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REGULAR ARTICLE

Effect of *d-f* Exchange Interaction on the Optical Properties of Fe/Gd_2O_3 Nanostructure in the Infrared Spectral Range

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The paper deals with the influence of *d-f* exchange interactions occurring in the contact zone of layers in Fe/REM oxide nanostructures on the features of their infrared absorption spectra. The time-distances, energies and force constants of vibrations of Gd-O and Yb-O atomic bonds in Fe/Gd_2O_3 and Fe/Yb_2O_3 nanostructures with significant and small values of the effective magnetic moment of REM, respectively, have been compared. It is shown that the difference between the absorption spectra of these nanostructures and the properties calculated from them indicates the presence of the influence of the *d-f* exchange interaction on the vibrations of the Gd-O bond and its absence for Yb-O. For the Gd-O bond, the increase in vibrational energy due to the *d-f* exchange interaction is 0.02-0.11 %. It is shown how the influence of the exchange interaction can be taken into account in the well-known quantum mechanical description of the anharmonicity of the oscillator vibrations by introducing an additional term in the expression for its potential energy. This approach makes it possible to show that the *d-f* exchange interaction also affects the value of the distance between the nuclei of Gd-O atoms.

Keywords: Fe, SEM oxide, IR spectroscopy, *d-f* exchange interaction.

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1. INTRODUCTION

In bulk samples of matter, the *d-f* exchange interaction between atoms with unfilled *d-* and *f*-electron shells has long attracted the attention of researchers [1-4] because of its potential for practical applications in various devices for displaying and processing optical information.

In thin film objects, the occurrence of *d-f* exchange interaction at the interface of contacting layers was first demonstrated by the contact of metals with unfilled *d-* and *f*-electron shells. The development of this field has led to a number of studies, the number of which is currently increasing.

Further studies have shown the possibility of realizing the exchange *d-f* interaction at the interface between layers of *d*-metals (Fe, Co, Ni) and their oxides (Fe_3O_4) with oxides of *f*-elements (rare earth metals – REM) [5], which are already semiconductors and dielectrics. Expanding the range of electrical properties of such multilayer structures increases the prospects for their practical application. At the same time, the possibility of enhancing many properties of the above materials by *d-f* exchange interactions proved to be particularly valuable. It has been shown that exchange interactions organize the magnetic structure of ferromagnetic layers (Fe, Co, Ni, Fe_3O_4) [6, 7], thereby increasing their magnetization and, accordingly, enhancing many properties of the layers that depend on this property, such as galvanomagnetic, magneto-optical [8], electronic paramagnetic resonance [9], anomalous Hall [10, 11], and conductivity of MDM structures [12]. Such amplification does not require energy consumption or the use of amplifying devices and can be achieved at the nanoscale, which is important for nanotechnology.

The aim of this work is to study the influence of the *d-f* exchange interaction on the optical properties of *d*-metal/REM oxide nanostructures in the infrared (IR) region of the spectrum. To achieve this goal, we determined the dependence of the shift of the absorption bands of the REM oxides in their transmission spectrum $T(\lambda)$ on the intensity of the *d-f* exchange interaction, which was controlled by selecting the value of the effective magnetic moment of the REM.

2. EXPERIMENTAL CONDITIONS

For experiments in the infrared region of the spectrum, Fe d-metal was used as the metal with the highest effective moment in the iron group $(\mu)_{Fe} = 7.13\ \mu_B$, i.e. it allows achieving a high value of the *d-f* exchange

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energy of interaction with the REM oxide.

Gd_2O_3 and Yb_2O_3 were used as the SEM oxides. These materials were selected because they have different properties that affect the frequency ν of the absorption bands: Gd has a high value of effective magnetic moment $(\mu)_{Gd} = 7.95\ \mu_B$, i.e. it can provide a large energy of exchange *d-f* interaction with Fe, and Yb has a very low value of $(\mu)_{Yb} = 0.41\ \mu_B$ and causes a weak *d-f* interaction. Therefore, the comparison of the transmission spectra $T(\lambda)$ of Fe/Gd_2O_3 and Fe/Yb_2O_3 nanostructures will allow us to study the process of the influence of the exchange *d-f* interaction on the vibrations of the Gd-O and Yb-O atomic bonds.

The Gd_2O_3, Yb_2O_3, and Fe films were successively deposited by electron beam evaporation of targets of similar composition on KBr substrates transparent in the studied spectral region. Deposition conditions: Fe-vacuum $3 \cdot 10^{-3}$ Pa, film growth rate $\upsilon = (5\text{-}10)$ nm/min, substrate temperature was $t = (30\text{-}40)$ °C; Gd_2O_3, Yb_2O_3-oxygen partial pressure $p_{O2} = 2 \cdot 10^{-2}$ Pa, film growth rate $\upsilon = (3\text{-}10)$ nm/min, substrate temperature $t = (30\text{-}50)$ °C. The thickness of the Fe layers was 120 nm, the thickness of the films was 80 nm.

During the deposition of the Fe film, a small amount of oxygen is incorporated into its composition. Calculation shows that at a given vacuum level, ten Fe atoms can account for less than one atom of simultaneously deposited oxygen. This means that in most of the contact area between Fe layers and REM oxides (Gd_2O_3 or Yb_2O_3), there is a close contact between *d*-atoms of Fe and *f*-atoms of REM (Gd or Yb), which is accompanied by the occurrence of *d-f* exchange interaction.

The surface of Fe films deposited on a layer of REM oxide is also partially oxidized during exposure to air. This is evidenced by a slow increase in the resistivity of the films, which stops after about three days. Fe films, even with a thickness of 120 nm, which is less than that used in the experiment, are oxidized by air oxygen only from the surface. This was demonstrated by their electronic phase analysis.

Figure 1 shows an electron micrograph of a 30 nm thick Fe film on a layer of RZM oxide, Gd_2O_3 (50 nm).

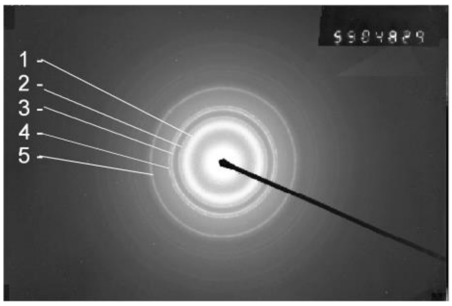

Fig. 1 – An electron diffraction pattern of a 30 nm thick Fe film on a layer of RZM oxide, Gd_2O_3 (50 nm). 1 – Fe_3O_4 line (d_1 = 0.2967 nm), 2 – Fe_3O_4 line (d_2 = 0.2532 nm), 3 – Fe line (d_1 = 0.20268 nm), 4 – common line for Fe (d_2 = 0.14332 nm) and Fe_3O_4 (d_3 = 0.1485 nm), 5 – Fe line (d_3 = 0.11702 nm)

From Fig. 1 it can be seen that the electron pattern contains three strong lines corresponding to the interplanar distances for Fe: $d_1 = 0.20268$ nm, $d_2 = 0.14332$ nm, $d_3 = 0.11702$ nm [13] and for Fe_3O_4: $d_1 = 0.2967$ nm, $d_2 = 0.2532$ nm, $d_3 = 0.1485$ nm [14]. This means that the Fe and Fe_3O_4 phases are present separately in the film. Therefore, it can be assumed that the configuration of the thicker (120 nm) film deposited on the RZM oxide is a layer of Fe with a protective layer of Fe_3O_4 on top. The electron micrograph also shows that such a Fe film is polycrystalline and the REM oxide layer is amorphous.

The following equipment was used for the experiments. The film nanostructures were obtained on an electron beam sputtering apparatus VU-1A. The thickness of the films was measured with an MII-4 interference microscope.

3. RESULTS AND DISCUSSION

It is known [15] that in the infrared transmission spectrum of REM oxides there are bands associated with valence vibrations of bonds between the f-metal and oxygen atoms. For the RSM oxides Gd_2O_3 and Yb_2O_3 selected in our work, the absorption maxima of the Gd-O and Yb-O bond vibrations appearing at wave numbers ν of 475.94 cm^{-1} and 418.14 cm^{-1} and 477.39 cm^{-1} and 419.15 cm^{-1}, respectively, were used as such bands. The change in ν of these maxima can be used as an indicator of the influence of the *d-f* exchange interaction on the REM oxides in contact with the *d*-metal Fe layer. At the same time, the valence vibrations of Fe-O have absorption bands at 580 cm^{-1} [16], which are far enough away from the above-mentioned bands of the REM oxides and do not interfere with the analysis of their ν changes.

For simplicity, if we consider the bond between Gd-O and Yb-O atoms as a bond in a two-atom molecule, then we can apply the known concepts corresponding to a harmonic oscillator [17]. The oscillation frequency of the oscillator is equal to

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \tag{1}$$

where K is the force constant of oscillation, $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$ is the reduced mass of the oscillator m_1 and m_2 are the masses of the atoms of the two-nuclear molecule, and the frequency is related to the wave number ν by the ratio $\nu = c \cdot \nu$ where c is the speed of light.

The energy corresponding to the oscillation frequency ν must satisfy the Bohr condition.

$$E = h\nu, \tag{2}$$

where *h* is the Planck constant.

When a layer of *d*-metal Fe is in contact with a layer of REM oxide, the *d-f* exchange interaction can be realized with the participation of intermediate oxygen atoms. Then it should affect the bonding of the *f*-atom with oxygen. Fig. 2 shows fragments of transmission spectra of Gd_2O_3 (a) and Yb_2O_3 (b) oxides in the region (400-1000) cm^{-1}, taken without and in contact with the Fe layer.

In the presence of a Fe layer in contact with REM oxides, an increase in the ν bands of the valence vibrations of the Gd-O bond is observed in the absorption spectrum of the Gd_2O_3 layer, while a decrease is observed for Yb_2O_3. That is, according to formulas (1) and (2), in the presence of contact with the Fe layer, the force constant K and the energy E of the valence vibrations of the Gd-O bond increase, while the Yb-O bond decreases.

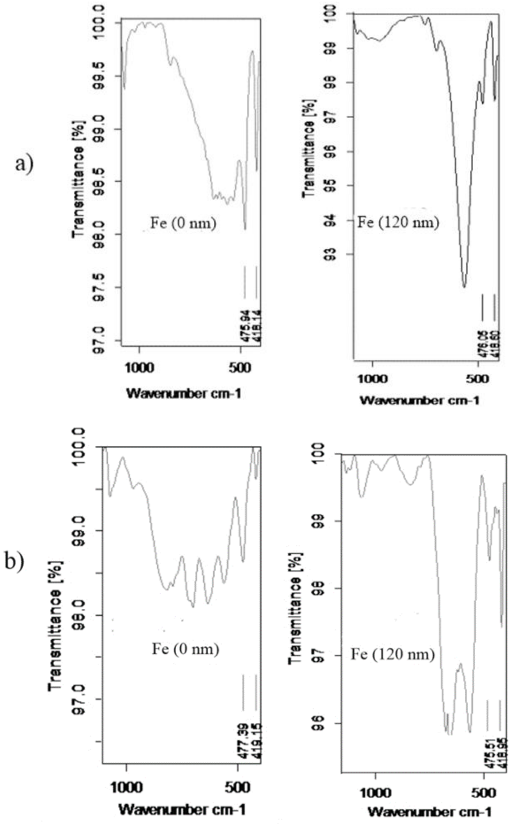

Fig. 2 – Transmission spectra of Gd_2O_3 (a) and Yb_2O_3 (b) oxides in the absence of Fe (0 nm) and in contact with a layer of Fe (120 nm)

Table 1 – Values of the force constant K and vibrational energy E of the molecular groups Gd-O (a) and Yb-O (b) corresponding to two absorption bands in the films of REM oxides without and with contact to the Fe layer

a)

Structure	Gd_2O_3		Fe/Gd_2O_3	
ν (cm^{-1})	475.94	418,14	476.05	418.6
K (N/m)	$1.93\cdot10^5$	$1.49\ 10^5$	$1.93\ 10^5$	$1.49\cdot10^5$
E (eV)	$59.0\cdot10^{-3}$	$51.8\cdot10^{-3}$	$59.0\cdot10^{-3}$	$51.9\cdot10^{-3}$

b)

Structure	Yb_2O_3		$Fe\ /\ Yb_2O_3$	
ν (cm^{-1})	477.39	419.15	475.51	418.95
K (N/m)	$1.96\cdot10^5$	$1.51\cdot10^5$	$1.94\cdot10^5$	$1.51\cdot10^5$
E (eV)	$59.1\cdot10^{-3}$	$51.9\cdot10^{-3}$	$58.9\cdot10^{-3}$	$51.9\cdot10^{-3}$

The increase in the values of K and E for Gd_2O_3 oxide and their decrease for Yb_2O_3 may be due to the influence of the exchange *d-f* interaction. The large value of the Gd magnetic moment, 7.95 μ_B, also determines the significant energy of its exchange *d-f* interaction, which significantly affects the frequency of oscillations of the Gd-O bond, as well as the values of K and E characterizing these oscillations.

At the same time, the small value of the magnetic moment of 0.41 μ_B in Yb causes a low energy of the *d-f* interaction, which makes its effect on the change of ν , K, and E imperceptible. On the contrary, a decrease in ν , K and E is observed after the deposition of a Fe layer on Yb_2O_3. This decrease may be due to the weakening of the Yb-O bond under the influence of a neighboring Fe atom on an oxygen atom. In the Gd_2O_3 layer, which has a strong *d-f* exchange interaction, this influence of the Fe atom is insignificant.

The effect of the exchange *d-f* interaction on the force parameter of the oscillations K of a harmonic oscillator, the Gd-O atomic bond, shows that it causes a perturbation ν , E. The latter leads to the appearance of anharmonicity in the transmission spectra (Fig. 1). The influence of external forces acting on the oscillator can be taken into account by introducing an additional cubic term in the expression for the potential energy V [17].

$$V=\frac{1}{2}Kq^2-Gq^3\ ,\ K\approx e\mu_0\left[\vec{v}\times\left(\vec{H}+\vec{M}\right)\right] \qquad (3)$$

where q is the amplitude of the harmonic oscillations $K\gg G$, μ_0 is the magnetic constant, and $\left(\vec{H}+\vec{M}\right)$ are vectors taking into account the influence of the exchange *d-f* interaction $H_{d\text{-}f}$ and $M_{d\text{-}f}$, respectively [18].

In the case of Gd-O atom bonding, the external forces can be both the influence of the *d-f* exchange interaction between Gd and Fe atoms and the influence of the chemical bond between Fe and O atoms. As shown in Table 1, the influence of these factors increases the value of E by (0.1-0.22) %.

4. CONCLUSIONS

The *d-f* exchange interaction in the Fe/Gd_2O_3 nanostructure increases the K-force parameter of the vibrations, which changes the wavenumber ν and the energy E of the Gd-O atomic bond in the Gd_2O_3 nanostructure. A similar effect is not observed in Fe/Yb_2O_3 nanostructures. This is due to the significant energy of the *d-f* interaction in Gd_2O_3 and the low energy in Yb_2O_3.

In the quantum mechanical consideration of the vibrational spectra of REM oxides, the influence of the *d-f* exchange interaction can be taken into account by introducing an additional term into the expression for the potential energy of the *f*-atom-oxygen bond, which takes into account the anharmonicity of the vibrational process [17].

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Вплив *d-f* обмінної взаємодії на оптичні властивості наноструктури Fe/Gd_2O_3 у інфрачервоному діапазоні спектра

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У роботі розглянуто вплив *d-f* обмінної взаємодії, що відбувається в приконтактній зоні шарів в оксидних наноструктурах Fe/REM, на особливості їхніх ІЧ-спектрів поглинання. Проведено порівняння частот, енергій і силових констант коливань атомних зв'язків Gd-O і Yb-O в наноструктурах Fe/Gd_2O_3 і Fe/Yb_2O_3 зі значними і малими значеннями ефективного магнітного моменту РЗМ відповідно. Показано, що різниця між спектрами поглинання цих наноструктур і розрахованими за ними властивостями свідчить про наявність впливу *d-f* обмінної взаємодії на коливання зв'язку Gd-O і його відсутність для Yb-O. Для зв'язку Gd-O збільшення енергії коливань за рахунок *d-f* обмінної взаємодії становить 0,02-0,11 %. Показано, як вплив обмінної взаємодії можна врахувати у відомому квантово-механічному описі ангармонічності коливань осцилятора, ввівши додатковий член у вираз для його потенціальної енергії. Такий підхід дає змогу показати, що обмінна взаємодія *d-f* також впливає на величину відстані між ядрами атомів Gd-O.

Ключові слова: Fe, РЗМ-оксид, ІЧ-спектроскопія, *d-f* обмінна взаємодія.