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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

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Experimental evidences of the shape-induced structural distortion of $SrTiO_3$ single crystals from impurity Mn^{4+} ions electron paramagnetic resonance

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A study of high-quality $SrTiO_3$ single crystals doped with the Mn^{4+} ions in the cubic phase ($T > 105$ K) with X-band electron paramagnetic resonance reveals direct correspondence between a shape of a sample and magnetic anisotropy of the impurity Mn^{4+} centers. In particular, for a sample with the shape of a square base rectangular prism, a size of $(a \times a \times h)$ and faces perpendicular to the $\langle 100 \rangle$ crystallographic directions, zero-field splitting parameter D is approximately proportional to $(a/h - 1)$ quantity. Temperature dependence of D indicates that this peculiar symmetry lowering is a feature characteristic for the cubic $Fm3m$ phase of the strontium titanate. Diminishing of the D value with the decrease of the surface roughness for a thin (001)-oriented $SrTiO_3$:Mn platelet shows that the observed effect originates from the sample surface.

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1. Introduction

Strontium titanate $SrTiO_3$ (STO) serves as an object of the scientific interest for several decades, however, still new intriguing phenomena are discovered [1]. Heteroepitaxial $SrTiO_3/LaAlO_3$ interfaces are of special importance due to the formation at them of the high-mobility electron gas [2] that experiences a transition to the superconducting state [3, 4]. Strontium titanate belongs to the group of the perovskite-like ABO_3 highly-polarizable oxides. At room temperature, strontium titanate is found in the cubic symmetry phase, space group $Fm3m$ (O_h). With the temperature lowering, it obeys the antiferrodistorsive structural phase transition at $T_c \sim 105$ K to the tetragonal phase, space group $I4mcm$ (D_{4h}^{18}) [5, 6]. On further cooling, its dielectric permittivity grows with the extrapolated T_c for the ferroelectric state of approximately 35 K; however, though the dielectric permittivity reaches very high values of the order of 10^4, it saturates at about 4 K, and paraelectric phase is retained down to the lowest temperatures due to the quantum-mechanical effects (quantum paraelectricity) [7]. Polar state can be induced at finite temperatures by different perturbations such as electric field, uniaxial stress or by doping with some off-center impurities (Ca, Ba, Mg, Pb) [8–12].

Below $T_c \sim 105$ K structural domains are formed in the crystalline samples with the tetragonal axes oriented along the three quasicubic $\langle 100 \rangle$ axes. The monodomain state may be induced by cooling through the T_c of an appropriately strained crystal; it is also realized spontaneously in thin, < 0.7 mm, (110)-oriented rectangular platelets elongated along the [001] direction after its thermal training [13]. The grounds beyond the last approach are not clear.

Manganese-doped STO is also studied for quite a long time. Electron paramagnetic resonance (EPR) spectroscopy has proven to be a powerful tool for investigations of the impurity center microscopic structure and properties in various diamagnetic crystalline materials including $SrTiO_3$. It has been reported in numerous papers that manganese incorporates into the STO host lattice in various oxidation states, e.g. Mn^{4+}, Mn^{2+} and Mn^{3+} [14]. The valence of the doped Mn-ions can be controlled in different ways: using MnO or MnO_2 oxides for doping, oxidizing or reducing atmosphere in the course of synthesis, various post-annealing procedures. An interest to the STO:Mn was revived recently due to the reports on the so-called "magnetoelectric multiglass" behavior with an observation of both the ferromagnetic and ferroelectric responses in heavily Mn^{2+}-doped ceramics at low temperatures [15, 16]. An open question was how the manganese impurity induced this multiglass phase. It has been found recently that the magnetic response is extrinsic, it is caused by ferrimagnetic Mn_3O_4 precipitates.

During our studies of high-quality single crystals of Mn-doped STO we have faced an intriguing phenomenon of a dependence of the Mn^{4+} ions EPR spectrum structure, as it looked initially, on a shape of a sample. Our confidence that this observation was not an artifact was based upon two considerations. First, it was reproduced systematically on samples from different sources and even grown by different techniques. Second, already in one of the earliest papers on the STO:Mn K. A. Müller reported that the EPR spectra of the Mn^{4+} centers in the cubic phase revealed a small but clearly detectable departure of the local symmetry from cubic to tetragonal [17]. It was preliminary associated with the off-center shifting of the Mn^{4+}-ion. However, no further studies were performed and no consistent explanation was proposed for this observation.

In this paper we report on a systematic study of the small tetragonal distortion detected by the EPR spectroscopy for the impurity Mn^{4+} centers in the high-quality STO:Mn single crystals. It is found that this distortion is a specific property of the cubic $SrTiO_3$ phase, its value scales with the shape anisotropy of a sample and depends strongly on its surface roughness.

2. Materials and methods

High-quality Mn-doped $SrTiO_3$ single crystals used in this study were grown at Furuuchi Chemical Corporation (Tokyo, Japan) using Verneuil method from the high purity (99.999%) initial components. We had at our disposal also $SrTiO_3$:Mn single crystals grown at the Vavilov State Optical Institute (St.-Petersburg, Russia) by Verneuil techniques and those grown at Kazan Federal University (Kazan, Russia) by floating-zone method with optical heating. All the samples of the STO:Mn series revealed in the room-temperature EPR spectra the signals of the manganese ions in the oxidation states of Mn^{4+}, Mn^{3+} and Mn^{2+}. An overall concentration of the manganese ions in the grown crystals was about 0.1 at.%. An effect reported in this paper revealed itself in the EPR spectra of the Mn^{4+} ions that due to the close values of the ionic radii and identical oxidation states substitute for the Ti^{4+} ions [17] and thus are found above T_c in the cubic-symmetry octahedral oxygen surrounding. Therefore, the samples containing predominantly the Mn^{4+} ions were studied in this work. Electronic configuration of the Mn^{4+} ions is $3d^3(t_{2g}^3)$, its ground state according to the Tanabe-Sugano diagram is the orbital singlet $^4A_2$, electronic spin is $S = 3/2$. Manganese is represented by ^{55}Mn isotope with the natural abundance of 100%; its nuclei have a spin $I = 5/2$ that causes the well known sextet hyperfine structure of Mn-ions EPR spectra.

Initially the reported effect was found in thin, about 0.5 mm, (001)-oriented platelets of STO:Mn with the lateral size of $\sim 2-3$ mm. In order to study the effect of the sample shape, we started with the square-base rectangular prism crystal with the faces perpendicular to $\langle 100\rangle$ directions and the size of $1.35 \times 1.35 \times 2.2$ mm^3. In the course of the experiment the sample height was reduced step-by-step from 2.20 mm to 0.20 mm. An accuracy of the sample size measurements was ±0.01 mm. Surface roughness for all the coarsely ground faces according to the atomic force microscopy (AFM) was ~ 150 nm (area $50{\times}50$ μm, $1024{\times}1024$ point resolution). Finely polished faces had a roughness of ~ 2 nm (1×1 μm area, 512×512 point resolution). Fine polishing was performed with the use of diamond pastes applied in a decreasing grain size order, starting from 20/14 μm and finishing with 1/0 μm grade. Roughness value corresponds to the full width at half-maximum of the height distribution about the average. Measurements were performed with the Bruker Dimension Fastscan atomic force microscope.

Samples were oriented using Bruker D8 Advance X-ray diffractometer with the Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å) equipped with the Euler cradle. Accuracy of the orientation was about ±2 degrees.

EPR spectra of the samples were measured with the commercial Bruker ESP300 EPR spectrometer operating in the microwave X-band (9.45 GHz) equipped with the standard Bruker ER4102ST rectangular cavity with the TE$_{102}$ microwave mode. Sample temperature was maintained and controlled by either the ER4112HV continuous-flow nitrogen system or with the ESR-9 liquid helium flow cryostat (Oxford Instruments).

Dielectric permittivity of pure STO at room temperature is about 300 and reaches tens of thousands below 10 K. It is essentially not modified in the range of $T > T_c$ on doping of SrTiO$_3$ with manganese [18]. This fact sets some experimental constraints; namely, the size of the sample should be as small as possible. Otherwise, the microwave field distribution may deviate strongly from the simple TE$_{102}$ mode with the sample being in a quasi-homogeneous oscillating magnetic field B_1. In the high-temperature range, a notable dependence of the cavity resonance frequency takes place (with the sample installed). Below 100 K, new cavity modes with peculiar microwave field configurations may appear, even with the electric component E_1 inside the sample.

For modeling and fitting of the EPR spectra the Easyspin [19] module for Matlab was used.

3. Results and Discussion

In Fig. 1(a), the EPR spectrum of the SrTiO$_3$:Mn sample that had a shape of the cube with the edge length of 1.35 mm is shown. The spectra were measured at $T = 150$ K, well above the $T_c = 105$ K. This temperature corresponds to the cubic symmetry phase of SrTiO$_3$. The temperature was decreased from the room one in order to reduce the natural width of the spectral components. The magnetic field was applied along one of the $\langle 100\rangle$ directions; spectra measured along all these directions are identical for this sample. Equivalency of the $\langle 100\rangle$ directions fits well the cubic structure of the STO.

The spectrum consists of six hyperfine components that arise due to the interaction of the electronic spin with the spin of the ^{55}Mn nucleus. Each hyperfine component reveals a structure composed of the central sharp line and the shoulders on its both sides. This is a manifestation of the EPR spectrum fine structure. The spectra of the impurity Mn^{4+} centers ($S = 3/2$) presented in this paper will be analyzed using the following spin-Hamiltonian:

$$H = g\beta\left(\mathbf{B}\cdot\mathbf{S}\right) + A\left(\mathbf{S}\cdot\mathbf{I}\right) + DS_z^2 - g_n\beta_n\left(\mathbf{B}\cdot\mathbf{I}\right), \qquad (1)$$

where the first term describes the electronic Zeeman interaction, the second stands for the hyperfine interaction, the third term accounts for a zero-field splitting (ZFS) due to a possible symmetry lowering from the cubic to axial and the last corresponds to the nuclear Zeeman effect. In all cases discussed in this paper the g-factor and the hyperfine interaction constant were considered isotropic (their possible modification due to the reported symmetry lowering could not be resolved) and thus were described by the scalar g and A quantities.

Green line in Fig. 1(a) shows the simulated Mn^{4+} ion EPR spectrum obtained with the parameter values of $g = 1.9908$, $A = 214.4$ MHz, $D = 0$ MHz, $g_n = 1.3819$ and equal (0.3 mT) width of Lorentzian-shape fine-structure components. We note here the splitting structure of hyperfine components that in the case of a cubic symmetry is nearly-symmetric with respect to the center of gravity of the spectrum. Clearly, simulation result differs from the measured spectrum: in the last the widths of the lines corresponding to the transitions of $|M_s = +1/2\rangle \leftrightarrow |M_s = -1/2\rangle$ (central sharp component) and $|M_s = \pm 1/2\rangle \leftrightarrow |M_s = \pm 3/2\rangle$ (shoulders) are different. The situation with the spectrum description was improved by introducing an inhomogeneous broadening of the EPR lines that appeared due to the local strains. This has been accounted for by the averaging over a Gaussian distribution of the D-value centered at $D = 0$. Result of the spectrum fitting within a described approach is shown in Fig. 1(a) by the red line; an estimate of the D-distribution width was $w = 27 \pm 3$ MHz.

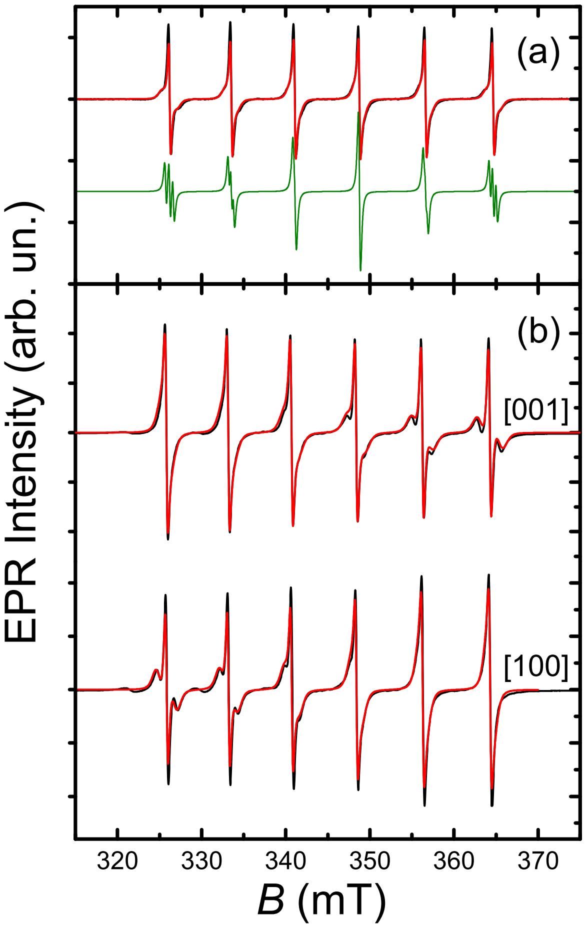

Figure 1. EPR spectra of $SrTiO_3$:Mn single crystals (black lines) and their fits (red lines): (a) for the sample with the shape of the cube, (b) for the (001)-oriented platelet shaped sample with the magnetic field along the [001] crystallographic direction (upper traces) and along the [100] direction (lower traces); $\nu = 9.4864$ GHz, $T = 150$ K. The spectrum shown in panel (a) with the green line was simulated assuming cubic symmetry of the paramagnetic center, suitable set of spin-Hamiltonian (1) parameters and equal (0.3 mT) widths of Lorenzian-shape spectral components (see text).

The splitting pattern of the Mn^{4+} ion spectrum changes significantly and qualitatively if the sample shape is changed. The effect is especially large if a sample has a shape of a square-base rectangular prism with $a \times a \times h$ size and faces perpendicular to $\langle 100 \rangle$ directions. Two types of a prism have been studied: a platelet ($h \ll a$) and a stick ($h \gg a$). In Fig. 1(b) EPR spectra of the $2.4 \times 2.4 \times 0.6$ mm^3 platelet are presented by the black lines for $\mathbf{B} \parallel [001]$ (out-of-plane, upper black trace) and $\mathbf{B} \parallel [100]$ (in-plane, lower black trace) orientations. The spectrum measured with $\mathbf{B} \parallel [010]$ is identical to the one with $\mathbf{B} \parallel [100]$. For a stick with the size of $0.6 \times 0.6 \times 3.4$ mm^3, to reproduce qualitatively the splitting patterns, the two spectra presented in Fig. 1(b) should be interchanged: the upper would be obtained with $\mathbf{B} \parallel [100]$ and the lower with $\mathbf{B} \parallel [001]$.

One notes immediately that the spectra of the platelet (stick) sample measured with the magnetic field applied along the nominally equivalent in the cubic phase [001] and [100] directions are no more identical. Moreover, both are different from the spectrum of a cube-shaped sample shown in Fig. 1(a). Clearly, an anisotropy is revealed in the spectra of the impurity Mn^{4+} ion ensembles, and this anisotropy is related somehow to the shape of the macroscopic crystalline samples. A similar anisotropy was reported for the $SrTiO_3$:Mn^{4+} crystalline samples in the early study by K.A. Müller [17]. In fact, we have faced such anisotropy in every sample of (001)-oriented thin, less than 1 mm, platelet (or stick) shaped sample of $SrTiO_3$:Mn or $SrTiO_3$:Fe crystals[†]. In the last the effect is observed at room temperature. In order to reproduce the structure of the spectra the simplest way is to introduce a non-zero D in Eq. (1). The results of the fits are shown in Fig. 1(b) with red lines. Obtained parameter values for the platelet were $D = -10 \pm 2$ MHz, D-strain distribution width $w = 29 \pm 3$ MHz. For the stick-like sample $D = 11 \pm 2$ MHz, $w = 30 \pm 3$ MHz. We see that while strain distribution width has left the same within experimental uncertainty compared to the cube-like sample, axial ZFS parameter D has acquired well resolved nonzero value. Parameter D even changes the sign on switching from the (001)-oriented platelet to the elongated prism. Thus, the spectrum of the whole ensemble of the Mn^{4+} ions in high-quality (001)-oriented $SrTiO_3$ single crystals reveals the symmetry lowering from cubic to axial (tetragonal) on changing a shape of a macroscopic sample from a cube to a platelet or a stick. Moreover, spectra structure indicates that the whole ensemble of the Mn^{4+} impurity centers reveals identical splitting. This could take place only if the anisotropic distortion originates from the host matrix.

In Fig. 2, we present a sequence of the EPR spectra of the same (001)-oriented STO:Mn crystalline sample that initially had the dimensions of $1.35 \times 1.35 \times 2.20$ mm^3 and then in a step-by-step manner its height was decreased from 2.20 mm down to 0.20 mm. We focus here at the fine structure of the high-field hyperfine component of the Mn^{4+} ions. Gradual modification of the splitting is clearly seen. Corresponding variation of the D-value obtained from the fitting of spectra is shown in the inset in Fig. 2. We find that (i) the distortion varies smoothly with changing a shape of a sample and (ii) its value is approximately proportional to $(a/h-1)$ quantity.

At the next step temperature dependencies of the EPR spectrum splitting for (001)-oriented STO:Mn platelet and stick described above were studied. Parameter D value of the spin-Hamiltonian Eq. (1) dependence on temperature is shown in Fig. 3 for a range of $100 - 170$ K. High-temperature limit of T is defined by a possibility to resolve fine EPR spectrum components related to its relaxation broadening on warming. The value of D for both samples was found almost temperature independent in the range of $120-170$ K. It starts to decrease on approaching the structural phase transition temperature T_c and at 100 K is found zero within the experimental uncertainty. This indicates that the observed phenomenon is specific for a cubic phase of the strontium titanate.

What could be an origin of the observed phenomenon? An absence of the orbital degeneracy of the Mn^{4+}-ion ground state excludes the Jahn-Teller effect [20] from this list. Another possible source is the residual stress. It usually appears due to the plastic deformations that arise during sample grinding/polishing. Plastic deformations are realized via generation and accumulation of dislocations. To create a quasi-homogeneous sample lattice distortion, dislocations have to be created homogeneously throughout the volume of samples.

[†] An extensive EPR study of a sample shape induced Fe^{3+} impurity ions anisotropy in STO crystals is in progress and will be reported elsewhere.

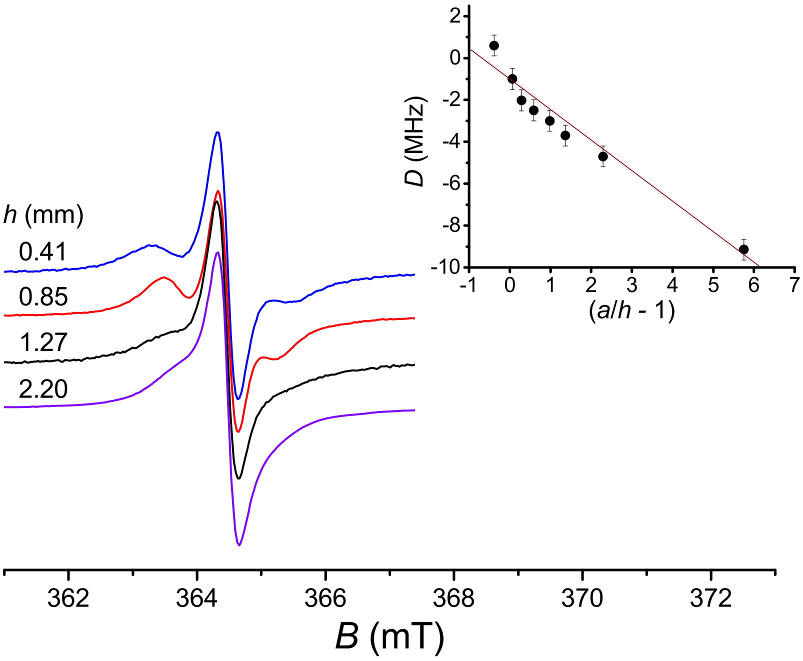

Figure 2. Shape effect on the low-field hyperfine component of the impurity Mn^{4+} ions in $SrTiO_3$ crystal EPR spectrum of a square 1.35×1.35 mm^2 base rectangular prism sample for various height h values; the faces of the prism are perpendicular to $\langle 100 \rangle$ directions, $\nu = 9.4892$ GHz, $T = 150$ K. The inset shows the dependence of the spin-Hamiltonian parameter D on the ratio of a/h.

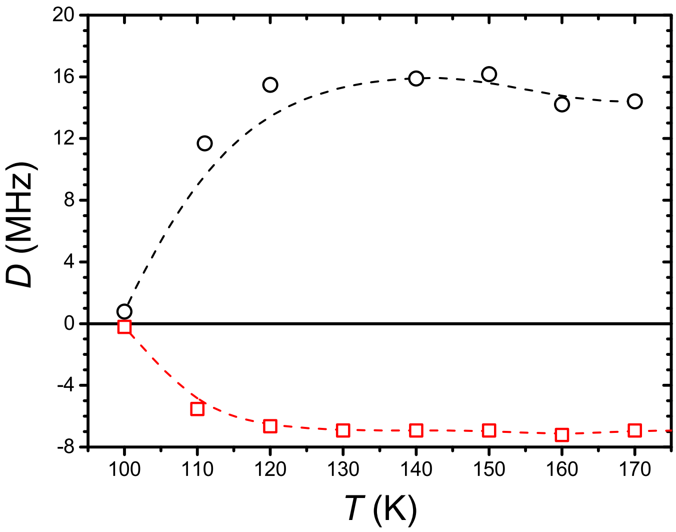

Figure 3. Temperature dependences of the ZFS D parameter of the spin-Hamiltonian Eq. (1) for a stick-like ($h \gg a$, circles) and platelet-like ($h \ll a$, squares) square-base rectangular prism $SrTiO_3$:Mn^{4+} crystalline samples. The lines are the guides for an eye only.

To check the relation of the residual stress to the observed symmetry lowering we have studied an influence of the sample surface roughness on the magnitude of ZFS parameter D. Results are presented in Fig. 4, where the fine structures of the low-field and the high-field hyperfine spectrum components measured with $\mathbf{B} \parallel [100]$ and $\mathbf{B} \parallel [001]$ directions, respectively, of the same thin (001)-oriented platelet are shown for the cases of the coarsely ground and finely polished (001)-faces. Surface roughness in the former case was ~ 150 nm and in the latter ~ 2 nm. Importantly, at the first step the spectra of the sample with coarse faces were measured (red lines in Fig. 4) then the faces were finely polished and the spectra were measured again (black lines). A clear decrease in the splitting value has taken place after faces polishing. This

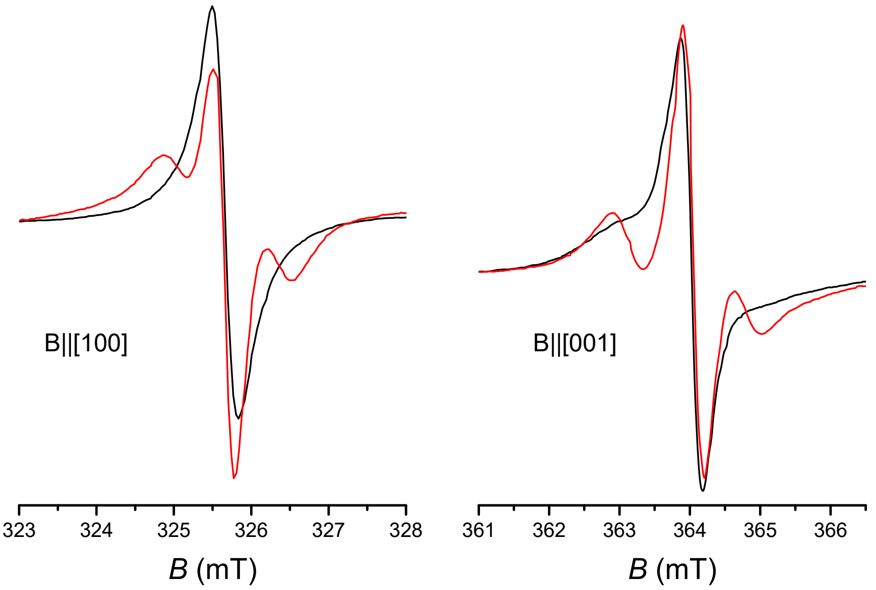

Figure 4. Fine structures of the low- and high-field hyperfine components of the EPR spectrum of Mn^{4+} ions in the same $SrTiO_3$ crystalline square (001)-oriented platelet with ground (red lines) and finely polished (black lines) faces and field $\mathbf{B}$ applied along [100] (left panel) and [001] (right panel) directions; $\nu = 9.4864$ GHz, $T = 120$ K.

observation is incompatible with a hypothesis of a residual stress origin of the sample shape-induced structural distortion of $SrTiO_3$ crystalline matrix because polishing can only increase the density of dislocation and the residual stress, respectively. It means that a different source of a distortion should be found. Another important conclusion is that the value of a distortion is related to the quality of the sample surface: it decreases with a decrease of a surface roughness. It looks that qualitatively the surface somehow induces a distortion while its roughness defines the effect quantitatively. However, to clarify the nature of the reported phenomenon, additional studies should be performed.

We note here that the distortion revealed in the EPR spectra of the impurity Mn^{4+} ions in the $SrTiO_3$ finely polished platelet decreased by $\sim 20\%$ after its annealing at 1100°C for 12 hours in the air. Observed reduction of the effect however can be associated either with the bulk structure recovery or with the surface reconstruction.

We would like to stress also that the observed phenomenon is highly unusual and to our knowledge was not reported for other bulk macroscopic crystalline samples studied with EPR before. There was no need to care about the shape, size and surface quality of such a sample before. Therefore, in our opinion, the observed phenomenon maybe unique for $SrTiO_3$. Then it may serve as an indication of a nontrivial structure and hidden instability of a nominally cubic phase of STO at $T > T_c$. Indeed, different kinds of STO lattice instabilities characterized by an onset of only the short-range order well above the T_c have been revealed by an advanced XRD diffraction analysis [21].

An observed shape-induced lattice distortion of the $SrTiO_3$ single crystals may serve as an origin for promoting a single-domain STO structure below the structural phase transition temperature [13]. The effect we report here undoubtedly should be taken into account in production of the microelectronic devices with $SrTiO_3$ substrates. Whether this effect is strongly pronounced or not in large samples is currently unclear. This question can be addressed by the micro-Raman spectroscopy. A direct approval of the observed effect may be performed by high-resolution X-ray diffraction.

4. Summary

We report in this communication an experimental observation of the structural distortion of the bulk crystalline SrTiO$_3$ samples revealed in the fine structure of the EPR spectra of impurity Mn^{4+} ions. The effect is most strongly pronounced for (001)-oriented platelets and sticks with the sign of the distortion depending on a sample shape anisotropy. It has been shown that the effect takes place at $T > T_c$, above the temperature of the structural phase transition; thus it is specific to the cubic phase of the strontium titanate. The value of a distortion depends on the quality of the sample faces and the anisotropy of its shape.

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