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Oscillation of the multiferroic/ferroelectric $GdMnO_3/SrTiO_3$ and $YbMnO_3/SrTiO_3$ interfaces in the EPR spectrum

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The electron paramagnetic resonance (EPR) method was used to study thin manganite ytterbium $YbMnO_3$ and gadolinium $GdMnO_3$ films, with a thickness of 100 nm, deposited on a $SrTiO_3$ virtual ferroelectric backing ($GdMnO_3/SrTiO_3$ and $YbMnO_3/SrTiO_3$). The most interesting results are obtained in the 40–100 K temperature interval for $GdMnO_3/SrTiO_3$, and 40–150 K for $YbMnO_3/SrTiO_3$. In these temperature ranges, in addition to the exchange-narrowed line from all film material, absorbed power oscillations were observed in the EPR spectra, with the amplitude of the oscillations depending on both the temperature and the magnitude of the external magnetic field. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4906316]

Introduction

There is interest in studying the physical properties of bilayer heterostructures in the form of thin multiferroic films deposited on a dielectric backing, because of their unusual physical properties and practical application potential. Regarding their unusual properties, it is known that at the interface between two dielectrics, such as a thin $SrTiO_3$ film on a $LaAlO_3$ backing, there is an observable transition into the superconducting state.[1] As far as practical applicability, studies of ferroelectric materials for possible use in microwave technology have been going on for quite some time. However, using a material with a high dielectric permittivity, which depends strongly on temperature, is fairly difficult. Therefore, the use of a ferroelectric thin film deposited on dielectric backing is suggested as a microwave device.[2] Therefore, thin films of $GdMnO_3$ and $YbMnO_3$ multiferroics deposited on a $SrTiO_3$ virtual ferroelectric, are selected as the objects of this study.

Experimental Results

Epitaxial thin films of gadolinium manganite $GdMnO_3$, and manganite ytterbium $YbMnO_3$, on backing made of single-crystal strontium titanate $SrTiO_3$, are created by rf magnetron sputtering. Analysis of the test samples by Rutherford backscattering showed that the thickness of the obtained films was ~100 nm, and the chemical composition corresponded to the declared stoichiometry. As a result of x-ray analysis of the structure, and the phase structure of the obtained films, it is established that all samples are single-phase. The thickness of the backing is ~0.6 mm (Fig. 1).

Measurements of EPR spectra were done at X-band, on an ELEXSYS E500 spectrometer, manufactured by Bruker, equipped with nitrogen and helium flow cryostats, and also on a spectrometer manufactured by Varian, in the temperature range from 4 to 400 K. The sample was placed in a quartz tube, and secured by melted paraffin, such that the constant magnetic field was parallel to the plane of the film/backing interface. The sample was placed in the cavity at the antinode of the microwave field, and the accuracy of the temperature measurement was within 1 K.

The EPR spectrum for the $GdMnO_3/SrTiO_3$ sample, at room temperature, showed a group of lines that represented the fine structure of the gadolinium paramagnetic center, the behavior of which is described in detail by Ref. 3. When the $YbMnO_3/SrTiO_3$ and $GdMnO_3/SrTiO_3$ thin films were studied in the 40–150 K and 40–100 K temperature intervals, respectively, two absorption curves were observed on the oscilloscope screen in the "tune" mode. At some temperatures, there were three absorption curves that succeed each other in time. The shape of the absorption curves on the oscilloscope screen at a temperature of 45 K is presented in Fig. 2 for $YbMnO_3/SrTiO_3$. The resonance frequency values of

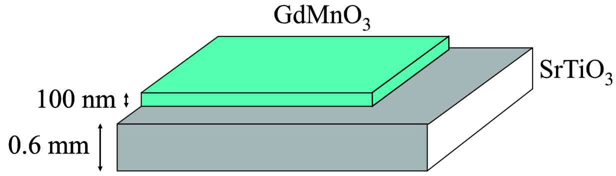

FIG. 1. Schematic view of the $GdMnO_3/SrTiO_3$ heterostructure.

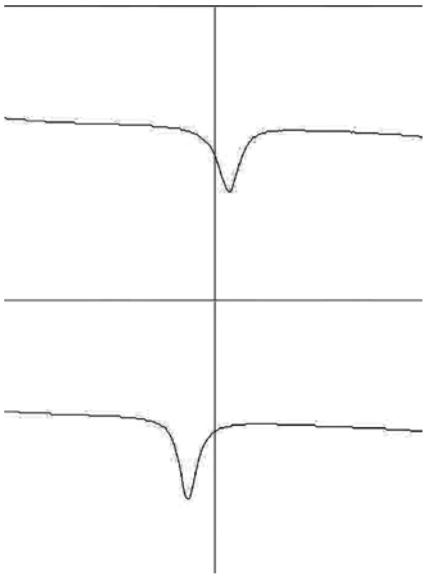

FIG. 2. The shape of the $YbMnO_3/SrTiO_3$ absorption lines on the oscilloscope screen of the Bruker ELEXSYS spectrometer, with a time difference of about 1 s at the temperature of 45 K. The center line is set to a frequency of 9.39 GHz.

additional absorption curves were measured on the Bruker ELEXSYS spectrometer, in the 80–160 K temperature range and are shown in Fig. 3; the temperature measurement is accurate within 0.2 K. As can be seen in Fig. 3, if the temperature is changed by 1 K, the frequency of the additional peak changes by 60 MHz.

Fig. 4 shows the shape of the spectrum for the $YbMnO_3$/$SrTiO_3$ thin film magnetic resonance for several temperatures, where absorbed microwave power oscillations are observed with an increasing magnetic field. As can be seen in the diagram, the amplitude of the oscillations depends on the magnetic field. Fig. 5 shows the dependence of the oscillations on the magnitude of the magnetic field. This dependence is described well by the expression: $C^*\exp(-\Delta/H)$, where $\Delta = 2000$ Oe, and H is the magnetic field strength. The vibrations are observed against the background of a broad line of approximately 8000 Oe from the $GdMnO_3$ film (see Fig. 6), and at a temperature of 78 K there is a sharp

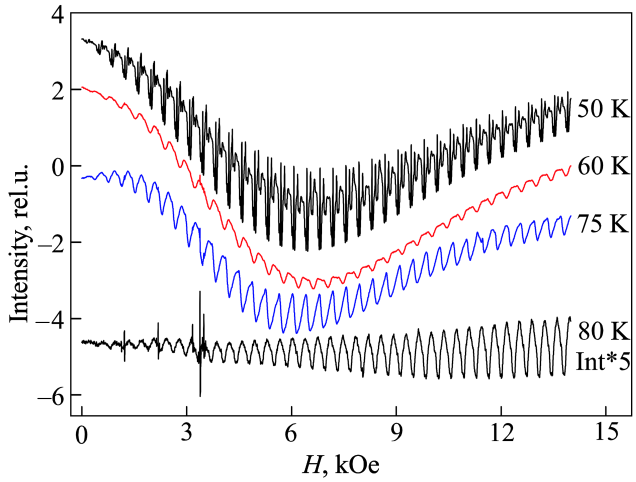

FIG. 4. The shape of the $GdMnO_3/SrTiO_3$ thin film magnetic resonance spectrum, at different temperatures.

decrease of the magnetic resonance line width down to 1000 Oe, which indicates a magnetic phase transition observed in $GdMnO_3$ single-crystals at a temperature of about 40 K.

Discussion

The shape of the oscillations in the magnetic resonance spectrum is similar to dimensional resonance curves, observed in thick metal plates (Gantmakher effect).[4] A similar pattern can be observed from a two-dimensional gas at the interface of two dielectrics (was reported in Refs. 5 and 6), which can represent a thin metal plate. However, an interface is a few lattice periods thick, which is not enough to excite the dimensional resonance.

As can be seen in Fig. 2, on the oscillogram of the microwave generation zone, within a fairly broad temperature zone, there are two absorption peaks for the thin multiferroic film sample on $SrTiO_3$ backing. One (let's call it "first") is due to the absorption of microwave energy by the loaded cavity. The second, most likely, occurs due to excitation of the bulk acoustic resonator (BAR) vibrations in the $GdMnO_3/SrTiO_3$ or $YbMnO_3/SrTiO_3$ sample.

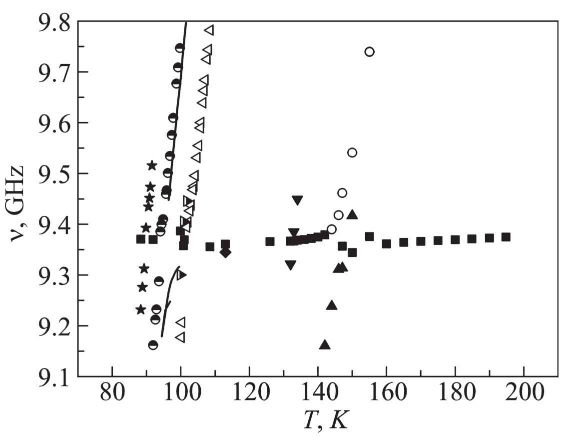

FIG. 3. Temperature dependence of the absorption frequency of the cavity, in which the $YbMnO_3/SrTiO_3$ thin film is placed. (■) symbols represent the resonance frequency of the cavity, and the rest of the symbols are the absorption frequencies of the sample. The solid line is the vibration frequency of $SrTiO_3$, after mechanical removal of the thin film.

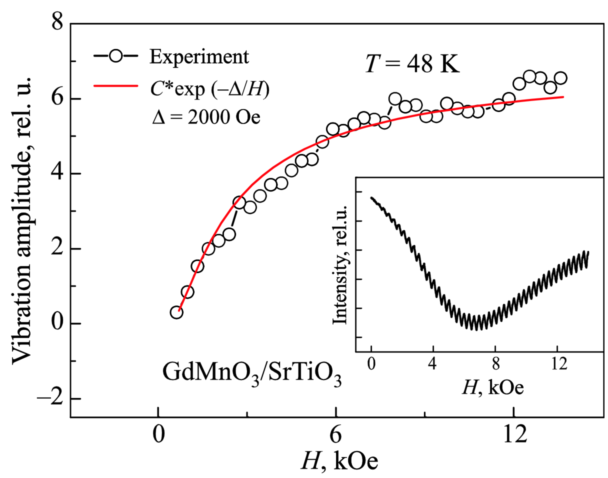

FIG. 5. The dependence of the vibration amplitude on the magnetic field. The inset shows the shape of the magnetic resonance spectrum of the $GdMnO_3/SrTiO_3$ thin film, at a temperature of 48 K.

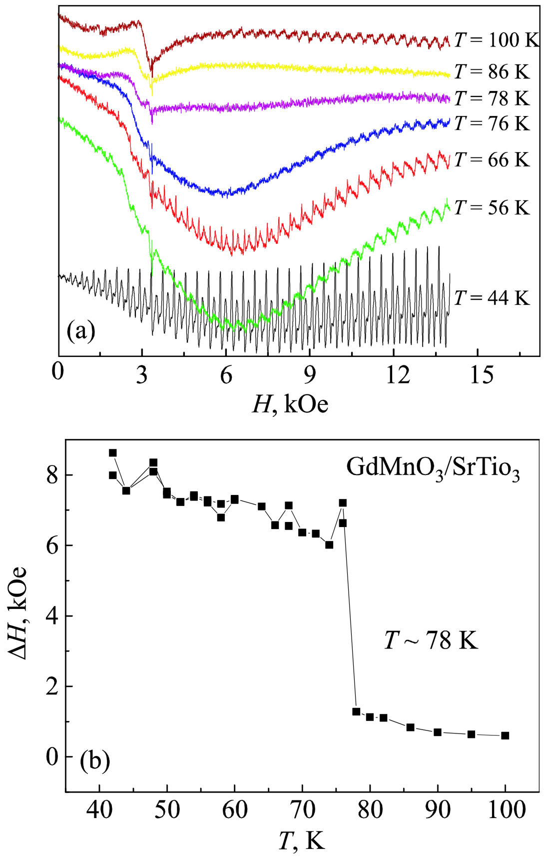

FIG. 6. Temperature dependence of the magnetic resonance spectrum in the X-band (a); temperature dependence of the magnetic resonance line width of the $GdMnO_3/SrTiO_3$ thin film (b).

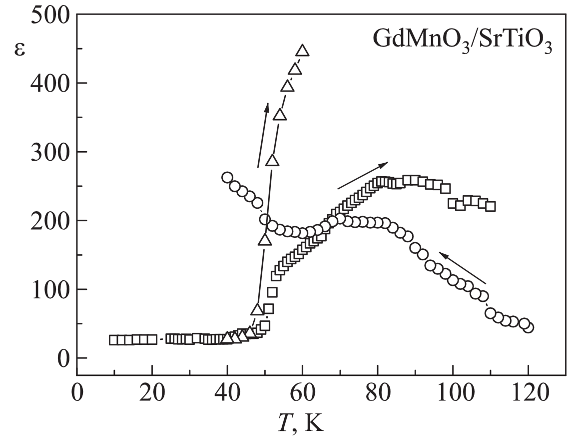

FIG. 7. Temperature dependence of the $GdMnO_3/SrTiO_3$ dielectric permittivity, (Δ) symbols represent the heating of the sample at 10 K/min, (□) symbols represent heating at 1 K/min, (○) symbols represent sample cooling.

Therefore, the mechanism creating oscillations at the microwave level in the cavity, and their observation in the magnetic resonance spectrum, are possibly tied to the function of the automatic frequency control (AFC) system using a PID (proportional integral differential) device to control temperature. As shown in Fig. 3, the resonance frequency of the second peak changes by about 60 MHz when the temperature is changed within 1 K (the set value of a PID temperature controller on a Bruker ELEXSYS spectrometer was 1 K when the experiments shown in Figs. 4–6 were conducted). At a certain ratio between the PID regulation parameters, the temperature fluctuates around the set value. The temperature fluctuations will have a periodic nature, which in turn, leads to periodic variations in the frequency of the $GdMnO_3/SrTiO_3$ and $YbMnO_3/SrTiO_3$ samples. Therefore, the automatic frequency control system can "capture" the first peak and the second with equal probability (if they are close enough together in frequency to be overlapped by AFC frequency modulation). Therefore, when the "second peak" periodically goes outside the boundaries created by AFC frequency modulation, the system "captures" the "first peak" which registers on the EPR spectrum as a change in the level of microwave power absorbed by the cavity, which creates the oscillations in the EPR spectrum of the test samples.

It is likely that such a strong variation due to temperature in the resonance frequency value of the second peak is due to the dielectric properties of the $SrTiO_3$ backing. Low-temperature dielectric properties of strontium titanate and barium crystals have been attracting the attention of researchers since the mid-1960s, mainly due to the fact that their dielectric permittivity has a pronounced dependence on the temperature and the applied static field. In recent years, interest has increased in these samples, since their usage allows for the construction of thin film microwave devices based on bulk acoustic waves, called bulk acoustic resonators (BAR).[7]

The temperature dependence of the $SrTiO_3$ dielectric permittivity was studied in Ref. 8. The authors discovered low-temperature anomalies of dielectric loss, associated with the formation of thin ferroelectric clusters, or the formation of regions with coherent reorientation of defect states in quantum paraelectrics. The dielectric properties of $SrTiO_3$ also vary greatly with doping. The study by Lemanov *et al.*[9] presents measurements of the dielectric relaxation of $SrTiO_3$, doped with manganese ions. It is found that the temperature dependence of the constant of dielectric absorption depends on the frequency of the measurements (see Figs. 3–5 in Ref. 9). The authors measured the constants of dielectric absorption for manganese-doped $SrTiO_3$ in the frequency range of 10 Hz to 1 MHz. In Fig. 3 of Ref. 9, the maximum value of the dielectric permittivity is approximately $\varepsilon'' = 450$ and $\varepsilon' = 2500$ (100 GHz) for $SrTiO_3$:$0.02Mn^{2+}$. Substituting these values into the expression $\lambda = \lambda_{SHF}/\sqrt{\varepsilon}$, where $\varepsilon = \sqrt{\varepsilon'^2 + \varepsilon''^2}$, gives us $\lambda \approx 0.6$ mm. This value is comparable to the thickness of the backing. It is possible that the $SrTiO_3$ backing with the $GdMnO_3$ or $YbMnO_3$ thin film multiferroic on top, serves as a generator of hypersound, i.e., an elastic wave with a frequency of about 10^9 Hz. The generation and reception of hypersound are based on the use of piezoelectricity and magnetostriction phenomena. As already noted, the use of $SrTiO_3$ and $BaTiO_3$ as the working media for microwave technology has been discussed for quite some time. $SrTiO_3$ is the ideal material for studying electrostriction, thanks to its large electrostriction coefficient and absence of piezoelectricity.[2] The authors of Ref. 10 suggested a model that would explain how, with the help of a planar capacitor, hypersonic waves become excited in ferroelectrics, by the piezoelectric effect. At $T = 78$ K they observed a significant increase in the nonlinear response to the biharmonic signal at frequencies that are close to the microwave.

Given the above, there is an obvious need to study the dielectric properties of $GdMnO_3/SrTiO_3$ and $YbMnO_3/SrTiO_3$ structures. In order to measure the dielectric permittivity of the $GdMnO_3/SrTiO_3$ thin film, we prepared a plate capacitor, in which the test sample was the dielectric between the plates. The prepared capacitor was placed into a helium flow cryostat, and the temperature dependence of electric capacity was measured at a frequency of 100 kHz. The temperature dependence changes with the direction of the temperature change (whether the sample is heated or cooled). The shape of the curves is shown in Fig. 7. The dielectric permittivity at the frequency 100 kHz was calculated according to the formula $\varepsilon = CS/(\varepsilon_0 d)$, where C is the measured capacitance, S is the area of the plates, d is the sample thickness, and ε_0 is the vacuum permittivity. When the temperature is lowered (below 120 K), the dielectric permittivity starts to increase sharply and falls to a minimum value at 40 K. When the temperature is increased above 40 K, the dielectric permittivity increases, but the absolute values are dependent on the temperature's rate of change. Such behavior of $\varepsilon(T)$ was observed in Ref. 11, which studied the effect of non-stoichiometric location of the Sr and Ti ions, on the ferroelectric properties of $SrTiO_3$ ceramics. The authors studied the dependence of the pyroelectric current in $SrTiO_3$ ceramics with an Sr/Ti = 0.96 ratio. At first the sample was cooled to a temperature of $T = 2$ K in an electric field ($E = 14$ kV/cm, with the direction of the electric field perpendicular to the plane of the sample, made in the form of a disc), and then after a short-circuit procedure, the temperature dependence of the pyroelectric current was measured. The data are obtained for three different heating rates (2, 4, and 6 K/min). The maximum of the current-temperature curve does not shift along the T axis, but as the rate at which the temperature changes increases, the maximum current value also increases: I_{max} (2 K/min) = 2 pA; I_{max} (6 K/min) = 5 pA. In the non-stoichiometric $SrTiO_3$ sample, polarization increases as the temperature drops below 10 K. Consequently, the dielectric properties are affected by lattice defects and thermal vibrations of the atoms close to equilibrium. Reference 12 is a study of the influence of quantum fluctuations on the structural phase transition in $SrTiO_3$ and $BaTiO_3$ compounds. For $SrTiO_3$, it was found that the quantum fluctuations fully suppress ferroelectric transitions and reduce the temperature of the transition to the tetragonal phase from 130 to 110 K, in which the oxygen octahedra rotate in opposite directions in adjacent unit cells, which leads to the quantum paraelectric phase at very low temperatures. The formation of a certain quantum coherent state[13] near 37 K, is indicated by a sharp decrease in the line width of the fine structure of the Fe^{3+} ion impurity, under external uniaxial pressure.

Conclusion

Magnetic resonance spectra of manganite ytterbium $YbMnO_3$ and gadolinium $GdMnO_3$ thin films, deposited on ferroelectric backing made of $SrTiO_3$, are measured in a broad range of temperatures. Within the 40–100 K temperature range for $GdMnO_3/SrTiO_3$, and 40–120 K for $YbMnO_3/SrTiO_3$, the magnetic resonance spectrum shows oscillation lines of absorbed microwave power, which are associated with two or more resonance absorption line widths in the cavity. One absorption line belongs to the cavity itself, and the second is caused by the sample's natural resonance properties.

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