Sextic anharmonicity and ferroelectricity in photoexcited SrTiO$_3$ at low temperatures

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New Journal of Physics 9 (2007) 320
Received 10 May 2007
Published 10 September 2007
Online at http://www.njp.org/
doi:10.1088/1367-2630/9/9/320

Abstract. Ultraviolet light induces ferroelectric domains in SrTiO$_3$ at low temperatures. The ferroelectric domains are related to anharmonic soft modes of the crystal. We show the sextic anharmonicity is the lowest order for the soft mode to give rise to ferroelectricity in SrTiO$_3$ after photoexcitation. The occurrence of a quartic anharmonicity and/or harmonicity for the soft mode potential will suppress the domain structure in the crystal.

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1. Introduction

The perovskite compound SrTiO$_3$ has a far larger dielectric constant than other dielectrics [1]. This characteristic is believed to come from its ferroelectric or soft mode behavior observed from Raman scattering [2, 3], neutron scattering [4] as well as infrared absorption [5, 6]. As is well known, anharmonicity is very important in describing this soft mode. The temperature dependence of the ferroelectric mode was explained by a nonlinear shell model, assuming an anisotropy in the oxygen polarizability [3], which automatically includes the coupling of the soft mode to an acoustic mode at low temperatures. In that work [7], it was stressed that a single mode theory cannot give a satisfactory fit to the experimental data.

Barrett [8] dealt with an ionic polarizability based on the quartic anharmonic model, which resulted in a Curie–Weiss law down to 50 K for SrTiO$_3$. This quartic anharmonicity was also confirmed for SrTiO$_3$ down to 10 K by two-phonon Raman spectroscopy [9]. However, for even lower temperatures, the quartic anharmonic theory becomes invalid [7]. With the hyper-Raman technique, the zone-center soft modes of SrTiO$_3$ were measured down to 5 K by Vogt [10], and the soft modes were suggested to be based on a sextic anharmonicity instead of a quartic one.

SrTiO$_3$ is already known to remain paraelectric at all temperatures [2]. Müller and Burkard [7] made a further study by measuring the temperature-dependent dielectric constant down to 0.3 K and even to 0.035 K for one sample. The constant dielectric behavior below 4 K was assigned to a quantum effect. The ferroelectric transition temperature of this crystal is so low that it falls into the quantum mechanics regime and thus the ferroelectric phase is suppressed by the quantum fluctuations. The intrinsic paraelectricity was confirmed by the stress-induced ferroelectricity in this crystal [11] and the quantum fluctuation was recently observed directly using x-ray absorption [12].

The above studies fundamentally concern the crystal in the electronic ground state, in which there are no electrons in the conduction band. Recently, it was shown that an ultraviolet illuminated SrTiO$_3$ crystal undergoes gigantic dielectric [13, 14] and conductive [15] enhancements at low temperatures. These are typical photo-induced phase transitions. Due to the photoexcitation, the valence band electrons are excited to the conduction band. Different from the valence band electrons, the interaction of these excited electrons with the phonons cannot be involved in the mean field on the electrons. In consequence, the electron and phonon (e–p) coupling is expected to play a special role in these photo-induced phase transitions. This was microscopically interpreted by the dual e–p coupling model with the odd parity phonon modes to be under a sextic anharmonicity, with a coupling with the photoexcited electron in a quadratic manner and with the even parity phonon modes assumed to be harmonic, coupled linearly with the electron [16]. The even breathing modes were shown to be associated with the localized state. The odd modes in sextic anharmonicity dominate the extended state, i.e. the super-para-electric (SPE) large polaron, which is actually a macroscopic ferroelectric domain and responsible for the photo-induced dielectric and conductive properties of the crystal [16]. Thus, the sextic anharmonicity for the odd soft modes potentials becomes the key point of the formation of the domain structure. However, the sextic anharmonicity in that work [16] was fundamentally an assumption. The origin of this sextic anharmonicity was not clarified.

In the following section, we will show that the sextic anharmonicity is the lowest order for the soft mode to give rise to ferroelectric domains in SrTiO$_3$ after photoexcitation at low temperatures. And in section 3, we will give a general argument on the influence of the harmonicity or quartic anharmonicity on the domain structure in the crystal.
2. Sextic anharmonicity and ferroelectricity

Since the photo-induced phase transition in SrTiO$_3$ is associated with polarons [16], next we investigate the fundamental single electron system. In an attempt to reflect the spatial extension of the polaron, we introduce a parameter of reciprocal localization length $\Delta$ into the wavefunction for the electronic state which is taken as

$$|p\rangle = \sum_l \varphi(l) a^\dagger_{l\sigma} |0\rangle, \quad \sum_l |\varphi(l)|^2 = 1,$$

where $|0\rangle$ is the true electron vacuum, $a^\dagger_{l\sigma}$ is the creation operator of an electron at the lattice site $l$ with spin $\sigma (= \alpha, \beta)$ in a simple cubic crystal and the trial function $\varphi(l)$ is assumed to be a Gaussian as

$$\varphi(l) \sim \exp \left[\frac{-\Delta^2 (l \cdot l)}{2}\right], \quad l = (l_x, l_y, l_z),$$

wherein, $l_x, l_y, l_z$ are the Cartesian components of $l$.

The ultraviolet light turns the SrTiO$_3$ crystal from a dielectric into a conductor [15]. However, the observed photo-conductivity is small in comparison with metallic conductivity. Thus, the photo-induced conductivity actually suggests a shallow bound state near the bottom of the conduction band. In contrast, the large Stokes-shift as deduced from a luminescence experiment [17] suggests a deep and localized state within the large energy gap of the crystal [18].

The above-mentioned two in-gap states practically correspond to two metastable states. Thus, we are encouraged to look for a model encompassing at least one shallow and extended state, and one deep and localized state, comprising of two minima on the energy surface of the ground state of the e–p coupling system.

For the complicated compound SrTiO$_3$, there exist various vibration modes. Fundamentally, we think of two types of vibration modes, even and odd parity modes as shown in figure 1. According to the appendix, the Hamiltonian of the e–p coupling can be expressed in the lowest order as

$$H = -T \sum_{l, l', \sigma} (a_{l\sigma}^\dagger a_{l'\sigma} + \text{h.c.}) - S_1 \sum_l B_l a^\dagger_{l\alpha} a_{l\alpha} + \frac{S_1'}{2} \sum_l \left(-\frac{\partial^2}{\partial B^2_l} + B^2_l\right) \left(-\frac{\partial^2}{\partial D^2_{l,i}} + D^2_{l,i}\right)$$

with $B_l$ and $D_{l,i}$ representing the normal coordinates of the even and odd modes, respectively. $S_i$ ($i = 1, 2$) are the corresponding e–p coupling strengths.

From the schematic diagram in figure 1, the restoring force for the even mode is usually greater than that of the odd mode. So the characteristic frequency of the former is usually larger than that of the latter. For the time being, we can strategically write the whole Hamiltonian of the e–p coupling system in the following way

$$H = -T \sum_{l, l', \sigma} (a_{l\sigma}^\dagger a_{l'\sigma} + \text{h.c.}) - S_1 \sum_l B_l a^\dagger_{l\alpha} a_{l\alpha} + \frac{S_1'}{2} \sum_l \left(-\frac{\partial^2}{\partial B^2_l} + B^2_l\right)$$

$$-S_2 \sum_{l,i} D_{l,i}^2 a^\dagger_{l\alpha} a_{l\alpha} + \frac{S_2'}{2} \sum_{l,i} \left(-\frac{\partial^2}{\partial D^2_{l,i}} + D^2_{l,i}\right).$$

Here, we assume a harmonicity for the even mode phonons. However for the odd mode phonons for the present, we assume a $2r$th-order of anharmonicity with $r$ being an integer. The index $i$
Figure 1. Schematic diagram of the vibration of a single TiO$_6$ unit for (a) an even mode and (b) an odd mode.

claims the three independent spatial degrees of freedom for each phonon. $S'_1$ and $S'_2$ are the constants related to the effective mass and the characteristic frequency of the two modes, respectively. $\{l, l'\}$ denotes that the electronic transfer is only between the adjacent sites. Compared with the phonon frequency ($\sim 30$ meV) from the absorption spectra in SrTiO$_3$ [17], the conduction bandwidth ($12 T = 2$ eV) [18] of the crystal is much larger. So we can seek the adiabatic property of the model for the boundary condition of the integer $r$.

Within the Helmann–Feynman theorem ($\langle \cdots \rangle \equiv \langle p | \cdots | p \rangle$)

$$\frac{\partial \langle H \rangle}{\partial B_l} = 0, \quad \frac{\partial \langle H \rangle}{\partial D_{l_i}} = 0,$$

(5)

the adiabatic energy of the Hamiltonian in equation (4) ($\equiv h_{ad}$) has the simple form

$$h_{ad} = -T \sum_{l, l', \sigma} \langle a^+_l \sigma a^i_l \sigma \rangle + \text{H.c.} - \frac{S'_1}{2S'_1} \sum_l \langle a^+_l a^i_l \rangle^2 - \frac{r - 1}{r} S_2 \left( \frac{2S_2}{S'_2 r} \right)^{(1/r - 1)} \sum_{l, i} \langle a^+_i a^i_l \rangle^{r/(r-1)}.$$

(6)

First, we expect from equation (6) to obtain a minimum (at $0 < \Delta < 1$) related to the shallow and extended state, which is associated with the conductive and dielectric enhancements [16]. In an attempt to get the analytic expression for the adiabatic energy with respect to the extension parameter $\Delta$, we employ the continuum approximation because in the extended state, the polaron extension is usually much larger than the lattice constant. Within this approximation,

$$-T \sum_{l, l', \sigma} \langle a^+_l \sigma a^i_l \sigma \rangle + \text{H.c.} \rightarrow -T \int_{-\infty}^{\infty} dl_x \int_{-\infty}^{\infty} dl_y \int_{-\infty}^{\infty} dl_z \varphi(l) \left( \frac{\partial^2}{\partial l_x^2} + \frac{\partial^2}{\partial l_y^2} + \frac{\partial^2}{\partial l_z^2} \right) \varphi(l).$$

Thus, equation (6) is reduced to

$$h_{ad} = -6 T + \frac{3T \Delta^2}{2} - \frac{S'_1}{2S'_1} \Delta^3 - 3S_2 \left( \frac{2S_2}{S'_2 r} \right)^{(1/r - 1)} \pi^{(3/2 - 2r)} \sqrt{\frac{r - 1}{r}} \Delta^{(3/r - 1)}.$$

(7)
Since the constant term $-6T$ merely lowers the whole adiabatic surface, we can expect the minima of the adiabatic surface from the combination of the second term with the third term or with the last term in equation (7). However, the combination of the second and the third terms can only possibly give one minimum at $\Delta < 1$, and this minimum can occur only at $\Delta = 0$. An extended state as this minimum represents, it is a free electronic state rather than a state that suffers any phonon scattering. For such a complicated compound as SrTiO$_3$, the conduction band electrons can never avoid being scattered by the phonons due to the e–p coupling. In consequence, the free electronic state ($\Delta = 0$) is not a metastable state. It is only a transient and unstable state, which is not responsible for the ferroelectric domains observed from the experiments [13]–[16]. Thereby, an extended metastable state can only be expected from the combination of the second and the last terms in equation (7), with $r$ being restricted to be greater than $5/2$. Therefore, the lowest order for the odd modes in the Hamiltonian of equation (4) is 6.

It should be mentioned that the harmonicity ($r = 1$) or the quartic anharmonicity ($r = 2$) alone for the odd modes in equation (4) is numerically invalidated because in such a case the shallow extended state or the ferroelectric domain is always suppressed.

For the localized metastable state (at $\Delta > 1$) as concerned with the large Stokes shift [17], it can be readily obtained from the first two terms of the discrete model in equation (6), given appropriate $S_1$ and $S'_1$.

3. Effect of quartic anharmonicity and harmonicity

In the above discussion, we have shown that the sextic anharmonicity alone is the lowest order for odd parity modes. In such a case, the macroscopic ferroelectric domains, substantially each equivalent to an extended and shallow in-gap state, will arise from the photoexcitation in the crystal and are responsible for the remarkable dielectric and conductive properties at low temperatures [17]. However, as the temperature or the restoring force of the soft mode increases, lower order anharmonicity or harmonicity are inclined to occur. To get further knowledge about the influence of the lower order cases on the sextic anharmonicity, we resort to numerically calculating the adiabatic surface of the Hamiltonian considering only the odd parity soft modes

$$H_{\text{sim}} = -T \sum_{\{l,l'\},\sigma} (a_{l,l',\sigma}^{\dagger} a_{l',\sigma} + \text{H.c.}) - \frac{S_d \omega_d}{2} \sum_{l,i} n_i D_{l,i}^2 + \frac{\omega_d}{2} \sum_{l,i} \left( x D_{l,i}^2 + \frac{D_{l,i}^6}{3} \right),$$

wherein, $\omega_d$ is assigned to be the frequency of the soft mode ($\sim 1$ meV) observed via the Raman scattering [2]. $x$ serves as a ratio to reflect the harmonic influence on the sextic terms. We employ the Gaussian type trial function for the variance of the degrees of freedom of the soft mode as $D_{l,i} = d \exp \left(-\frac{(l-l_i)^2}{2\Delta_{l,i}^2}\right)$, with $d$ and $\Delta_{l,i}$ being the amplitude and the half-width, respectively. The electronic trial function is stated in equation (1). For a particular e–p coupling constant $S_d = 60$ and the lattice size of $100 \times 100 \times 100$, we obtain the corresponding adiabatic surface as shown in figure 2. We can see that a shallow gap state survives, but only when $x$ is very small ($\sim 0.0001$). Even if $x$ is as small as 0.001, the extended state will be lifted up into the conduction band. So it is clear that the introduction of the harmonic terms for the soft mode produces too large a restoring force, which will suppress the domain structure.

If we replace the harmonic terms $D_{l,i}^2$ in equation (8) with the quartic anharmonic terms $D_{l,i}^4/2$, we can obtain the same consequence, except that the critical value for $x$ to suppress the

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shallow in-gap state is about 0.01–0.1. As a result, compared with the sextic anharmonicity, the lower order anharmonic terms or the harmonic ones must have a very small ratio if they co-occur with sextic terms. So, we can temporarily neglect them in the investigation of the low temperature properties of SrTiO$_3$.

4. Conclusion

Subject to ultraviolet irradiation, the SrTiO$_3$ crystal shows ferroelectric domain structures [16], which are the origin of the experimentally observed photo-induced dielectric enhancement [13, 14] and photo-conductivity [15] of this crystal. The photo-induced ferroelectricity of this crystal is microscopically related to a kind of e–p interaction effect.

In this paper, we show that the sextic anharmonicity is the lowest order anharmonicity for the odd parity phonon modes coupled with the electron and this kind of e–p coupling gives rise to macroscopic polaronic droplets and ultimately to ferroelectric domains in light soaked SrTiO$_3$. However, as the temperature or the restoring force of the soft mode of the crystal increases, a lower-order quartic anharmonicity or harmonicity will occur. In such a case, the e–p coupling only stimulates disordered vibrations in the lattice and the crystal will not show domain structures after photoexcitation.

Acknowledgments

Y Qiu is grateful to Dr K Ishida for his suggestion of inspecting the harmonic effect. This work was partly supported by the Research Fund of Zhejiang Normal University, China, partly by the NAREGI Nano-science Project, Ministry of Education, Culture, Sports, Science and Technology, Japan and Peta-computing Nano-science Grand-challenge Project by the Japanese Ministry of Education, Science and Culture.
Appendix

The e–p interaction can usually be expressed in the Einstein model as

\[ -S \sum_l Q_l a_l^\dagger a_l, \quad (A.1) \]

\( S \) is the common notation of the coupling strength. The normal coordinates \( Q_l \) can be expanded by the real displacements of the crystal ions. For a lattice with \( N \) unit cells and \( s \) atoms or ions in each, the expansion can be written as

\[ Q_l \eta \sim \sum_{i=1}^N \sum_{\xi=1}^s u_{i,\xi} \cdot h_{i,\eta}^\xi e^{-iR_0^i}, \quad (A.2) \]

wherein, \( u_{i,\xi} \) is the transient vibrating displacement of the \( \xi \)th ion in the \( i \)th unit cell, whose center of mass coordinate is \( R_0^i \), and \( h_{i,\eta}^\xi \) is the polarization vector of the corresponding mode. By setting up a rectangular coordinate system with a proper choice of its origin point in the crystal, we can always find an \( O_2^- \) with a transient displacement of \(-u_{i,\xi}\) pertaining to a particular TiO_6 cell centered at \(-R_0^i\), given an \( O_2^- \) with the transient displacement of \( u_{i,\xi} \) pertaining to the cell centered at \( R_0^i \), meeting

\[ u_{i,\xi} = u_{i,\xi} \quad R_0^i = R_0^i. \quad (A.5) \]

Inserting equation \( (A.5) \) into \( (A.4) \) yields \( I = I' \). Therefore, according to the symmetry of the even mode, it is clear that \( Q_{l,\eta} \) stays invariant by a space inversion operation. Following the same arguments, however, we can prove that for the odd mode, the normal coordinate \( Q_{l,\eta} \) changes its sign by the space inversion operation. Thereby, the normal coordinates of the odd mode must be involved in the Hamiltonian in an even power to keep the energy invariant by the space inversion operation. While for the even mode, there is no restriction on the power of its coordinates. As the lowest order approximation, we take the linear terms for the even modes and quadratic terms for the odd modes and obtain the e–p coupling Hamiltonian as expressed by equation \( (3) \) in the text.

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