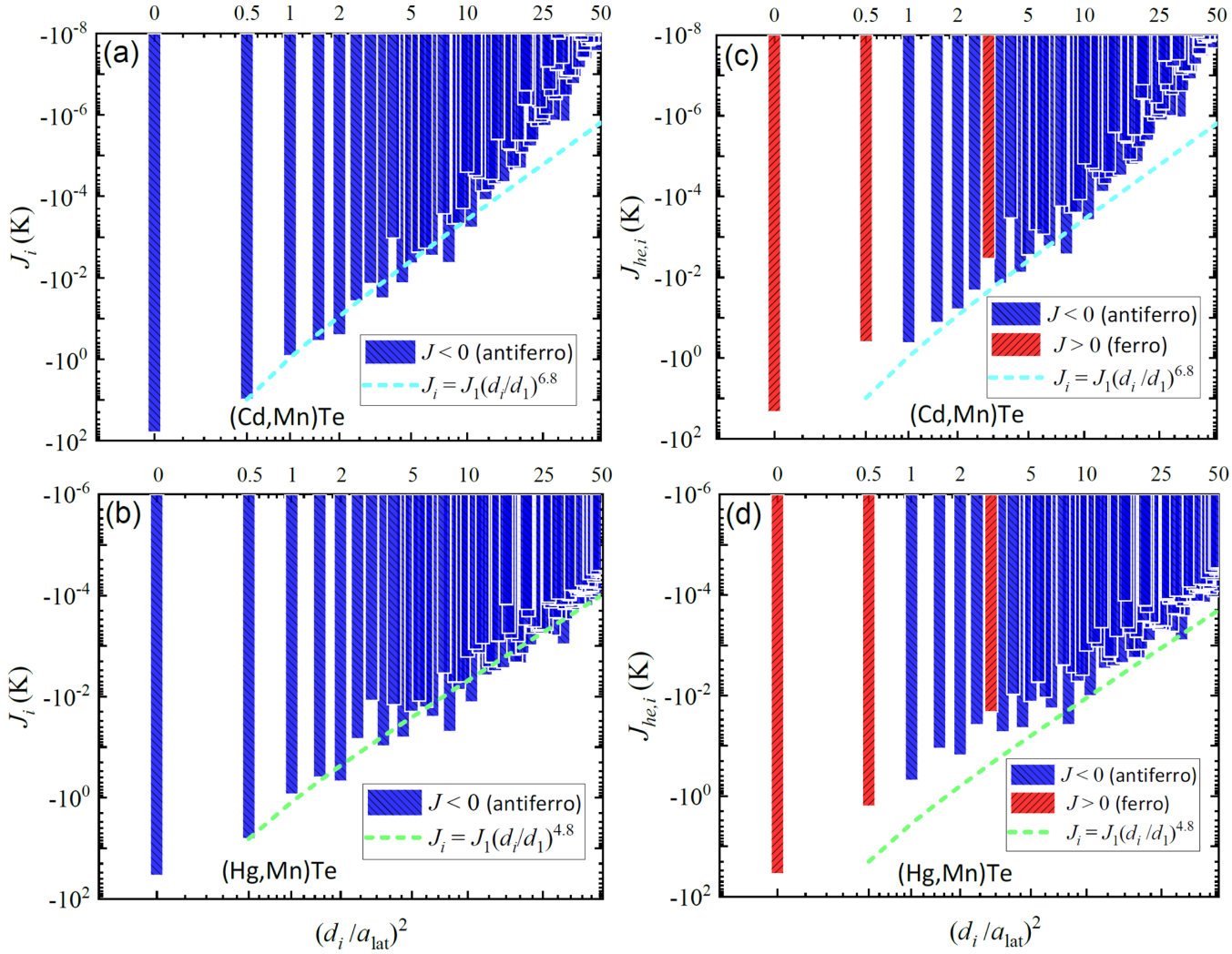

FIG. 2. (a),(b) Computed total exchange energies J_i and (c),(d) the interband BR contribution $J_{i,he}$ for Mn pairs (including the self-interaction values J_0) vs Mn-Mn distances d_i in the unit of the lattice parameter $a_{\rm lat}$ for (a),(c) CdTe and (b),(d) HgTe. Dashed lines indicate $J_i \sim d_i^{-n}$ with $n = 6.8$ and 4.8, as found experimentally for $Cd_{1-x}Mn_xTe$ [49] and $Hg_{1-x}Mn_xTe$ [50], respectively.

the Van Vleck mechanism [9,10]. (i) These impurities appear isoelectronic [9,10,27], which means that d orbitals remain fully occupied or empty. Moreover, as in other DMSs, correlations, together with the Jahn-Teller effect and dilution, enhance the d orbital localization further on. Accordingly, the double-exchange scenario, put forward when interpreting *ab initio* results [28,30], is not valid. (ii) Another *ab initio* study reveals the insensitivity of the spin-spin coupling energy of the band inversion [29], with the finding contradicting the Van Vleck model. (iii) Recent studies of x-ray magnetic circular dichroism and resonant photoelectron spectroscopy demonstrate similarities of p-d hybridization effects in V- or Cr-doped $(Bi_xSb_{1-x})_2Te_3$ [30] and II-VI DMSs [40], in particular, stronger hybridization of t_{2g} TM levels compared to the e_g case, which implies a similar physics of spin-spin coupling as found in tetrahedrally coordinated DMSs. (iv) As superexchange prevails over the interband Van Vleck mechanism in the zero-gap case, it should dominate even more strongly in the gapped topological systems. (v) From the direct computations for tetrahedral systems carried out here and previously [36,37,58], supported by experimental data [39,49,50,59,60], we know that the superexchange is ferromagnetic for d^3 and d^4, whereas it is antiferromagnetic for d^5 and d^6 cases. According to the experimental results [9,10,27] and *ab initio* studies [28], the same sequence occurs in tetradymite topological insulators, except for the Mn case, as Mn acts as an acceptor [61], so that the RKKY interaction accompanies the antiferromagnetic superexchange, such as in (Ga,Mn)As [6,62]. Altogether, these arguments indicate that the TM charge state and coordination, more than a topological class, govern the magnetic properties of DMSs.

Acknowledgments. The work is supported by the Foundation for Polish Science through the International Research Agendas program co-financed by the European Union within the Smart Growth Operational Programme. J.A.M. acknowledges the support of the National Science Centre (Poland) under Grant No. UMO-218/31/BST3/03758. We acknowledge the access to the computing facilities of the Interdisciplinary Center of Modeling at the University of Warsaw (ICM UW), Grant No. G68-12.

[1] R. M. White, *Quantum Theory of Magnetism* (Springer-Verlag, Berlin, 2007), pp. 1–213.

[2] C. Zener, Interaction between the *d* shells in the transition metals, Phys. Rev. **81**, 440 (1951).

[3] T. Dietl and J. Spałek, Effect of Fluctuations of Magnetization on the Bound Magnetic Polaron: Comparison with Experiment, Phys. Rev. Lett. **48**, 355 (1982).

[4] T. Dietl, Spin dynamics of a confined electron interacting with magnetic or nuclear spins: A semiclassical approach, Phys. Rev. B **91**, 125204 (2015).

[5] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Zener model description of ferromagnetism in zinc-blende magnetic semiconductors, Science **287**, 1019 (2000).

[6] T. Dietl and H. Ohno, Dilute ferromagnetic semiconductors: Physics and spintronic structures, Rev. Mod. Phys. **86**, 187 (2014).

[7] T. Jungwirth, J. Wunderlich, V. Novák, K. Olejník, B. L. Gallagher, R. P. Campion, K. W. Edmonds, A. W. Rushforth, A. J. Ferguson, and P. Němec, Spin-dependent phenomena and device concepts explored in (Ga,Mn)As, Rev. Mod. Phys. **86**, 855 (2014).

[8] T. Dietl, A. Haury, and Y. M. d'Aubigne, Free carrier-induced ferromagnetism in structures of diluted magnetic semiconductors, Phys. Rev. B **55**, R3347 (1997).

[9] He Ke, Yayu Wang, and Qi-Kun Xue, Topological materials: Quantum anomalous Hall system, Annu. Rev. Cond. Mat. Phys. **9**, 329 (2018).

[10] Y. Tokura, K. Yasuda, and A. Tsukazaki, Magnetic topological insulators, Nat. Rev. Phys. **1**, 126 (2019).

[11] Cui-Zu Chang, Jinsong Zhang, Xiao Feng, Jie Shen, Zuocheng Zhang, Minghua Guo, Kang Li, Yunbo Ou, Pang Wei, Li-Li Wang, Zhong-Qing Ji, Yang Feng, Shuaihua Ji, Xi Chen, Jinfeng Jia, Xi Dai, Zhong Fang, Shou-Cheng Zhang, Ke He, Yayu Wang *et al.*, Experimental observation of the quantum anomalous Hall effect in a magnetic topological insulator, Science **340**, 167 (2013).

[12] Di Xiao, Jue Jiang, Jae-Ho Shin, Wenbo Wang, Fei Wang, Yi-Fan Zhao, Chaoxing Liu, Weida Wu, M. H. W. Chan, N. Samarth, and Cui-Zu Chang, Realization of the Axion Insulator State in Quantum Anomalous Hall Sandwich Heterostructures, Phys. Rev. Lett. **120**, 056801 (2018).

[13] Y. Fan, P. Upadhyaya, X. Kou, M. Lang, So Takei, Z. Wang, J. Tang, L. He, Li-Te Chang, M. Montazeri, G. Yu, W. Jiang, T. Nie, R. N. Schwartz, Y Tserkovnyak, and K. L. Wang, Magnetization switching through giant spin-orbit torque in a magnetically doped topological insulator heterostructure, Nat. Mater. **13**, 699 (2014).

[14] Q. L. He, L. Pan, A. L. Stern, E. C. Burks, X. Che, G. Yin, J. Wang, B. Lian, Q. Zhou, E. S. Choi, K. Murata, X. Kou, Z. Chen, T. Nie, Q. Shao, Y. Fan, S.-C. Zhang, K. Liu, J. Xia, and K. L. Wang, Chiral Majorana fermion modes in a quantum anomalous Hall insulator–superconductor structure, Science **357**, 294 (2017).

[15] M. Kayyalha, Di Xiao, R. Zhang, J. Shin, J. Jiang, F. Wang, Yi-Fan Zhao, R. Xiao, L. Zhang, K. M. Fijalkowski, P. Mandal, M. Winnerlein, C. Gould, Qi Li, L. W. Molenkamp, M. H. W. Chan, N. Samarth, and Cui-Zu Chang, Absence of evidence for chiral Majorana modes in quantum anomalous Hall-superconductor devices, Science **367**, 64 (2020).

[16] R. Yu, W. Zhang, H.-J. Zhang, S.-C. Zhang, X. Dai, and Z. Fang, Quantized anomalous Hall effect in magnetic topological insulators, Science **329**, 61 (2010); see Eq. (S1) in Supporting Online Material.

[17] N. Bloembergen and T. J. Rowland, Nuclear spin exchange in solids: Tl^{203} and Tl^{205} magnetic resonance in thallium and thallic oxide, Phys. Rev. **97**, 1679 (1955).

[18] G. Bastard and C. Lewiner, Indirect-exchange interactions in zero-gap semiconductors, Phys. Rev. B **20**, 4256 (1979).

[19] C. Lewiner and G. Bastard, Indirect exchange interaction in extremely non-parabolic zero-gap semiconductors, J. Phys. C: Solid State Phys. **13**, 2347 (1980).

[20] Ven-Chung Lee, Indirect exchange interaction in the zero-gap semiconductor $Hg_{1-x}Mn_xTe$, Phys. Rev. B **37**, 8849 (1988).

[21] C. Śliwa and T. Dietl, Thermodynamic perturbation theory for noninteracting quantum particles with application to spin-spin interactions in solids, Phys. Rev. B **98**, 035105 (2018).

[22] C. Autieri, C. Śliwa, R. Islam, G. Cuono, and T. Dietl, Momentum-resolved spin splitting in Mn-doped trivial CdTe and topological HgTe semiconductors, Phys. Rev. B **103**, 115209 (2021).

[23] B. E. Larson, K. C. Hass, H. Ehrenreich, and A. E. Carlsson, Theory of exchange interactions and chemical trends in diluted magnetic semiconductors, Phys. Rev. B **37**, 4137 (1988).

[24] A. Savoyant, S. D'Ambrosio, R. O. Kuzian, A. M. Daré, and A. Stepanov, Exchange integrals in Mn- and Co-doped II-VI semiconductors, Phys. Rev. B **90**, 075205 (2014).

[25] J. Spałek, A. Lewicki, Z. Tarnawski, J. K. Furdyna, R. R. Galazka, and Z. Obuszko, Magnetic susceptibility of semimagnetic semiconductors: The high-temperature regime and the role of superexchange, Phys. Rev. B **33**, 3407 (1986).

[26] A. Lewicki, J. Spałek, J. K. Furdyna, and R. R. Gałazka, Magnetic susceptibility of diluted magnetic (semimagnetic) semiconductors: Further evidence for superexchange, Phys. Rev. B **37**, 1860 (1988).

[27] Y. Satake, J. Shiogai, G. P. Mazur, S. Kimura, S. Awaji, K. Fujiwara, T. Nojima, K. Nomura, S. Souma, T. Sato, T. Dietl, and A. Tsukazaki, Magnetic-field-induced topological phase transition in Fe-doped $(Bi, Sb)_2Se_3$ heterostructures, Phys. Rev. Materials **4**, 044202 (2020).

[28] M. G. Vergniory, M. M. Otrokov, D. Thonig, M. Hoffmann, I. V. Maznichenko, M. Geilhufe, X. Zubizarreta, S. Ostanin, A. Marmodoro, J. Henk, W. Hergert, I. Mertig, E. V. Chulkov, and A. Ernst, Exchange interaction and its tuning in magnetic binary chalcogenides, Phys. Rev. B **89**, 165202 (2014).

[29] J. Kim, S.-H. Jhi, A. H. MacDonald, and R. Wu, Ordering mechanism and quantum anomalous Hall effect of magnetically doped topological insulators, Phys. Rev. B **96**, 140410(R) (2017).

[30] T. R. F. Peixoto, H. Bentmann, P. Rüßmann, A.-V. Tcakaev, M. Winnerlein, S. Schreyeck, S. Schatz, R. C. Vidal, F. Stier, V. Zabolotnyy, R. J. Green, C. H. Min, C. I. Fornari, H. Maaß, H. B. Vasili, P. Gargiani, M. Valvidares, A. Barla, J. Buck, M. Hoesch *et al.*, Non-local effect of impurity states on the exchange coupling mechanism in magnetic topological insulators, npj Quantum Mater. **5**, 87 (2020).

[31] T. Dietl, (Diluted) magnetic semiconductors, in *Handbook of Semiconductors*, Vol. 3B, edited by S. Mahajan (North Holland, Amsterdam, 1994), p. 1270.

[32] T. Dietl, H. Ohno, and F. Matsukura, Hole-mediated ferromagnetism in tetrahedrally coordinated semiconductors, Phys. Rev. B **63**, 195205 (2001).

[33] D. Ferrand, J. Cibert, A. Wasiela, C. Bourgognon, S. Tatarenko, G. Fishman, T. Andrearczyk, J. Jaroszynski, S. Kolesnik, T. Dietl, B. Barbara, and D. Dufeu, Carrier-induced ferromagnetism in p-$Zn_{1-x}Mn_x$ Te, Phys. Rev. B **63**, 085201 (2001).

[34] J. Ginter, J. Kossut, and L. Świerkowski, Indirect exchange interaction via electrons in spin-orbit coupled bands in semiconductors, Phys. Stat. Solidi (B) **96**, 735 (1979).

[35] J. Blinowski and P. Kacman, Superexchange in $A^{II}B^{VI}$ diluted magnetic semiconductors with Mn, Fe and Co ions, Acta Phys. Pol. A **87**, 539 (1995).

[36] J. Blinowski, P. Kacman, and J. A. Majewski, Ferromagnetic superexchange in Cr-based diluted magnetic semiconductors, Phys. Rev. B **53**, 9524 (1996).

[37] C. Simserides, J. A. Majewski, K. N. Trohidou, and T. Dietl, Theory of ferromagnetism driven by superexchange in dilute magnetic semi-conductors, EPJ Web Conf. **75**, 01003 (2014).

[38] M. Sawicki, T. Devillers, S. Gałęski, C. Simserides, S. Dobkowska, B. Faina, A. Grois, A. Navarro-Quezada, K. N. Trohidou, J. A. Majewski, T. Dietl, and A. Bonanni, Origin of low-temperature magnetic ordering in $Ga_{1-x}Mn_x$ N, Phys. Rev. B **85**, 205204 (2012).

[39] S. Stefanowicz, G. Kunert, C. Simserides, J. A. Majewski, W. Stefanowicz, C. Kruse, S. Figge, Tian Li, R. Jakieła, K. N. Trohidou, A. Bonanni, D. Hommel, M. Sawicki, and T. Dietl, Phase diagram and critical behavior of a random ferromagnet $Ga_{1-x}Mn_xN$, Phys. Rev. B **88**, 081201(R) (2013).

[40] P. Kacman, Spin interactions in diluted magnetic semiconductors and magnetic semiconductor structures, Semicon. Sci. Technol. **16**, R25 (2001).

[41] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.104.L220404 for additional information on (i) the various exchange mechanisms, (ii) a comparison of the second-order perturbation theory in the p-d exchange integral compared to the fourth-order perturbation theory in the hybridization matrix elements, and (iii) issues with the integration method adopted in Refs. [18–20]. The Supplemental Material also contains additional Refs. [63–65].

[42] S. Froyen, Brillouin-zone integration by Fourier quadrature: Special points for superlattice and supercell calculations, Phys. Rev. B **39**, 3168 (1989).

[43] L. Liu and E. Tosatti, Dielectric Constant and Mobility of a Doped Zero-Gap Semiconductor, Phys. Rev. Lett. **23**, 772 (1969).

[44] J. G. Broerman, Anomalous Mobility and Dielectric Singularity of α-Sn, Phys. Rev. Lett. **24**, 450 (1970).

[45] B. E. Larson, K. C. Hass, and R. L. Aggarwal, Effects of internal exchange fields on magnetization steps in diluted magnetic semiconductors, Phys. Rev. B **33**, 1789 (1986).

[46] R. R. Galazka, W. Dobrowolski, J. P. Lascaray, M. Nawrocki, A. Bruno, J. M. Broto, and J. C. Ousset, Nearest neighbor exchange constants in $Hg_{1-x}Mn_xTe$, $Hg_{1-x}Mn_xSe$ and other semimagnetic semiconductors, J. Magn. Magn. Mater. **72**, 174 (1988).

[47] R. V. Cherbunin, V. M. Litviak, I. I. Ryzhov, A. V. Koudinov, S. Elsässer, A. Knapp, T. Kiessling, J. Geurts, S. Chusnutdinow, T. Wojtowicz, and G. Karczewski, High-resolution resonance spin-flip Raman spectroscopy of pairs of manganese ions in a CdTe quantum well, Phys. Rev. B **101**, 241301(R) (2020).

[48] J. P. Lascaray, A. Bruno, J. C. Ousset, H. Rakoto, J. M. Broto, and S. Askenazy, Quasi-static pulsed high magnetic field used to study magnetic properties of semimagnetic semiconductors, Phys. B: Condens. Matter **155**, 353 (1989).

[49] A. Twardowski, H. J. M. Swagten, W. J. M. de Jonge, and M. Demianiuk, Magnetic behavior of the diluted magnetic semiconductor $Zn_{1-x}Mn_xSe$, Phys. Rev. B **36**, 7013 (1987).

[50] R. R. Gałązka, Influence of electron subsystem on magnetic properties of semimagnetic semiconductors, J. Magn. Magn. Mater. **140-144**, 13 (1995).

[51] M. Sawicki, E. Guziewicz, M. I. Łukasiewicz, O. Proselkov, I. A. Kowalik, W. Lisowski, P. Dluzewski, A. Wittlin, M. Jaworski, A. Wolska, W. Paszkowicz, R. Jakiela, B. S. Witkowski, L. Wachnicki, M. T. Klepka, F. J. Luque, D. Arvanitis, J. W. Sobczak, M. Krawczyk, A. Jablonski *et al.*, Homogeneous and heterogeneous magnetism in (Zn,Co)O: From a random antiferromagnet to a dipolar superferromagnet by changing the growth temperature, Phys. Rev. B **88**, 085204 (2013).

[52] R. R. Galazka, S. Nagata, and P. H. Keesom, Paramagnetic–spin-glass–antiferromagnetic phase transitions in $Cd_{1-x}Mn_xTe$ from specific heat and magnetic susceptibility measurements, Phys. Rev. B **22**, 3344 (1980).

[53] D. A. Smith, The zero-frequency susceptibility of spin glasses and micromagnets, J. Phys. F **5**, 2148 (1975).

[54] A. Mycielski, C. Rigaux, M. Menant, T. Dietl, and M. Otto, Spin glass phase transition in $Hg_{1-k}Mn_kTe$ semimagnetic semiconductors, Solid State Commun. **50**, 257 (1984).

[55] G. Bednik, Antiferromagnetism and spin density waves in three-dimensional Dirac metals, Phys. Rev. B **102**, 125119 (2020).

[56] Cui-Zu Chang, Peizhe Tang, Yi-Lin Wang, Xiao Feng, Kang Li, Zuocheng Zhang, Yayu Wang, Li-Li Wang, Xi Chen, Chaoxing Liu, Wenhui Duan, Ke He, Xu-Cun Ma, and Qi-Kun Xue, Chemical-Potential-Dependent Gap Opening at the Dirac Surface States of Bi_2Se_3 Induced by Aggregated Substitutional Cr Atoms, Phys. Rev. Lett. **112**, 056801 (2014).

[57] J. Růžička, O. Caha, V. Holý, H. Steiner, V. Volobuiev, A. Ney, G. Bauer, T. Duchoň, K. Veltruská, I. Khalakhan, V. Matolín, E. F. Schwier, H. Iwasawa, K. Shimada, and G. Springholz, Structural and electronic properties of manganese-doped Bi_2Te_3 epitaxial layers, New J. Phys. **17**, 013028 (2015).

[58] J. Blinowski, P. Kacman, and J. A. Majewski, Superexchange in diluted magnetic semiconductors, Mater. Sci. Forum **182-184**, 779 (1995).

[59] A. Twardowski, Magnetic properties of Fe-based diluted magnetic semiconductors, J. Appl. Phys. **67**, 5108 (1990).

[60] R. Watanabe, R. Yoshimi, M. Kawamura, M. Mogi, A. Tsukazaki, X. Z. Yu, K. Nakajima, K. S. Takahashi, M. Kawasaki, and Y. Tokura, Quantum anomalous Hall effect driven by magnetic proximity coupling in all-telluride based heterostructure, Appl. Phys. Lett. **115**, 102403 (2019).

[61] Y. S. Hor, P. Roushan, H. Beidenkopf, J. Seo, D. Qu, J. G. Checkelsky, L. A. Wray, D. Hsieh, Y. Xia, S.-Y. Xu, D. Qian, M. Z. Hasan, N. P. Ong, A. Yazdani, and R. J. Cava, Development of ferromagnetism in the doped

topological insulator $Bi_{2-x}Mn_xTe_3$, Phys. Rev. B **81**, 195203 (2010).

[62] K. Sato, L. Bergqvist, J. Kudrnovský, P. H. Dederichs, O. Eriksson, I. Turek, B. Sanyal, G. Bouzerar, H. Katayama-Yoshida, V. A. Dinh, T. Fukushima, H. Kizaki, and R. Zeller, First-principles theory of dilute magnetic semiconductors, Rev. Mod. Phys. **82**, 1633 (2010).

[63] A. Bonanni and T. Dietl, A story of high-temperature ferromagnetism in semiconductors, Chem. Soc. Rev. **39**, 528 (2010).

[64] J. R. Schrieffer and P. A. Wolff, Relation between the Anderson and Kondo Hamiltonians, Phys. Rev. **149**, 491 (1966).

[65] R. Winkler, *Spin-Orbit Coupling Effects in Two-Dimensional Electron and Hole Systems*, Springer Tracts in Modern Physics, Vol. 191 (Springer, Berlin, 2003).