Observation of a Near-Surface Structural Phase Transition in SrTiO$_3$
by Optical Second Harmonic Generation

E. D. Mishina,$^1$ T. V. Misuryaev,$^1$ N. E. Sherstyuk,$^1$ V. V. Lemanov,$^2$ A. I. Morozov,$^1$ A. S. Sigov,$^1$ and Th. Rasing$^3$

$^1$Moscow Institute of Radioengineering, Electronics and Automation, Moscow 117454, Russia
$^2$A.F. Ioffe Physical Technical Institute, 194021 St. Petersburg, Russia
$^3$Research Institute for Materials, University of Nijmegen, Toernooiveld 1, NL-6525 ED Nijmegen, The Netherlands

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A near-surface structural phase transition on a SrTiO$_3$ single crystal, occurring at $T^*$ about 45 K above the bulk cubic-to-tetragonal transition, is observed by means of optical second harmonic generation. The temperature dependence of the second harmonic field in the vicinity of $T^*$ is described with a phenomenological Landau-type model.

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The study of phase transitions in low-dimensional systems such as clusters or surfaces is not only fascinating from a fundamental point of view, but also has technological relevance for nanostructures where surfaces and interfaces play a more-and-more important and sometimes dominating role. The shift of a surface phase transition temperature with respect to a bulk $T_c$ was first predicted for magnetic [1] and later for structural phase transitions [2]. Experimentally, enhancements of surface Curie temperature of more than 20 K were observed [3]. Although this shift may depend on surface quality (defects, adsorbates, dislocations, stress), even the ideal surface of a crystal may drive the surface distortions conjugated to the surface order parameter to a temperature that differs from the bulk value [4].

First order and order-disorder surface phase transitions (PT) have been studied comprehensively in past decades by various surface sensitive techniques [5]. In contrast, (structural) displacive second order PT’s, found in a wide range of nonlinear dielectric materials, have been studied systematically only by neutron and x-ray diffraction techniques. In these studies, surface effects reflect themselves by changes of scattering profiles and the appearance of a second length scale in the scattering profiles. The temperature range in which such surface effects appear depends on the surface preparation as well as on the probing depth and was reported to extend up to $\Delta T_c = 50$ K [6]. In SrTiO$_3$ a $\Delta T_c = 220$ K was predicted based on an interpolation of the penetration depth dependence of x-ray-scattering parameters [7].

In recent years, optical second harmonic generation (SHG) was proven to possess both a high surface sensitivity as well as a high sensitivity to (structural) symmetry changes. Since the early SHG observation of time-resolved laser-induced silicon melting [8], SHG was applied successfully for studying surface reconstructions [9], phase transitions in molecular monolayers [10], and the ferromagnetic-paramagnetic PT in a magnetic thin film [11].

In this Letter, we report the direct observation of a near-surface structural phase transition in a dielectric material by means of SHG that is shown to be of the same type as that in the bulk (second order displacive), but occurs at a much higher temperature with $\Delta T_c = 45 \pm 5$ K.

We used the model perovskite system SrTiO$_3$, revealing a tetragonal-to-cubic bulk phase transition at the critical temperature $\Delta T_c = 105$ K. The use of reflection and transmission geometries and appropriate polarization combinations of fundamental and SH waves allowed us to separate surface and bulk contributions to the SHG signal. This is mostly based on the fact that coherence lengths for SHG in reflection and transmission are different: $l_{coh} = \pi/(2k_z\omega \pm k_{2\omega}) = \lambda_{2\omega}/4(n_\omega \pm n_{2\omega})$, with $n_\omega$ and $n_{2\omega}$ being the refractive indices for the fundamental and SHG waves, and $(\pm)$ refers to the reflection (transmission) geometry, respectively. In this way we can probe surface and bulk order parameters separately.

The SrTiO$_3$ single crystal used in our experiments was grown by an optical zone-melting technique, polished to optical quality and oriented with an accuracy of $\pm 0.05^\circ$ to a (110) face. Below $T_c$, the crystal has $4/mmm$ symmetry, whereas for $T > T_c$, the symmetry is $m3m$. For the SHG measurements the output of a Ti:sapphire laser at 760 nm with a pulse width of about 100 fs and a repetition rate of 82 MHz was used, with an average power of 100 mW focused onto a spot of about 100 $\mu$m in diameter on the (110) crystal face. The crystal was mounted in a stress-free way in an optical flow cryostat (Oxford Instrument, 5–300 K) that did not allow further surface preparation and characterization. The SHG signal generated either in reflection (angle of incidence $45^\circ$) or in transmission (normal incidence) was filtered by color filters and a monochromator and detected by a photomultiplier tube. The incoming fundamental wave was polarized either in the plane ($p$-in) or perpendicular ($s$-in) to the plane of incidence for the reflection geometry. Polarization of the SH wave was analyzed by rotating an analyzer around its normal. For the transmission geometry it gives a variation of polarization combination from parallel ($\parallel$) to crossed ($\perp$). The choice of the azimuthal angle $\Psi = 0$ in our experiments was determined by the requirement of suppressing the bulk contribution in the reflection geometry (see below).
SH polarization diagrams for both reflection and transmission geometry are presented in Fig. 1 (top panels) and show a strong temperature dependence in intensity and shape. The temperature dependence of the polarization angle $\Phi_{2\omega}$ corresponding to the maximum of the SH intensity is plotted in the bottom panels. For the transmission geometry it is almost constant, except for an abrupt change of about 90° near the bulk transition temperature $T_c = 105 \, \text{K}$. Similar behavior is observed in the reflection geometry, but at $T^* = 150 \, \text{K}$.

Generally, the SH radiation from a nonlinear medium consists of two parts: coherent and incoherent (scattered). For a perfect crystal only fluctuations in the vicinity of a PT give incoherent hyper-Rayleigh and hyper-Raman scattering (HRS). Therefore the SHG polarization diagrams for an $\alpha$-polarized fundamental wave can be written as

$$I_s^{\alpha}(\phi) = I_{\text{HRS}}^{\alpha} + [(E_{2\omega}^{\alpha,\alpha})^2 \cos^2 \phi + (E_{2\omega}^{\alpha,\phi})^2 \sin^2 \phi - 2E_{2\omega}^{\alpha,\alpha}E_{2\omega}^{\alpha,\phi} \cos \phi \sin \phi \cos \Delta],$$

(1)

where $I_{\text{HRS}}^{\alpha}$ is the measured HRS intensity, $\Delta$ is the phase difference between $E_{2\omega}^{\alpha,\alpha}$ and $E_{2\omega}^{\alpha,\phi}$ that may arise due to the complex character of both linear and nonlinear susceptibilities and to the birefringence in the low temperature phase (LTP). For the reflection geometry, $E_{2\omega}^{\alpha,\alpha}$ and $E_{2\omega}^{\alpha,\phi}$ are $p$- and $s$-polarized components of the SH field, respectively, $\alpha = p, s$. For the transmission geometry, $\alpha = t$ in our experiments, and $E_{2\omega}^{\alpha,\alpha}$ gives parallel and $E_{2\omega}^{\alpha,\phi}$ perpendicular polarization combinations, respectively (see Fig. 1 and Fig. 3 below). The solid lines in Fig. 1 are fits to Eq. (1).

For both geometries, $I_{\text{HRS}}^{\alpha}$ increased smoothly with decreasing temperature without any discontinuities at either $T_c$ or $T^*$. For the transmission geometry it is consistent with the results in Ref. [12]. The temperature dependences of $E_{2\omega}^{\alpha,\alpha}$, $E_{2\omega}^{\alpha,\phi}$ are presented in Fig. 2. For the transmission geometry (left panel) the SH field increases sharply with decreasing temperature below $T_c$. In the reflection geometry for the $s$-in, $s$-out polarization combination (right top panel) the same feature exists but at a different temperature $T^*$. The same is observed for the $s$-in, $p$-out (right bottom panel), but now the SH intensity sharply decreases below $T^*$. In both sets of reflection data a discontinuity at $T_c$ was also observed. The phase difference $\Delta$ was zero within the error bar for all geometries, indicating that the coherent SH wave was linearly polarized and $\Phi_{2\omega}$ is indeed the polarization angle. A careful analysis of the possible nonlinear sources contributing to the SHG in both geometries allows us to attribute these features to structural phase transitions, as will be shown below.

Optical SHG derives its surface sensitivity from the fact that the normally strongest (electric dipole) contribution to the SHG response is forbidden in the bulk of centrosymmetric materials, but necessarily allowed at symmetry breaking surfaces. Higher order (quadrupole) contributions are responsible for the bulk SHG. The total SHG field of a centrosymmetric crystal can then be written as

$$E_{i,2\omega} \propto \chi^{(2)D}_{ijkl} E_j(\omega) E_k(\omega) + i \chi^{(2)Q}_{ijkl} E_j(\omega) k_l E_i(\omega),$$

(2)

where $E_j(\omega)$ and $k_j$ are the electric field and wave vector of the incoming fundamental wave, respectively, and $\chi^{(2)D}_{ijkl}$ and $\chi^{(2)Q}_{ijkl}$ are the surface dipole and the bulk quadrupole nonlinear susceptibilities, respectively.
Within the frame of the Ginzburg-Landau theory [13], the temperature dependence of the bulk nonlinear susceptibility $\chi_{ijkl}^{Q,4nm}$ in the LTP can be written as

$$\Delta \chi_{ijkl}^{Q} = \frac{\partial^{2} \Delta\chi_{ijkl}^{Q}}{\partial \eta^{2}} + \Delta \chi_{ijkl}^{Q}, \quad (3)$$

where $\Delta \chi_{ijkl}^{Q} = \theta_{ijklmn}^{Q} \eta_{n} \eta_{m}$, $\chi_{ijkl}^{Q}$ is the bulk quadrupole susceptibility and $\theta_{ijklmn}^{Q}$ is a sixth order tensor, both corresponding to the symmetry of the high temperature phase (HTP), and $\eta$ is the bulk order parameter that is zero above $T_c$. For SrTiO$_3$, $\eta$ is the angle of rotation of the oxygen octahedron around one of its axes of symmetry. Below $T_c$, $\eta$ can be expressed as a function of reduced temperature $\tau = (T - T_c)/T_c$ as $\eta \propto \tau^{1/2}$, whereas the normal temperature dependence of $\chi_{ijkl}^{Q,m3n}$ (i.e., not correlated with the phase transition) can be taken into account as a second order polynomial in $(T_c - T)$, analogous to the temperature dependence of the refractive index [14]. Therefore below $T_c$ an additional temperature dependent term appears:

$$\Delta \chi_{ijkl}^{Q} \propto (T_c - T). \quad (4)$$

To obtain the temperature dependence of the surface order parameter $\eta_s$ as well as the surface transition temperature $T^*$, surface-induced terms should be taken into account in the expression for the free energy. Following Levanyuk [4] this gives, for the second order PT,

$$F = S \int \frac{dz}{0} dz \left[ \frac{2}{a} \eta + \frac{B}{4} \eta^{4} + \frac{2}{2} \left( \frac{d \eta}{dz} \right)^{2} + \frac{d_0 \tilde{A}}{2} \eta_0^{2} \right],$$

where $S$ is the crystal surface area, $A = a(T - T_c)$, $\tilde{A} < 0$, $d_0$ is the thickness of the surface layer, $B > 0$, and $a$ and $A$ are constants, and $z$ is directed into the bulk of the crystal. $\eta$ decays exponentially inside the crystal with a correlation length $r_c$ of the bulk order parameter: $\eta = \eta_0 \exp(-z/r_c)$. This gives

$$\eta_0^2 = -8(Ar_c + d\tilde{A})/Br_c \propto (T^* - T), \quad (6)$$

where $T^*$ is the temperature at which a nonzero value of the order parameter appears, i.e., the temperature of a surface phase transition.

The surface nonlinear optical susceptibility can then be written as

$$\chi_{ijkl}^{D,m} = \chi_{ijkl}^{D,2nm} + \Delta \chi_{ijkl}^{D}, \quad (7)$$

where $\Delta \chi_{ijkl}^{D} = \theta_{ijklmn}^{D} \eta_{n} \eta_{m}$ or $\Delta \chi_{ijkl}^{D} = \theta_{ijklmn}^{D} \eta_{n} \eta_{m} + \theta_{ijklmn}^{D} \eta_{n} \eta_{m}$ and where the surface order parameters can be expressed in the bulk order parameters by Euler transformations (see Fig. 3). Similar to the bulk, this gives a linear temperature dependence of the surface susceptibilities below the surface phase transition temperature $T^*$:

$$\Delta \chi_{ijkl}^{D} \propto (T^* - T). \quad (8)$$

The nonzero components of $\chi^{(2)D}$ and $\chi^{(2)Q}$ are determined by the symmetry of the surface and bulk of the crystal. Their contributions to the SHG signal are largely dependent on the Fresnel factors and the coherence lengths. In particular, we get for the reflection geometry $l_{coh}^{ref} = 40$ nm and for the transmission $l_{coh}^{trans} = 420$ nm. It means that, although for both geometries the total SH field is given by $E_{2\omega} = E_{coh}^{ref} + E_{coh}^{trans}$, the relative contributions of surface and bulk to the SH signal are very different due to the different integration volumes. As a result, the surface contribution is comparable to or dominating the bulk in the reflection geometry, whereas for transmission the bulk contribution, if allowed by symmetry, dominates by at least an order of magnitude. Moreover, in reflection, by choosing the azimuthal angle of the crystal ($\Psi = 0$), the bulk contribution can be suppressed completely due to the symmetry of $\chi^{Q,m3n}$.

For normal incidence, none of the nonzero $\chi^{Q,m3n}$ components can give a contribution to the SHG field. Therefore, for these experimental conditions, no coherent SHG appears in the HTP in the transmission geometry, consistent with the experimental results (Fig. 2). This is also true for the LTP if $\eta = \eta_z$. When $\eta = \eta_x$, $\Delta \chi_{ijkl}^{D}$ yields a nonzero SH field linear in $(T_c - T)$, in perfect agreement with the experimental results (see Fig. 2). Within the frame of this model the polarization angle $\Phi_{2\omega}$ should be constant in the LTP and change abruptly at $T_c$, in excellent agreement with Fig. 1.

For the reflection geometry, the temperature dependence of the SH field still reveals a feature at $T_c$ but also an additional one at $T^*$ (see Fig. 2). To determine the nonzero
surface susceptibility tensor components, the symmetry of the surface layer should be analyzed. Figure 3 shows the atomic arrangement for the ideal (110) SrTiO$_3$ crystallographic plane within the first crystallographic layer. By assuming that no additional order parameters appear at the surface in comparison with the bulk this corresponds to a $2nm$ surface symmetry in the HTP and an $m$ surface symmetry in the LTP for any orientation of the order parameter. For these symmetries above $T^*$ a surface $\chi_{ijk}^{m,3m}$ (as well as a bulk $\chi_{ijk}^{0,m3m}$) yields a nonzero SHG field for $s$-in, $p$-out and a zero SH field for the $s$-in, $s$-out polarization combinations. The solid lines in Fig. 3 are fits to Eq. (2) [with the nonlinear susceptibilities given by Eqs. (3) and (8)] and show an excellent agreement with those theoretical predictions. From these data the near-surface phase transition temperature appears to be $T^* = (150 \pm 5)$ K.

The polarization angle $\Psi_{2\omega}$ that follows from these considerations for a temperature range $T_c < T < T^* \tan\Psi_{2\omega} = E_{ps}/E_{ss} \approx [C_1 + C_2/(T - T_c)]$ (with $C_1$ and $C_2$ being constants) is also in excellent agreement with the experimental results (see solid line in Fig. 1, right bottom panel).

From the theoretical considerations we can also make an estimate of the expected $T^*$:

$$T^* = T_c + \frac{(\Delta d_0)^2}{4D}. \quad (9)$$

With $a = 5.4 \times 10^{-3}$ eV $\cdot$ K$^{-1}$, $D = 3.7 \times 10^{-15}$ eV $\cdot$ cm$^2$ [15] and supposing that $\Delta \sim aT_c$ and $d_0$ is given by the lattice constant, Eq. (9) predicts $T^* = 130$ K, in good agreement with the experimental results.

Note that, though our experiment could not be done in an ultrahigh vacuum environment, the presence of an isotropic adsorbate layer will have no effect on the $ss$ SHG response due to the so-called $ss$ selection rule [16]. However, such a layer may contribute to the regular temperature dependence for the $sp$ polarization combination. It is important to realize that, as the surface contribution comes from several top layers of the crystal, the use of a stabilized surface (with or without an adsorbate on top) is not critical for the observation of a near-surface (or subsurface) phase transition. In high vacuum, it is very likely that the contribution of a reconstructed surface (that has been observed even at room temperature [17]) is anisotropic and might dominate the contribution from the PT occurring in the top layers.

In conclusion, we have reported the observation of a second order displacive structural near-surface phase transition on a single crystal by means of optical second harmonic generation by using the intrinsic sensitivity of the SHG technique for inversion symmetry breaking. The temperature of the surface phase transition for a (110) face of a SrTiO$_3$ single crystal was obtained and appeared to differ from the temperature of the bulk phase transition by 45 K. Both $T^*$ and the temperature dependence of the surface order parameter could be described by a phenomenological Landau theory.

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