Observation of a Near-Surface Structural Phase Transition in $SrTiO_3$ by Optical Second Harmonic Generation

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(Received 6 May 1999; revised manuscript received 14 January 2000)

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.

PACS numbers: 68.35.Rh, 42.65.Ky, 77.80.Bh

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: $l_{\mathrm{coh}} = \pi/(2k_{z,\omega} \pm k_{z,2\omega}) = \lambda_\omega/4(n_\omega \pm n_{2\omega})$, with n_ω and $n_{2\omega}$ being the refractive indices for the fundamental and SHG waves, and $+$ $(-)$ 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 $\pm 0.05°$ 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 μm 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°) 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 ($\|$) 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).

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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 SHG 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 $T_c = 105$ K. Similar behavior is observed in the reflection geometry, but at $T^* = 150$ 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 α-polarized fundamental wave can be written as

$$I_{2\omega}^{\alpha}(\phi) = I^{\mathrm{HRS}} + [(E_{2\omega}^{\alpha,u})^2 \cos^2\phi + (E_{2\omega}^{\alpha,t})^2 \sin^2\phi - 2E_{2\omega}^{\alpha,u} E_{2\omega}^{\alpha,t} \cos\phi \sin\phi \cos\Delta], \quad (1)$$

where I^{HRS} is the measured HRS intensity, Δ is the phase difference between $E_{2\omega}^{\alpha,u}$ and $E_{2\omega}^{\alpha,t}$ 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, $E_{2\omega}^{\alpha,u}$ and $E_{2\omega}^{\alpha,t}$ are p- and s-polarized components of the SH field, respectively, $\alpha = p, s$. For the transmission geometry, $\alpha = t$ in our experiments, and $E_{2\omega}^{\alpha,t}$ gives parallel and $E_{2\omega}^{\alpha,u}$ 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^{HRS} 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 $E_{2\omega}^{\alpha,u}$, $E_{2\omega}^{\alpha,t}$ 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 SHG intensity sharply decreases below T^*. In both sets of reflection data a discontinuity at T_c was also observed. The phase difference Δ 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

$$E_{i,2\omega} \propto \chi_{ijk}^{(2)D} E_j(\omega) E_k(\omega) + i\chi_{ijkl}^{(2)Q} E_j(\omega) k_k E_l(\omega), \quad (2)$$

where $E_j(\omega)$ and k_j are the electric field and wave vector of the incoming fundamental wave, respectively, and $\chi_{ijk}^{(2)D}$ and $\chi_{ijkl}^{(2)Q}$ are the surface dipole and the bulk quadrupole nonlinear susceptibilities, respectively.

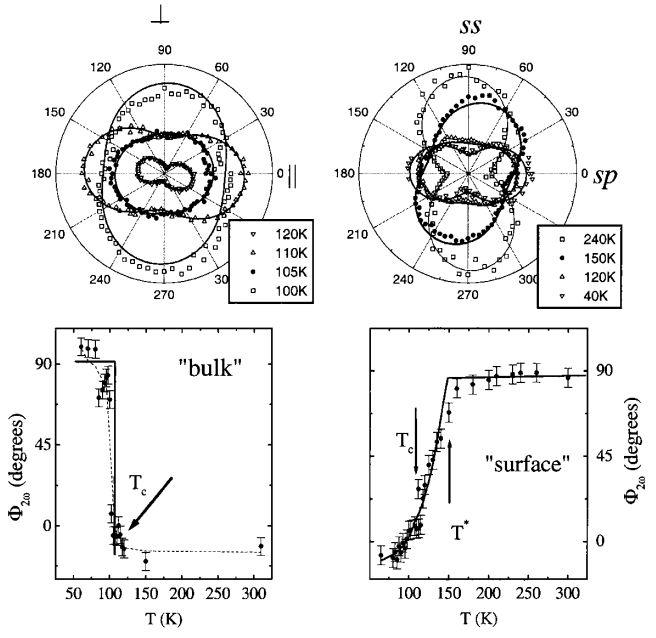

FIG. 1. Top: polarization diagrams of SH intensity for azimuthal angle $\Psi = 0$. Solid lines are fits to Eq. (1). Bottom: temperature dependence of the SHG polarization angle $\Phi_{2\omega}$. Left panels correspond to transmission and right panels correspond to the reflection geometry. Solid lines are fits to the data (see text). The dashed line is a guide for the eye. The fundamental radiation is $s(t)$ polarized.

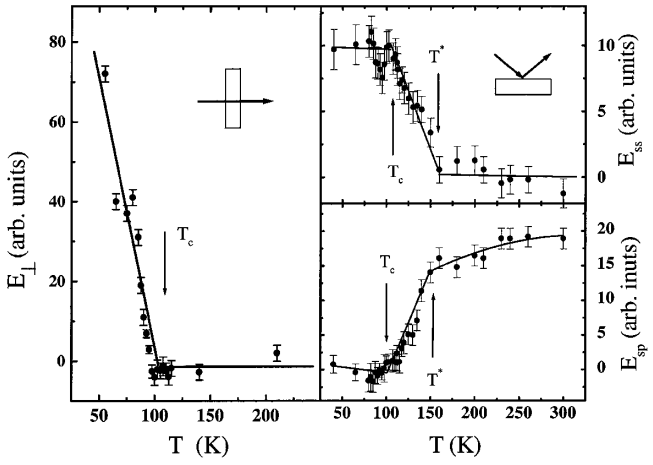

FIG. 2. Left: temperature dependence of SH intensity in transmission for crossed polarization combinations. Right: temperature dependence of s-polarized (top) and p-polarized (bottom) SHG field in reflection. The fundamental wave is $s(t)$ polarized. Solid lines are fits to the data using Eq. (5).

Within the frame of the Ginzburg-Landau theory [13], the temperature dependence of the bulk nonlinear susceptibility $\chi^{Q,4mmm}_{ijkl}$ in the LTP can be written as

$$\chi^{Q,4mmm}_{ijkl} = \chi^{Q,m3m}_{ijkl} + \Delta\chi^{Q}_{ijkl}, \quad (3)$$

where $\Delta\chi^{Q}_{ijkl} = \theta_{ijklmm}\eta_m\eta_m$. $\chi^{Q,m3m}_{ijkl}$ is the bulk quadrupole susceptibility and θ_{ijklmn} is a sixth order tensor, both corresponding to the symmetry of the high temperature phase (HTP), and η is the bulk order parameter that is zero above T_c. For $SrTiO_3$, η is the angle of rotation of the oxygen octahedron around one of its axes of symmetry. Below T_c, η can be expressed as a function of reduced temperature $\tau = |T_c - T|/T_c$ as $\eta \propto \tau^{1/2}$, whereas the normal temperature dependence of $\chi^{Q,m3m}_{ijkl}$ (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:

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

To obtain the temperature dependence of the surface order parameter η_0 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,

$$F = S\int_0^\infty dz\left[\frac{A}{2}\eta^2 + \frac{B}{4}\eta^4 + \frac{D}{2}\left(\frac{d\eta}{dz}\right)^2\right] + \frac{d_0\tilde{A}}{2}\eta_0^2, \quad (5)$$

where S is the crystal surface area, $A = a(T - T_c)$, $\tilde{A} < 0$, d_0 is the thickness of the surface layer, $B > 0$, D and a are constants, and z is directed into the bulk of the crystal. η 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

$$\chi^{D,m}_{ijk} = \chi^{D,2mm}_{ijk} + \Delta\chi^{D}_{ijk}, \quad (7)$$

where $\Delta\chi^{D}_{ijk} = \theta_{ijkzz}\eta_{0z}\eta_{0z}$ or $\Delta\chi^{D}_{ijk} = \theta_{ijkxx}\eta_{0x}\eta_{0x} + \theta_{ijkyy}\eta_{0y}\eta_{0y}$ 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^*:

$$\Delta\chi^{D}_{ijk} \propto (T^* - T). \quad (8)$$

The nonzero components of $\hat{\chi}^{(2)D}$ and $\hat{\chi}^{(2)Q}$ 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

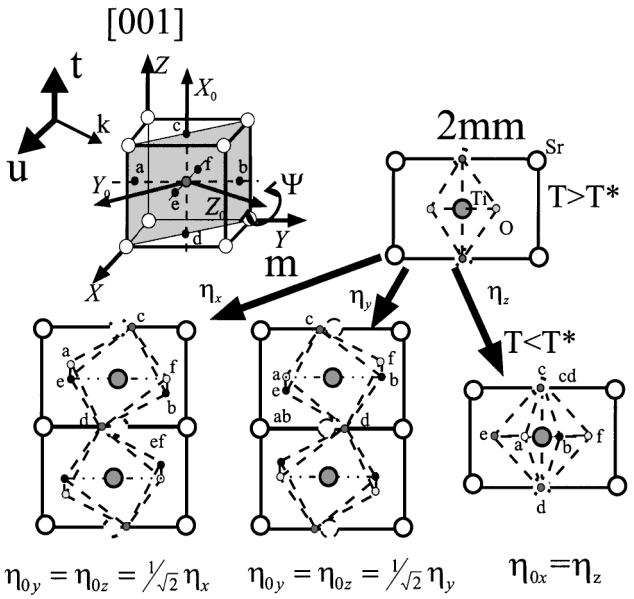

FIG. 3. Left top: mutual orientation of the crystallographic and surface unit cells for (110) face. Azimuthal angle Ψ equals zero when the Z_0 axis of the crystallographic frame is parallel to the t axis of the laboratory frame. *tuk* is the laboratory frame with k parallel to the propagation direction of the fundamental beam. The atomic arrangements correspond to the first crystallographic layer in the HTP (top right) and LTP (bottom). η and η_0 are the order parameter components in the bulk and surface, respectively. To follow the axes of rotation, oxygen atoms are denoted by letters.

lengths. In particular, we get for the reflection geometry $l^{\text{refl}}_{\text{coh}} = 40$ nm and for the transmission $l^{\text{tr}}_{\text{coh}} = 420$ nm. It means that, although for both geometries the total SH field is given by $\vec{E}_{2\omega} = \vec{E}^{D}_{2\omega} + \vec{E}^{Q}_{2\omega}$, 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 $\hat{\chi}^{Q,m3m}$.

For normal incidence, none of the nonzero $\hat{\chi}^{Q,m3m}$ 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 $\eta = \eta_{x(y)}$, $\Delta\chi^{Q}_{ijkl}$ 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 $2mm$ 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 $\chi_{ijk}^{D,2mm}$ (as well as a bulk $\chi_{ijkj}^{Q,m3m}$) 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 $\Phi_{2\omega}$ that follows from these considerations for a temperature range $T_c < T < T^*$ $\tan\Phi_{2\omega} = E_{ps}/E_{ss} \propto [C_1 + C_2/(T - T_c)]$ (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^*:

$$T^* = T_c + \frac{(\tilde{A}d_0)^2}{aD}. \tag{9}$$

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 $\tilde{A} \sim aT_c$ 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.

This work is supported by INTAS, NWO, RFBR, and ISSEP. We would like to thank Professor O. A. Aktsipetrov and Dr. A. N. Rubtsov for useful discussions. E. D. M. thanks the Research Institute for Materials of the University of Nijmegen for their hospitality.

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