Superexchange in Dilute Magnetic Dielectrics: Application to 
\((\text{Ti,Co})\text{O}_2\)

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Abstract

We extend the model of ferromagnetic superexchange in dilute magnetic semiconductors to the ferromagnetically ordered highly insulating compounds (dilute magnetic dielectrics). The intrinsic ferromagnetism without free carriers is observed in oxygen-deficient films of anatase TiO\(_2\) doped with transition metal impurities in cation sublattice. We suppose that ferromagnetic order arises due to superexchange between complexes [oxygen vacancies + magnetic impurities], which are stabilized by charge transfer from vacancies to impurities. The Hund rule controls the superexchange via empty vacancy related levels so that it becomes possible only for the parallel orientation of impurity magnetic moments. The percolation threshold for magnetic ordering is determined by the radius of vacancy levels, but the exchange mechanism does not require free carriers. The crucial role of the non-stoichiometry in formation of the ferromagnetism makes the Curie temperatures extremely sensitive to the methods of sample preparation.

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I. INTRODUCTORY NOTES

Recent experimental and theoretical investigations of dilute ferromagnetic semiconductors are concentrated mostly on II-VI and III-V materials doped with Mn impurities (see, e.g., Ref. 1). The theoretical explanation is based on the Vonsovskii-Zener model, which implies existence of a direct exchange interaction between the localized spins of magnetic ions (Mn) and itinerant spins of free carriers (holes in case of (Ga,Mn)As and related materials). This interaction generates RKKY-type indirect exchange between Mn ions, and the latter is claimed to be the source of long-range FM order in dilute magnetic semiconductor (DMS) alloys. It was shown recently that the kinematic exchange interaction (specific version of superexchange between localized Mn moments via empty valence states of the host material) arises in p-type III-V DMS. This mechanism works together with the RKKY interaction because of the noticeable hybridization between d-electrons of Mn ions and p-holes near the top of the valence band. Both mechanisms are characterized by a direct proportionality between the carrier concentration and Curie temperature $T_C$. However, it was pointed out recently that an application of the RKKY based model to disordered DMS may be questionable if one properly takes oscillating character of the RKKY interaction into account.

Meanwhile, another family of dilute ferromagnetic alloys was discovered during the recent five years, where the ferromagnetic order with a high $T_C$ exists in spite of the low carrier concentration. The ferromagnetic order was observed even in the insulating materials with carriers frozen out at $T \to 0$. These are metal oxides doped with transition metal ions (see, e.g., Ref. 5 for a review). The absence of free carriers leaves no room for a RKKY interaction in this case, so the question about the origin of ferromagnetism arises anew.

The metal oxides like ZnO, SnO$_2$, TiO$_2$ are classified as wide-gap semiconductors. In this sense they are close to the wide-gap III-V nitrides GaN and AlN. We analyzed the case of $n$-(Ga,Mn)N in Ref. 3, where the leading interaction mechanism is the Zener type double exchange via empty states in the impurity band. Magnetic ions (MI) in all these compounds substitute for metallic cations. From this point of view, the difference between the two groups is in the charge state of substitutional impurity: the neutral state of an impurity should be MI$^{3+}$ in nitrides and MI$^{4+}$ in oxides. This difference implies different structures of spin multiplets, which is important for the magnetic properties of metallic alloys. However, due to a noticeable covalency of the host materials, MI should saturate the
broken bonds by its own valent electrons, which are donated by the 3d shells. This means that the violation of the electronic structure inserted by the dopants cannot be ignored in the studies of magnetic properties of DMS. Moreover the recent paper emphasizes the role of bound exciton states in ZnO bases compounds and indicates the correlation between the experimentally observed chemical trends in ferromagnetism and the electron binding energies to various MI.

Among the most salient features of magnetism in dilute ferromagnetic oxides one should mention an extreme sensitivity of the magnetic order to the growth and annealing conditions. We believe that this is an integral feature of magnetism in these materials, and the ferromagnetic ordering with high $T_C$ is mediated by intrinsic or extrinsic defects, which form complexes with magnetic dopants. Such point of view is supported by recent experimental studies of Co-doped and Cr-doped TiO$_2$. It was noticed, in particular, that in the most perfect (Ti, Cr)O$_2$ crystals the hysteresis loop at a given temperature is essentially less distinct than in 'bad quality' samples. Besides, the enormous scatter of effective magnetic moment per cation is observed in all ferromagnetic oxides, and the concentration of magnetic dopants lies far below the percolation threshold $x_c$ associated with the nearest-neighbor cation coupling. Basing on these facts, one concludes that non-magnetic defects are also involved in formation of the localized magnetic moments. They influence their magnitude and localization, and this influence is sensitive to the growth and annealing regimes.

Recent theories of magnetism in $n$-type dilute magnetic oxides appeal to magnetic polarons as mediators of indirect exchange between magnetic dopants. In this case the extrinsic defects are donor impurities, which donate free electrons occupying the bottom of conduction band. These electrons form shallow spin-polarized polaronic states due to strong exchange with the localized magnetic moments of transition metal dopants. A large radius of these states makes the polaronic percolation threshold essentially lower than $x_c$.

One should note, however, that the carrier concentration in these compounds is vanishingly small, and that is why they have been proposed to be called dilute magnetic dielectrics (DMD). It means that we need now to find an exchange mechanism, which works in the case of really insulating oxides. In this paper we construct a model of insulating oxide, which considers intrinsic non-magnetic defects as an integral part of the ordering mechanism. We concentrate mainly on the superexchange between magnetic ions mediated by
oxygen vacancies, which is believed to be the source of ferromagnetic order in TiO$_2$ diluted with Co.

**II. MODEL OF DILUTE MAGNETIC OXIDE**

As has been established three decades ago, the basic microscopic Hamiltonian, which gives an adequate quantitative and qualitative description of electronic and magnetic properties of semiconductors doped by transition metal ions is the Anderson Hamiltonian (see summarizing monographs). Indirect RKKY, superexchange and double exchange interactions between magnetic ions may be derived microscopically from the multisite generalization of the Anderson model. The Hamiltonian of this model reads

$$H = H_h + H_d + H_{hd},$$

where $H_h$ describes the electronic structure of the host semiconductor, $H_d = \sum_j H_{dj}$ is the Hamiltonian of strongly interacting electrons in the $d$-shells of magnetic ions located in the lattice sites $j$, and $H_{hd} = \sum_j H_{hdj}$ is the hybridization Hamiltonian describing the covalent bonding between the impurity $3d$-electrons and the host $p$ electrons (the contribution of hybridization with the host $s$ electrons in the effective exchange is generally negligibly small). Usually the direct $dp$ exchange is neglected in the Anderson model, since the indirect exchange coupling dominates in the covalent materials.

From the point of view of the Anderson model, the crucial difference between the narrow-gap and wide-gap semiconductors is in the position of $d$-levels of the impurity electrons relative to the top of the valence band. Due to a strong electron-electron interaction in the $3d$ shell (Coulomb blockade), the impurity energy level $\varepsilon_d$ should be defined as an "addition energy" for the reaction $d^{n-1} + e_b \rightarrow d^n$, i.e. the energy cost of adding one more electron, $e_b$, from the band continuum to the impurity $3d$-shell,

$$\varepsilon_d = E(d^n) - E(d^{n-1})$$

where $E(d^p)$ is the total energy of a "pseudo-ion" consisting of an impurity in a configuration $3d^p$ and distorted electron distribution in the host semiconductor.

In this definition the energy is counted from the top of the valence band, which is the source of additional electrons for the impurity. It is known, e.g. that Mn, the most popular
magnetic impurity, has especially deep $d$ level corresponding to the half-filled $d$ shell in the configuration 3$d^6$. This level is always occupied in such narrow-band semiconductors as (Ga,Mn)As, (Ga,Mn)P, (In,Mn)As. This means that the addition energy $\varepsilon_d = E(d^5) - E(d^4)$ is well below the energy, $\varepsilon_p$, of the top of the valence band. On the contrary, $\varepsilon_d > \varepsilon_p$ in the wide gap semiconductors like GaN\textsuperscript{19} and the occupation of this state depends on the type and concentration of other defects.

One should compare this picture with the energy spectra of magnetically doped metal oxides. Situation with the transition metal impurities in ZnO is apparently close to that in GaN. Both these materials are wide band gap semiconductors, and the only difference is that the neutral state of magnetic impurity in ZnO is MI$^{2+}$. The corresponding energy levels arise, as a rule, within the band gap, and the states with other oxidation numbers may appear only due to an additional $n$- or $p$-doping.

The calculation\textsuperscript{20} of addition energies for MI$^{n+}$ states in rutile TiO$_2$ has shown that the "energy levels" $\varepsilon_d$ for neutral MI$^{4+}$ states are usually deep in the valence band for heavy transition metal ions (starting with Mn), whereas the condition $\varepsilon_d > \varepsilon_p$ is fulfilled for the addition energies of charged MI$^{3+}$ and MI$^{2+}$ ions. Recent LSDA+U calculations\textsuperscript{21} for anatase TiO$_2$ doped with Mn, Fe and Ni are in a general agreement with those earlier cluster calculations.

This means that the ground state of this system should be TiO$_2$:MI$^{4+}$. In this situation the Anderson Hamiltonian may be immediately transformed into the $sd$-exchange model by means of the Schrieffer-Wolff transformation. In the absence of free carriers the short-range effective inter-impurity exchange interaction is exponentially weak and there is no chance for magnetic ordering with reasonably high $T_C$. However, the situation in real materials is quite different. Leaving aside early results for the samples with secondary phase inclusions\textsuperscript{5} we concentrate on the recent data for the materials, which are believed to be genuine ferromagnetic DMD free from magnetic precipitates. As was mentioned above, the room temperature ferromagnetic order was detected in Cr and Co doped anatase TiO$_2$, and in both cases native defects are involved in formation of the ferromagnetic order.\textsuperscript{2,10} In the latter case these defects are apparently oxygen vacancies. Below, we adapt our theory\textsuperscript{3} for vacancy mediated indirect exchange. The case of (Ti,Cr)O$_2$ will be discussed in the concluding section.
III. VACANCY-RELATED SUPEREXCHANGE MECHANISM

In the highly insulating ferromagnetic (Ti,Co)O$_2$, magnetic ions are in Co$^{2+}$ state. A seeming contradiction with the requirement of electrical neutrality of the substitutional impurities$^{20}$ may be resolved, if one takes into account the intrinsic non-stoichiometry of the samples: oxygen vacancies $V_O$, are created in the process of sample preparation. It follows from the general neutrality consideration that an oxygen vacancy binds two electrons on a discrete level in the band gap to saturate the dangling bonds. In the process of annealing a noticeable amount of oxygen vacancies are captured by Co substitution impurities in cation sites. In the case, when $V_O$ arises in the octahedron containing a Co ion, the double defect Co$^2-$ $V_O$ is formed, and its stability (or metastability with respect to formation of Ti$^-$ $V_O$ complexes) is determined by the charge transfer of these two electrons in accordance with the reaction

$$V_O^0(p^2) + \text{Co}^{4+}(d^5) \rightarrow [\text{V}_O^{2+}\text{Co}^{2+}(d^7)]. \quad (3)$$

A presumable scheme of the energy levels, which substantiates such charge transfer is shown in Fig. 1. The configurations $d^n$ of 3$d$ shells corresponding to different charge states of Co and Cr impurities are pointed out. The dashed band shows the position of vacancy-related levels below the bottom of conduction band $\varepsilon_c$.

As a result of charge transfer reaction (3), the vacancy related electrons are captured by [V$O^{2+}\text{Co}^{2+}$] complexes, the system remains insulating and the magnetic interaction between these complexes predetermines the magnetic properties of the system.

In this section we construct a microscopic model of impurity-vacancy complexes basing on our previous studies$^3$ of double ferromagnetic exchange in (Ga,Mn)As and the electronic structure of complexes Cr-$V_O$ in (Ga,Cr)As$^{22}$ as well as on the numerical calculations of the electronic structure of $V_O$ defects in TiO$_2$ $^{20}$ and doped non-stoichiometric (oxygen deficient) (Ti,Co)O$_2$ $^{21,30}$.

The structure of Hamiltonian, which describes the oxygen deficient (Ti,Co)O$_2$ is the same as in Eq. (1), but the oxygen vacancies should be taken into account in the host Hamiltonian $H_h$. We start with a quantum-chemical picture of an isolated defect cell, which contains both Co impurity substituting for a Ti cation and the vacancy in one of the apices of oxygen octahedra. We mark the cell by the index $j$ and consider the Hamiltonian

$$H_{Vj} = H'_{hj} + H_{dj} + H_{hdj}. \quad (4)$$
FIG. 1: Impurity-related and vacancy-related energy levels in cation substituted non-stoichiometric TiO₂.

Now the first term $H'_{hj}$ describes the host crystal with the vacancy, $V_O$, in the cell $j$. This Hamiltonian may be diagonalized, and the resulting spectrum contains the band continuum distorted by the vacancy potential and the discrete levels $\epsilon_{v\mu}$ for electrons bound on the dangling bonds in the defect cell.

The Hamiltonian $H_{hdj}$ rewritten in this basis contains terms describing hybridization with both continuum and discrete states of $H'_{hj}$. The general form of $H_{hdj}$ is

$$H_{hdj} = \sum_{\mu\nu\sigma} \sum_{\tau_d\tau_o} \left( V_{j\nu\mu}(\tau_d, \tau_o) d_{j+\tau_d,\mu\sigma}^\dagger c_{j+\tau_o,\nu\sigma} + h.c. \right)$$

$$+ \sum_{\kappa\mu\sigma} \sum_{a=v,c} \left( V_{j\kappa\mu}(\tau_d, \kappa) d_{j+\tau_d,\mu\sigma}^\dagger c_{\kappa\sigma a} + h.c. \right).$$

(5)

Here the operators $d_{j+\tau_d,\mu\sigma}$ and $c_{j+\tau_o,\nu\sigma}$ stand for the localized $d\mu$ - and $p\nu$ - orbitals on the impurity site $R_i = R_j + \tau_d$ and the vacancy cite $R_o = R_j + \tau_o$, respectively, and the operators $c_{\kappa\sigma a}$ describe the continuous states in the host crystal valence ($a = v$) and conduction ($a = c$) bands.

Information about the vacancy-related states in anatase TiO₂ is rather scanty so we
refer to the data available for oxygen-deficient rutile TiO$\textsubscript{2}$. In accordance with numerical calculations\textsuperscript{29,30}, which correlate with the experimental observations, $V_{O}$ creates donor levels $\varepsilon_{o}$ a few tenth of an eV below the conduction band. The donor electrons saturate the dangling bonds with the neighboring atoms, so that the defect wave function has the largest amplitude at the next Ti neighbor of the vacancy and extends to several coordination spheres. The extended defect states form a band of donor levels already for 1% concentration of oxygen vacancies, i.e. the wave functions of the vacancy states effectively overlap when the vacancies are separated by a distance of about 5 interatomic spacings. This observation will be used below when estimating the Curie temperature. The calculated electronic structure for Co-doped oxygen deficient anatase TiO$\textsubscript{2}$ gives similar picture for the charge distribution and the density of states\textsuperscript{28}.

This observation verifies the model Hamiltonian (5) for the Co substitutional impurities. Its form implies a strong nearest-neighbor hybridization between the vacancy and impurity related states. Since the conduction band of TiO$\textsubscript{2}$ is formed mainly by the $d$-states of Ti sublattice, the matrix elements $V_{c\mu}$ in the second term in this Hamiltonian describe the hybridization of the Co impurity $d$-states with those in the cationic sublattice. Apparently one may neglect the hybridization $V_{c\mu}$ in comparison with $V_{j\nu\mu}$, and retain in this term only the hybridization $V_{j\nu\mu}$ with the oxygen-related p-states in the valence band.

We return now to are the energy level scheme Fig. 1 substantiating the charge transfer reaction (3). It is emphasized that we compare the one-electron energy levels of the oxygen vacancy with the corresponding levels of Co impurities in different charge states. These levels are defined as addition energies (2) corresponding to recharging processes $\text{Co}^{m+}/\text{Co}^{(m-1)+}$. These energies may be taken, i.e. from Ref. 20. Hybridization $V_{j\nu\mu}$ allows for an electron transfer of the two electrons from the vacancy level first to the level $\varepsilon_{d}(3+/4+)$ and then to the level $\varepsilon_{d}(2+/3+)$ and formation of the complex defect $[V_{O}^{2+}\text{Co}^{2+}]_{j}$ with seven electrons occupying the 3d-shell of the ion Co$^{2+}$ and empty extended V$\textsubscript{O}$-related states.

Indirect exchange interaction arises when the wave functions of two complexes centered in the cells $j$ and $i$ overlap. It is clear that the overlap is controlled by the radius of extended V$\textsubscript{O}$-related state. An obvious interaction mechanism is the superexchange, where two magnetic impurities exchange electrons via empty vacancy levels. It will be shown below that this interaction favors ferromagnetic ordering in the system.

The simplest way to construct an effective superexchange interaction operator is to
project the two-impurity Hamiltonian $H_{ji} = H_{dj} + H_{di} + H'_{hji} + H_{hdi} + H_{hhdj} + H_{hdj}$ onto the subspace $\langle ji | \ldots | ji \rangle_{2+}$ with fixed Co$^{2+}$ configurations of the two magnetic ions and also project out the charged impurity states Co$^{3+}$, which arise due to the hybridization $H_{hhdj} + H_{hdj}$. Here $H'_{hji}$ is the host Hamiltonian with two oxygen vacancies in the cells $j, i$. Then the fourth order term in the impurity-vacancy hybridization

$$
\langle ji | H_{hdy} \frac{1}{E_0 - H_{hji}^0} H_{hdi} \frac{1}{E_0 - H_{hji}^0} H_{hdi} \frac{1}{E_0 - H_{hji}^0} H_{hdy} | ji \rangle_{2+}
$$

(6)
gives the effective exchange vertex, represented graphically in Fig. 2. The resolvents, which appear in (6) correspond to the ground state $E_0$ of the non-hybridized Hamiltonian $H_{hji}^0 = H_{dj} + H_{di} + H'_{hji}$. The solid lines in this diagram stand for the definite charge and spin state of the impurity in the site $i$ or $j$ (Co$^{2+}$(d$^7$) and (Co$^{3+}$(d$^6$) in a given spin and orbital configuration). The vertices correspond to various terms in the hybridization Hamiltonian (5), which changes the impurity state from $d_i^7$ to $d_i^6$ and v.v. In the vertex $V_{\sigma \nu}$ an electron appears on the empty vacancy $\nu$ - orbital with the spin $\sigma$. In the vertex $V_{\alpha \mu}$ a hole (electron) appears in the valence (conduction) band. Yet, a similar process $d_i^7 \rightarrow d_i^6 + \nu'\sigma$ occurs around the counterpart site $j$. Then the two p-electrons change their "hosts" (two dashed lines in Fig. 2), and this is the end of the superexchange process. This scheme allows one to roughly estimate the effective exchange coupling as

$$
J_Z \sim V^4 / \Delta_{do}^2 D_o,
$$

(7)

where $\Delta_{do}$ is the energy of the transition (3), and $D_o$ is the characteristic energy scale of the vacancy related band under the bottom of conduction band.
A similar estimate may be found, e.g. in Refs. 23, where the superexchange between singly occupied states in the 4f-shell via empty states in conduction band was studied ($D_o$ in that case is the conduction band width). In the case of a singly occupied shell $f^1$ or $d^1$ there is no Hund interaction in the unfilled shell. As a result antiferromagnetic part of this interaction prevails (ferromagnetic channels are blocked by the Pauli principle)\textsuperscript{23}. In our case the superexchange mechanism favors the ferromagnetic alignment of spins since the intrashell Hund interaction suppresses the exchange by the electrons with antiparallel spins (see next section).

There seems to be much in common between the vacancy-related mechanism represented by Eqs. (6), (7) and the spin-polaron mechanism offered in Ref. 8. In both cases the effective radius of magnetic interaction is controlled by the extended donor states. It should be emphasized, however, that unlike the indirect exchange via the states in the donor impurity band\textsuperscript{8}, in our case the band of vacancy states may be empty (provided all the electrons from the vacancy levels are captured by acceptor-like magnetic impurities), so that this mechanism may be realized in highly insulating materials. On the other hand, the empty donor band of extended vacancy related states plays, in oxygen deficient (Ti)O$_2$, the role similar to that played by the empty states in the hole pockets of $p$-type (Ga,Mn)As in superexchange between magnetic ions (see Ref. 3). We will return to the comparison of superexchange mechanism in various dilute magnetic compounds in the concluding section.

IV. MICROSCOPIC THEORY OF SUPEREXCHANGE IN DMD

The simple estimate (7) by means of the fourth order perturbation equation (6) may be essentially improved. Basing on the theory of \textit{isolated} transition metal impurities in semiconductors,\textsuperscript{15,16} one may consider the effects of single-site hybridization between the $d$-orbitals of impurity and oxygen-related states in the valence band and vacancy levels and then use the perturbation theory approach for the \textit{intersite} hybridization effects responsible for the superexchange.

It is known that the main result of this hybridization is ‘swelling’ of the wave functions of the impurity $d$-electrons.\textsuperscript{15,16} These functions acquire ‘tails’ formed by a superposition of Bloch waves from valence and conduction bands. A localized vacancy state is also a superposition of the same Bloch waves. All these covalent effects modify the simple estimate (7),
which necessitate a more refined analysis within the microscopic Anderson-like Hamiltonian.

In this section we will derive equations for the superexchange interaction in the system of defects $[\text{Co}_{\text{Ti}}, \text{V}_{\text{O}}]$ by means of the Green function method developed in Ref. 3. For the purpose of practical calculations within this method, it is more convenient to write the term $H'_{h_j}$ in the model Hamiltonian (1) in the form

$$H'_{h_j} = \sum_{\kappa\alpha\sigma} \varepsilon_\kappa c_{\kappa\alpha\sigma}^\dagger c_{\kappa\alpha\sigma} + \sum_{\nu\sigma} \varepsilon_{\nu\sigma} c_{\nu\sigma}^\dagger c_{\nu\sigma} + \tau_{\nu\sigma} v_{\nu\sigma}.$$  \hspace{1cm} (8)

It is assumed in Eq. (8) that the host Hamiltonian with vacancies has been diagonalized, and the band states are classified by the index $\kappa$. Each vacancy in the site $j + \tau_\nu$ creates a localized level in the gap. It was found in the previous numerical calculations $^{20,29}$ that both the oxygen-related $p$-states in the valence band and the titanium-related $d$-states from the valence band contribute to formation of localized vacancy states, and the vacancy-related level arises slightly below the bottom of conduction band.

The term $H_d$ describing the subsystem of magnetic impurities in the Hamiltonian (1) has the form

$$H_d = \sum_j H_{d_j} = \sum_j \sum_{\mu\sigma} \varepsilon_\mu d_{\mu\sigma}^\dagger d_{\mu\sigma} + H_j^{\text{corr}}.$$  \hspace{1cm} (9)

Here the site indices are introduced in accordance with the definition given in (5), $H_j^{\text{corr}}$ includes all the Coulomb and exchange interactions responsible for the Hund rule within the $3d$-shells of Co ions. In accordance with this rule the Co $d$-shell contains seven electrons, five of which form the closed ‘inert’ $d_{\uparrow}^5(t_2^2e^2)$ subshell and the remaining two electrons form the open ‘active’ $d_{\downarrow}^2(t_\mu e_{\mu'})$ subshell. Only the electrons in the open subshell are involved in the hybridization induced superexchange. The reason for this discrimination is the above mentioned swelling of the impurity electron wave functions due to the hybridization with the host electrons, which is stronger for the open subshell than for the closed one.$^{15,16}$

It is easily seen from (8) that the fourth order transition

$$\langle d_{j_1}^5 d_{j_4}^2, d_{i_1}^5 d_{i_4}^2 | d_{i_1}^\dagger c_{\nu_1}^\dagger R_{ji}^2 d_{j_1}^\dagger c_{\nu_1}^\dagger R_{ji} d_{j_1} c_{\nu_1}^\dagger d_{j_1} | d_{j_1}^\dagger d_{j_4}^2, d_{i_1}^\dagger d_{i_4}^2 \rangle$$

for ferromagnetically aligned spins of two impurities is possible, whereas the similar process

$$\langle d_{j_1}^5 d_{j_4}^2, d_{i_1}^5 d_{i_4}^2 | d_{i_1}^\dagger c_{\nu_1}^\dagger R_{ji}^2 d_{j_1}^\dagger c_{\nu_1}^\dagger R_{ji} d_{j_1} c_{\nu_1}^\dagger d_{j_1} | d_{j_1}^\dagger d_{j_4}^2, d_{i_1}^\dagger d_{i_4}^2 \rangle$$

is suppressed due to the Hund rule for the occupation of subshells. Here $R_{ji} = (E_0 - H_{ji})^{-1}$ is the zeroth order resolvent.
Our task is to calculate the energy gain due to the electron exchange between the impurities with parallel spin alignment. Since no spin-flip occurs in the course of the exchange, the spin index may be omitted in the Hamiltonian $\text{5, 8, 10}$. This energy gain is given by the following equation$^{3, 25}$

$$E_{\text{magn}} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} \varepsilon \text{Tr} \Delta G[\varepsilon - i\delta \text{ sign}(\varepsilon - \eta)]d\varepsilon,$$

(10)

where $\Delta G$ is the part of the single electron Green function related to the spin-dependent interaction of magnetic impurities,

$$\Delta G(z) = (z - H)^{-1} - (z - H'_{ij})^{-1},$$

$\eta$ is the chemical potential. The integral in (10) contains contributions from both the valence band continuum and occupied discrete states in the energy gap.

When calculating $\Delta G(z)$, we exploited the following features of our problem.

(i) Since we are interested in the energy gain due to the parallel spin ordering, the spin-flip processes do not contribute to the relevant part of the system of Dyson equations for the Green function and these equations allow for an exact solution.$^{15}$

(ii) The calculation procedure may be radically simplified by using the analytical properties of $\text{Tr} \Delta G(z)$, which allow one to calculate the energy by summing over the empty states instead of integrating over the whole occupied part of the energy spectrum$^3$.

(iii) We are interested only in the trace of the Green function defined in the subspace $\langle d_j^\dagger d_i^\dagger | \ldots | d_i^\dagger d_j^\dagger \rangle$ (see Eq. (6)).

As was discussed above, the leading contribution to the formation of complex defect is due to the hybridization between the d-shells of magnetic impurities and the empty states in the band of vacancy related states below the bottom of conduction band. Thus, our next task is to calculate the upward shift of the $V_O$-related levels. For this sake one has to find the poles of the single electron Green function $G$. This function has the following block structure

$$G = \begin{pmatrix}
G_{\mu\mu'} & G_{\mu
u'} & G_{\mu
u'} \\
G_{\nu\mu'} & G_{\nu\nu'} & 0 \\
G_{\nu\mu'} & 0 & G_{\nu\nu'}
\end{pmatrix},$$

(11)

where the diagonal blocks are the two impurity ($G_{\mu\mu'}$), band ($G_{\nu\nu'}$) and single-vacancy ($G_{\nu\nu'}$) Green functions, respectively, and the off-diagonal blocks stand for two types of hybridization. Only valence band states are taken into account in the band component.
As shown above the exchange energy $E_{\text{magn}}$ is given by the shifts of the $V_O$ levels which are determined by the poles of $G$. It is sufficient to study the block $G_{\nu\nu}$ only since it has the same poles. Moreover, as follows from Eq. (10), we need only its diagonal part $\tilde{G}_{\nu\nu}$ in order to calculate its trace. It reads

$$\tilde{G}_{\nu\nu} = g_\nu + g_\nu^2 \sum_{i=1,2} V_{\nu\mu}(R_i) G_{i\mu,i\mu} V_{\nu,\mu}(R_i) +$$

$$g_\nu^2(\varepsilon) \sum_{i,j=1,2; \mu, \mu', \nu'} V_{\nu\mu}(R_i) G_{i\mu,i\mu}(\varepsilon) V_{\nu',\mu}(R_i) g_{\nu'}(\varepsilon) V_{\nu',\mu'}(R_j) G_{j\mu',j\mu'}(\varepsilon)V_{\nu',\mu'}(R_j).$$

We have kept the leading terms in the hybridization of the vacancy and impurity states contributing to the intersite exchange. Hybridization of the empty conduction band states and the impurity states is neglected in calculation of this exchange (see discussion after Eq. (5) in Section III). Since the spin-flip processes are not involved in the calculation of $E_{\text{magn}}$, the equations may be solved for each spin projection separately, and we omit below the spin index for the sake of brevity.

We represent the impurity Green function in terms of the irreducible representation of the symmetry group of axial defect $[\text{Co}_T, V_O]$, so that the impurity Green functions are diagonal in this representation

$$G_{d;i\mu,i\mu} = [\varepsilon - \varepsilon_{d;i\mu} - \Sigma_{d;i\mu}(\varepsilon)]^{-1}$$

with the mass operator

$$\Sigma_{d;i\mu}(\varepsilon) = \sum_{\kappa} V_{\kappa\mu}(R_i) g_{\kappa}(\varepsilon) V_{\kappa\mu}(R_i) G_{d;i,i\mu}.$$ 

which results from the exact solution of corresponding single impurity problem for a given spin. Here the index $\kappa = \{v, \nu\}$ unites both band and vacancy indices. The bare propagators are defined as

$$g_v = \frac{1}{\varepsilon - \varepsilon_v}, \quad g_\nu = \frac{1}{\varepsilon - \varepsilon_\nu}, \quad g_{d;i\alpha} = \frac{1}{\varepsilon - \varepsilon_{i\alpha}}.$$

Using Eqs. (12) and (10) we can find the change of the total energy due to the interaction of the vacancy and impurity states. The second order correction in the vacancy - impurity hybridization $V_{\mu,\nu}(R_i)$ in Eq. (12) is a single impurity effect and has nothing to do with the exchange interaction. The latter appears only in the last term of Eq. (12), which is of the
fourth order and describes a shift of the vacancy levels due to the electron exchange between two impurities, which is possible only provided the spins of two impurities are parallel.

The upward shift of the empty vacancy levels corresponds to lowering of the total energy of the system (see discussion after Eq. (10)). Hence, we come to the equation for the energy gain due to an indirect exchange (superexchange) between the two magnetic impurities,

\[ E^{\text{magn}}_{ij} = 2 \sum_{\nu \neq \nu'} V_{\nu \mu}^* (\mathbf{R}_i) V_{\nu' \mu'} (\mathbf{R}_i) V_{\nu' \mu'}^* (\mathbf{R}_j) V_{\nu' \mu'}^* (\mathbf{R}_j) \left[ \epsilon_{\nu} - \epsilon_{\nu'} - P_{d;i\mu} (\epsilon_{\nu}) \right] \left[ \epsilon_{\nu'} - \epsilon_{d;\nu' \mu'} - P_{d;j\mu'} (\epsilon_{\nu'}) \right] \]

where \( P_{d;ia} (\epsilon) = \text{Re} \Sigma_{d;ia} (\epsilon) \). Eq. (14) has a structure similar to that of eq. (10) of our paper. The role of hole pockets is now played by the empty vacancy states, and the fact that there is no free carriers and, hence no Fermi surface, so important for the RKKY model, play now no role whatsoever. Besides, contrary to the polaronic model, the ferromagnetism with high enough \( T_C \) arises in our model without additional enhancement due to spin polarization of the vacancy related band (see more detailed discussion below).

The fourth order exchange energy can be interpreted by means of the diagram presented in Fig. 2. Now the dashed lines in this diagram correspond to the two vacancy states virtually occupied in the superexchange act. Two multipliers in the denominator in (14) are the energies \( \tilde{\Delta}_{do, i} \) required for the two "reactions" \( \text{Co}(d^7) \rightarrow \text{Co}(d^6) + V_O(p) \) in the sites \( i, j \). These energies, include also the ligand field shifts \( P_{d;i\mu} \) of the impurity \( d \) levels. The vacancy band is empty so that the summation in Eq. (12) is carried out over all the states of the band. As a result the third multiplier, \( (\epsilon_{\nu} - \epsilon_{\nu'}) \), in the denominator is of the order of the vacancy band width \( D_o \). Thus the calculation of exchange energy by the Green function method by means of Eqs. (10), (14) confirms the qualitative estimate (7).

Now we are in a position to derive the effective spin Hamiltonian for interacting magnetic defects. Since we integrated out all the charge degrees of freedom when calculating the energy \( E^{\text{magn}}_{ij} \), this Hamiltonian has the simple form

\[ H_{ex}^{\text{eff}} = \frac{1}{2} \sum_{(ij)} J_{(ij)} S_i S_j, \]

where \( S_i \) is the spin of the ion \( \text{Co}(d^7) \), and the exchange constant \( J_{(ij)} \) is determined as the energy difference per bond between the parallel and antiparallel orientations of spins in the pair \( (ij) \). One may identify the coupling constants as \( 2J_{(ij)} S(S+1) = E^{\text{magn}}_{ij} \). Since these coupling constants are negative, they lead to a ferromagnetic ordering at temperatures below
the Curie temperature $T_C$. Well beyond the percolation threshold (which may be identified with the minimal vacancy concentration sufficient for formation of the vacancy band) $T_C$ may be estimated as

$$T_C = \frac{1}{k_B} \frac{zS(S + 1)}{3} |J| = \frac{z}{6k_B} |E^{\text{mag}}|.$$ \hspace{1cm} (16)

Here $|E^{\text{mag}}|$, and respectively $|J|$, is the typical value of the superexchange interaction in the pair of impurities separated by a distance not exceeding the double localization radius $R_O$ of the vacancy state. $z$ is the number of Co impurities within the corresponding volume. As was mentioned above the fact that 1% of vacancies is sufficient for formation of a band, meaning that the typical distance between them is smaller than $2R_O$. Since nearly each Co atom forms a complex with an oxygen vacancy, a 2% concentration of Co atoms substitutions means a 1% vacancy concentration when the vacancy states form a band. This fact guaranties that each Co atom interacts not only with its own vacancy but also with other neighboring vacancies, which form pairs with other Co atoms.

Magnetic ordering with a high $T_C$ in $(\text{Ti, Co})\text{O}_2$ is observed at higher Co concentrations up to 6% or 3% of the concentration of vacancies captured by the Co impurities. A 1% concentration of vacancies creates a band in the forbidden energy gap so that we may expect that the coordination number for such a concentration may be at least 4. At a three times higher concentration the coordination number will certainly become higher and a rough estimate $z \approx 10$ seems to be quite reasonable. We do not dispose precise experimental data concerning positions of the $V_O$ level in anatase TiO$_2$, so we refer the data available for the rutile modification where the donor levels related to an isolated $V_O$ are found at a few tenth of 1 eV below the bottom of conduction band. Using for the forbidden band width the experimental value 3.2 eV and basing on the calculations of Co-related d-level positions in the forbidden energy gap presented in Ref. \cite{21}, one may estimate the $pd$ charge transfer gap $\tilde{\Delta}_{pd} \sim 1$eV. The width of the vacancy band $D_o$ as well as the magnitude of hybridization parameter strongly depend on the specific characteristics of the sample (vacancy concentration, annealing regime etc). Besides, the vacancy band may or may be not partially filled due to uncontrollable donor impurities. Taking for an estimate the average value of $V_{\nu\mu} \sim 0.1$ eV, assuming the same estimate for $D_o$, and substituting the value of $S = 3/2$ into Eq. (16) one gets $T_C \sim \gamma z \cdot 10^{-4}$eV $\approx \gamma 100$K for $z = 10$. The coefficient $\gamma$ includes all the uncertainties (degeneracy factor of vacancy and impurity levels, difference between the intracell and intercell hybridization parameters, uncertainties in the effective
coordination number \( z \) etc. We expect the factor \( \gamma \) to be ideally close to one. However, it may deviate, and even strongly, from this value depending on the preparation history of each particular sample. Unfortunately, it is rather difficult to find optimal conditions for high \( T_C \) in such a multifactor situation.

V. CONCLUDING REMARKS

Among many dilute magnetic dielectrics only one example has been chosen, namely oxygen deficient \( \text{(Ti,Co)O}_2 \), and it has been shown that the imperfection of this crystal is crucially important for the formation of a long-range magnetic order. This idea is supported by the recent experimental observation: ferromagnetism is suppressed in Co doped \( \text{TiO}_2 \) film with high structural quality. Similar correlations between the quality of films and the magnetism were discovered in Ref. 10 for \( \text{(Ti,Cr)O}_2 \). It follows directly from our theory that without additional defects creating shallow levels under the bottom of conduction band, the radius of magnetic correlation is too short to overcome the percolation threshold, so that improvement of the film quality is detrimental for magnetic ordering in DMD.

It is also noticed in Ref. 10 that the charge state of chromium impurities in \( \text{TiO}_2 \) is \( \text{Cr}^{+3} \). This fact is easily understood within the framework of our hypothesis about the origin of magnetic order in DMD. Indeed, the difference between Co and Cr from the point of view of their electronic levels in host \( \text{TiO}_2 \) [in fact, the addition energies defined in Eq. (2) for the two impurities] is the position of these levels relative to the shallow defect levels. In correlation with the experimental data on ESR signal and theoretical calculations of the addition energies, the level of \( \text{Cr}^{2+} \) state in rutile \( \text{TiO}_2 \) is higher than the levels of shallow impurities and apparently higher than the bottom of conduction band. We assume that the situation is similar in anatase \( \text{TiO}_2 \), so that the same charge transfer mechanism, which binds the ions \( \text{Co}^{2+} \) with oxygen vacancies, should stabilize chromium impurities in a state \( \text{Cr}^{3+} \) (see Fig. 1). It is worth also mentioning that generally we may expect that the chemical trends in the Curie temperature for various transition metal impurities should correlate with the deep level energies (e.g., 7).

Another experimental fact, which demands theoretical explanation is a strong sample dependent scatter of saturation magnetic moment \( M_s \), which also depends on the fabrication conditions. This fact may be easily explained if one recognizes that only part of oxygen
vacancies is bound to magnetic impurities. “Free” vacancies, $V_O$, retain their electrons and eventually donate them to the vacancy band. The partially occupied band is spin polarized, and this polarization may enhance or partially compensate the magnetization of transition metal ions depending on the net sign of effective exchange in this band.\textsuperscript{8,28,30}

To conclude, we have proposed in this paper a mechanism of ferromagnetic exchange in dielectric non-stoichiometric TiO$_2$ doped with transition metal impurities, which involves the interaction between magnetic ions and oxygen vacancies and proposed a qualitative explanation of the basic properties of these materials. A quantitative calculations of electronic structure of magnetically doped TiO$_2$ based on the model described in this paper will be presented in forthcoming publications.

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