On the nature of ferromagnetism in oxide semiconductors doped with 3d-elements

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Abstract. The origin and mechanisms of ferromagnetism in the new class of magnetic materials, oxide-diluted magnetic semiconductors (ODMS), are examined in a framework of the Stoner-Anderson model. Within the Green function formalism, a condition (the Stoner criterion) for nucleation of ferromagnetism is obtained for itinerant electrons in the narrow defect (vacancy) band, and an additional contribution due to interaction with 3d magnetic ions is derived. The “trigger” character of the transition to the ferromagnetic state in ODMS is discussed in its dependence on the type and concentration of 3d magnetic impurity dopant. The results of calculations are compared with the experimental data for the spontaneous magnetic moment in semiconducting titanium dioxide (TiO₂) doped with 3d magnetic ions and containing various concentrations of oxygen vacancies.

1. Introduction
At present, there is an elevated interest to new class of magnetic materials – oxide-diluted magnetic semiconductors which exhibit the room temperature ferromagnetism [1], [2]. Diluted magnetic semiconductors could be a key spintronic material intended to control both spin and charge degrees of freedom of carriers in semiconductor devices.

Nowadays there exist several models of ferromagnetism in ODMS [3]–[5]. Most of researchers associate ferromagnetism with the localized magnetic moments on 3d-impurities which order by indirect exchange interactions. However, there are studies in which ferromagnetism is ascribed to electrons of defect band of the oxide crystal [5]. Which mechanism of magnetic ordering is realized in a particular system remains an open question. Therefore, the aim of this study is to clarify mechanisms of the long-range magnetic order in defective oxide semiconductors for the case when impurities are distributed in a sample in the form of a solid solution by substituting cations of the matrix.

2. Basics of ferromagnetism model in diluted magnetic oxide semiconductors.
We took titanium dioxide (TiO₂) rutile structure as a model ODMS which will be considered in this paper. Band structure and magnetic properties of rutile doped by 3d-elements are shown in figure 1a. It is well known that conductivity of pure titanium dioxide is provided by ionized point defects (as a rule by oxide vacancies) which are electronic donors [6], [7]. Energy levels of oxide defects lie in the
band-gap of TiO$_2$ at 0.3 eV below the bottom of conduction band (figure 1a). This levels form narrow quasi-continuous band with 0.3-0.4 eV width. We will argue below what the narrow defect band can be responsible for the ferromagnetism nucleation.

Our experimental studies revealed abrupt rise of the saturation magnetic moment of 3d-implanted TiO$_2$ films with increasing the concentration of 3d-elements. These findings are shown in figure 1b. The figure presents dose dependence of the magnetic moment per impurity atom in the single-crystal TiO$_2$ films. An important circumstance is that the above feature is observed in samples where the impurity is distributed in the form of dilute solution with substitution concentration of a few percent [8]. This allows to conclude that direct exchange can be neglected. Then, the origin of the ferromagnetism should be searched for in the host, but not in the magnetic moments of impurity alone.

**Figure 1.** Electrical and magnetic properties of rutile doped by 3d-elements: a) band structure and d-levels energy of 3d-elements [6], [7]; b) dose dependence of the spontaneous magnetic moment of Co-implanted single-crystal TiO$_2$ films. Theoretical concentration dependence of the magnetic susceptibility (dash line) is calculated using expression (6). Transition to the ferromagnetic state is observed at dose of 0.75×10$^{17}$ ion/cm$^2$.

Let’s consider in detail transition from the paramagnetic state to the ferromagnetic in ODMS under the influence of dopant 3d-elements. Our hypothesis is that the magnetic transition is caused by spin-splitting of the vacancy band. A mechanism of the magnetism implies itinerancy of electrons in the vacancy band, and existence of the exchange-type interaction $I$ (analog of the Stoner exchange) between them. We assume that the vacancy band is narrow with high density of states $N(E_F)$ in vicinity of the Fermi level $E_F$ (the Stoner criterion is close to fulfillment $IG(E_F)=1$), and completed defects percolation in the sample (overlapping of the electron states otherwise localized on the defects).

The model we use can be formalized by the Hamiltonian:

$$H = H_J + H_d + H_{s-d}.$$

(1)

Here $H_J$ is the Stoner Hamiltonian of the free-electrons systems in the second-quantization notations:
\[ H_s = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} + \frac{I}{2N_e} \sum_{n\sigma, d, \sigma} c_{n-d, \sigma}^+ c_{n-d, \sigma}^c c_{k, \sigma}^c c_{k, \sigma} , \]  

(2)

\( \varepsilon_k \) is the energy of the free-electron state with momentum \( k \), \( c^+ (c) \) - the creation (annihilation) operators, \( I \) is the exchange integral, \( N_e \) - the number of electron states in the vacancy band.

The second term \( H_d \) describes electrons localized on the impurity atoms [9]:

\[ H_d = \sum_{i, \sigma} E_d d_{i\sigma}^+ d_{i\sigma} + \frac{U}{2} \sum_{i, \sigma} d_{i\sigma}^+ d_{i\sigma}^+ d_{i\sigma} d_{i\sigma} , \]  

(3)

here \( E_d \) is the energy of the impurity d-level, \( d^+ (d) \) is the creation (annihilation) operators at impurity cites, \( U \) is parameter of the Coulomb repulsion of electrons at a d-orbital. The summation on the index \( i \) runs over all impurities the number of which is \( N_d \).

The third term \( H_{s-d} \) is the s-d hybridization energy of the localized and the itinerant electrons [10], [11]:

\[ H_{s-d} = \sum_{i, \sigma} \left( V_{i\sigma} c_{i\sigma}^+ d_{i\sigma} + V_{i\sigma}^* a_{i\sigma}^+ c_{i\sigma}^c \right) , \]  

(4)

where \( V_{i\sigma} \) is the potential of hybridization.

3. Ferromagnetism criterion

To find the modified criterion of ferromagnetism, we can calculate the transverse dynamic susceptibility of electrons in the vacancy band using the formalism of double-time thermodynamic Green functions. The Fourier component of the transverse dynamic susceptibility of the electron system is expressed in terms of Fourier component of the Green function \( \langle \langle B(q) | B^*(q) \rangle \rangle \) [12]:

\[ \chi^\perp (q, \omega) = 2\pi \langle \langle B(q) | B^*(q) \rangle \rangle_{\omega} , \]  

(5)

where \( B(q) = \sum_k c_{k\uparrow}^+ c_{k\downarrow} \) and \( B^*(q) = \sum_k c_{k\uparrow}^c c_{k\downarrow}^\dagger \).

We solve the problem up to the second order term in \( V_h \), which is a small parameter compared with the energy of the Coulomb repulsion \( U \) and the exchange integral \( I \). In the limit \( q \to 0 \), \( \omega \to 0 \) we have the following expression for the susceptibility:

\[ \chi^\perp (0,0) = \frac{G(E_F) \left( 1 + \frac{N_d |V_F|^2}{N_e (E_F - E_d + I/2 - Un/2)^2} \right)}{1 - IG(E_F) \left( 1 + \frac{N_d |V_F|^2}{N_e (E_F - E_d + I/2 - Un/2)^2} \right)} . \]  

(6)

Then, the criterion of ferromagnetism takes the following form:

\[ IG(E_F) \left( 1 + \frac{N_d |V_F|^2}{N_e (E_F - E_d + I/2 - Un/2)^2} \right) = 1 . \]  

(7)

Here \( E_F \) is the energy of the itinerant electron state on the Fermi level, \( V_F \) is the matrix element of the hybridization on the Fermi level.

4. Discussion

Expression (6) describes paramagnetic susceptibility of electrons in the vacancy band of ODMS. The susceptibility indefinitely increases at a certain concentration \( N_d / N_e \) of magnetic impurity. This
moment correspond to the spontaneous polarization of electrons in the vacancy band ("trigger" behavior). The calculated concentration dependence of the susceptibility is shown on figure 1b. Fitted to the experimental data (figure 1b) susceptibility goes to infinity at dose $\sim 0.7 \times 10^{17}$ ion/cm$^2$ that corresponds to the mean concentration of 6-7 atomic percent.

First of all, ferromagnetism of ODMS is determined in the first place by parameters of the narrow vacancy band but not by magnetic parameters of the dopant. It is just we observe in our experiments: the magnetic ordering temperature (700-800 K for cobalt) and the spontaneous magnetization are almost independent on the impurity concentration.

The nucleation of the ferromagnetic state depends on the impurity concentration, square of the hybridization matrix element $V_F$ at the Fermi level, and location of the localized energy level of the impurity $E_J$ relative to the Fermi level. In fact, it means that the transition threshold depends on the type of impurity. For example, figure 2 presents values of the spontaneous magnetic moments per impurity for different 3d-elements: Ti, V, Cr, Mn, Fe, Co, Ni, Cu. There is a wide range of magnetic moments for the particular 3d-impurity, however, we can single out general trend for the data set (see the solid curve in figure 2). Notably, V and Co have highest values of the mean magnetic moment. This fact, it is in agreement with our mechanism of ferromagnetism.

![Figure 2](image-url)

**Figure 2.** Value of the magnetic moment of TiO$_2$ single-crystalline plates implanted by 3d-elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu) at room temperature. For comparison, the data of papers [13]-[24] are shown.

According to the suggested mechanism, ferromagnetism of ODMS is spatially inhomogeneous and confined to areas of percolated impurities. Consequently, increase in the concentration of defects (actually, the oxygen vacancies) leads to escalation of the ferromagnetic areas and hence, to increase of the total magnetic moment. Particularly, this explains a wide spread of the saturation magnetic moments in the samples prepared by different techniques. Our measurements show that the oxide vacancies injection strongly affects the saturation magnetic moment. Figure 3 shows hysteresis loops before and after the vacancy injection from copper electrode by an electric field [25]. The saturation magnetic moment increases several times after the oxygen vacancies injection. At the same time, the temperature of the magnetic ordering ($\sim$720 K) and the coercive field remain almost steady. Therefore, the mechanism of the magnetic ordering is the same for both cases.
5. Conclusion
The long-range magnetic ordering mechanism in ODMS with high concentration of defects is suggested. Spin-splitting of the vacancy band and the “trigger” (on the concentration of the defects) behavior of transition to the ferromagnetic state are the main features of the suggested mechanism. The qualitatively new result is that ferromagnetic properties of ODMS are determined mainly by exchange interaction of electrons in narrow vacancy band. This result is in a qualitative agreement with our experimental data.

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