

Band structure change in the transition from the cubic to the tetragonal phase in single-domain SrTiO₃, determined from two-photon absorption spectra

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(Submitted 3 March 1986)

Zh. Eksp. Teor. Fiz. **64**, 1436–1443 (October 1986)

Two-photon absorption spectra are presented for the SrTiO₃ crystal for several temperatures in the cubic and tetragonal phases. Various segments of the two-photon absorption spectrum are shifted by different amounts in the phase transition at ~ 105.5 K without onset of polarization dichroism of the two-photon absorption. It is found that the threshold energies of the indirect transitions *A* (3.35 eV, 300 K) and *B* (3.56 eV, 300 K) and of the first direct transition *C* (3.80 eV, 300 K) do not change in the structural transformation. The threshold energies of the subsequent direct transitions are changed by different amounts, by ~ 10 meV (83 K) for the transition *D* to the tetragonal phase (3.960 eV, 300 K) and by ~ 15 meV for transitions *E* (4.085 eV, 300 K) and *F* (4.215 eV, 300 K). An analysis of the observed changes in the two-photon absorption spectra is carried out on the basis of the SrTiO₃ band-edge structure determined in our previous papers. It is found that in the structural transformation in SrTiO₃ there is an unequal shift of only the three valence subbands *D*, *E*, and *F* located at the *X* point of the Brillouin zone. The conduction band is not split, either at the Γ point, where the first direct transition (*C*) is located, or at the *X* point. Our results account for the absence of changes in the single-photon spectra in the 105.5 K phase transition and provide new information on the changes in the deeper band states.

INTRODUCTION

It is known that phase transitions produce changes in the unit cell of a crystal. Therefore, one might expect some changes also at the edges of the band structure and in the intrinsic optical absorption. Up to the present time the change in the band structure that occurs in the ferroelectric transition in SrTiO₃ (at the temperature 105 K) has not been determined (in contrast to the ferroelectric transition in BaTiO₃). The point is that in the transition from the para- to the ferroelectric phase the BaTiO₃ unit cell undergoes a strong tetragonal distortion. In this distortion the largest displacement of the Ti ion is in the [001] direction relative to the center of the oxygen octahedron, while the center itself remains essentially unchanged. This structural distortion, as was predicted theoretically¹⁻³ and recently observed experimentally,⁴⁻⁶ produces a splitting of the minima of the conduction band at the Γ and *X* points. This results in polarization dichroism of the intrinsic absorption, since the optical transitions to the upper of the split states of the conduction band are permitted only for light polarized parallel to the tetragonal axis of the crystal, while the transitions to the lower of the states are permitted only for light polarized perpendicular to the crystal axis *c*.

In the transition to the tetragonal phase the unit cell of SrTiO₃ changes only very slightly. Neighboring TiO₆ octahedra rotate in opposite directions around the *c* axis by a small angle $\pm \varphi$ ($\varphi + 2.1^\circ$ at 4.2 K) in the transition.⁷ The ratio of the tetragonal *c* axis to the cubic *a* axis is 1.0006. The nearest-neighbor distance and the bond angles of the Ti in the oxygen octahedron do not change. It is therefore difficult to expect significant changes in the edge structure of the

bands, which are made up mainly of the 3*d* orbitals of the Ti ion and the 2*s* and 2*p* orbitals of the oxygen ions.¹⁻³

Mattheis,⁷ using a simplified model, calculated the changes in the band structure of SrTiO₃ in the transition to the tetragonal phase. According to this calculation, the minimum of the conduction band, Γ_{25} , is split (not counting the spin-orbit splitting) into a lower twofold degenerate level Γ_{5+} and an upper nondegenerate level Γ_{4+} . The splitting is proportional to φ^2 and has the very small value ~ 90 meV at 4.2 K. This band splitting should produce a dichroism in the intrinsic edge absorption opposite in sign to that observed in BaTiO₃ in the ferroelectric phase.⁷ However, various careful studies of the edge absorption of SrTiO₃ in the region of the phase transition⁸⁻¹⁰ failed to reveal any changes in the edge absorption that might with some confidence be related to band-structure changes.

It must be noted that these investigations⁸⁻¹⁰ were carried out in the region of the indirect edge absorption, so that it is difficult to observe distortions in the spectra caused by changes in the energies of the band edges. Moreover, most of these experiments were carried out on multidomain SrTiO₃ samples. Therefore the absence of changes in the edge absorption in SrTiO₃ is still not sufficient proof of an invariant structure. It is possible that the small changes in the energies of the band edges could not be observed simply because the samples were multidomain.

The purpose of this investigation was to study experimentally the changes in the band structure that occur in the ferroelectric phase transition in single-domain SrTiO₃, using two-photon spectroscopy, a method that we have previously used successfully to determine the true edge structures of the energy bands of a series of perovskites^{4-6,11,12} and the change of the structure in the phase transition in BaTiO₃.

EXPERIMENTAL

The experiments were carried out with a single-crystal sample of SrTiO_3 of high optical quality with dimensions $7 \times 3 \times 3$ mm. The faces of the sample were oriented along the $\langle 001 \rangle$ directions. The two-photon spectra of this crystal, as has been found previously, are determined only by the intrinsic two-photon absorption,^{5,6,11,12} while the "singularities" in the spectra (the kinks) are due to the various indirect and direct transitions between the extrema of the valence band at the R , M , Γ , and X points and of the conduction band at the Γ and X points.^{5,6}

On transition to the tetragonal phase the crystal was formed into a single domain by biaxial pressure along the $[100]$ and $[010]$ axes. To produce this pressure we have developed a new and simple method which makes it possible to form large crystals reliably into a single domain. In this method, after the single-domain state is established, the pressure on the sample is removed. Therefore, the experimental results can be attributed to the intrinsic changes in the energy spectrum of the SrTiO_3 in the tetragonal phase, without any additional distortion associated with the external pressure. A description of this method for producing single domains will be published later.

The method we used to measure the two-photon spectra has been described in previous publications.^{4,6} It is distinguished by very high sensitivity and accuracy, which allow a study of not only the direct two-photon absorption, but also a broad range of the indirect two-photon absorption, typical of perovskites.^{4-6,11,12} The crystal temperature was lowered by a glass liquid-nitrogen cryostat.⁶ The sample was placed in a vacuum, between two coaxial diaphragms through which a laser beam and a beam from a xenon lamp were sent in opposite directions. The sample temperature was measured with a copper-constantan thermocouple, and it was varied with a special heater placed directly over the sample.

Figure 1 shows the edge portions of the two-photon absorption constant β in the cubic (O_h) and the tetragonal (D_{4h}) (Ref. 9) phases as a function of the total energy of the laser photons ($\hbar\omega_L = 1.17$ eV) plus the photon energy $\hbar\omega_p$ of the probe radiation from the lamp, for a number of temperatures. These spectra consist of four segments with different slopes, separated by cusps designated symbols a_1 , a_2 , e_1 , and e_2 . Upon reducing the temperature in the cubic phase from 423 to 126 K (curves 1, 2, and 3), there is a shift of the spectra of β to higher energy, accompanied by a change in the shape and a decrease in the amplitude values. From a detailed analysis of this temperature behavior of the edge regions of the SrTiO_3 two-photon absorption spectra, in which the contribution of each segment to the energy dependence of β was separated, we were able to show^{6,12} that in the energy range from 3.27 to 3.81 eV the spectra of β for SrTiO_3 are governed by two indirect two-photon transitions, with threshold energies designated A and B . At 126 K the portions of the spectrum (a_1 and a_2) corresponding to two-photon transitions with the absorption of phonons (phonon energies $\hbar\Omega_1 = 55$ meV and $\hbar\Omega_2 = 50$ meV) are frozen out and the edge spectra of β consists of only the two branches e_1 and e_2 , corresponding to two-photon absorption with the emis-

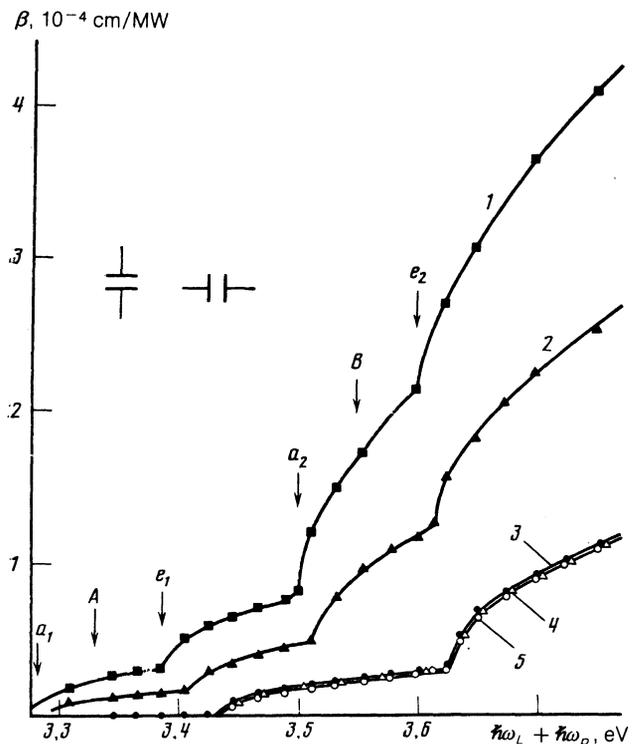


FIG. 1. Edge regions of the two-photon absorption spectra of SrTiO_3 for temperatures T : 1) 423 K; 2) 301 K; 3) 126 K; 4) 100 K; and 5) 83 K. A and B are the energies of the indirect edges; a_1 and a_2 are threshold energies of the sections of the spectrum with absorption of phonons; e_1 and e_2 are the threshold energies of the sections with emission of phonons (the arrows indicate only the thresholds for $T = 423$ K).

sion of these phonons. It can be seen from Fig. 1 that upon transition of the crystal to the single-domain state of the tetragonal phase (curves 4 and 5) the spectrum of β is practically indistinguishable from the spectrum for the cubic

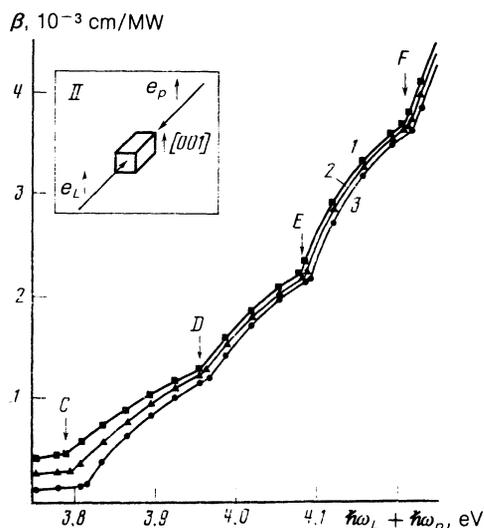


FIG. 2. Two-photon absorption spectra of SrTiO_3 in the region of direct absorption for temperatures T : 1) 423 K; 2) 301 K; 3) 126 K. C , D , E , and F are the energies of the direct edges. The inset shows polarization configuration II $e_L \parallel e_p \parallel [001]$.

phase near the phase transition (curve 3). This is apparently a consequence of the fact that the threshold energies of the indirect two-photon transitions *A* and *B* are not shifted appreciably by the phase transition in SrTiO₃.

Figure 2 shows the two-photon absorption spectrum of SrTiO₃ in the region of the direct transitions in the cubic phase. These spectra are governed by four direct two-photon transitions, of which the threshold energies are denoted by the letters *C*, *D*, *E*, and *F*. When the temperature is lowered (curves 1, 2, 3) the spectra are shifted towards higher energies with practically no change in shape. This temperature behavior of the β spectra corresponds to the usual increase in the gaps between the bands as the temperature is lowered. The temperature coefficients $\partial E_i / \partial T$ of the deeper transitions *D*, *E*, and *F* are significantly smaller than the corresponding coefficients of the edge transitions *A*, *B*, and *C*: $\partial E_A / \partial T = 1.6 \cdot 10^{-4}$ eV/deg, $\partial E_B / \partial T = -0.8 \cdot 10^{-4}$ eV/deg, $\partial E_C / \partial T = -0.8 \cdot 10^{-4}$ eV/deg, $\partial E_D / \partial T = \partial E_E / \partial T = \partial E_F / \partial T = 0.4 \cdot 10^{-4}$ eV/deg.

Figure 3 shows the changes in the β spectra, brought about by the transformation of the crystal to the single-domain tetragonal state, in the region of the direct two-photon transitions. It is readily seen that the phase transition brings about a shift, different for the various portions of the β spectra, towards lower energy (curves 2 and 3) relative to the position of the spectra in the cubic phase at a temperature close to the phase transition (curve 1). The threshold energy of the first direct transition *c* is practically unchanged, and

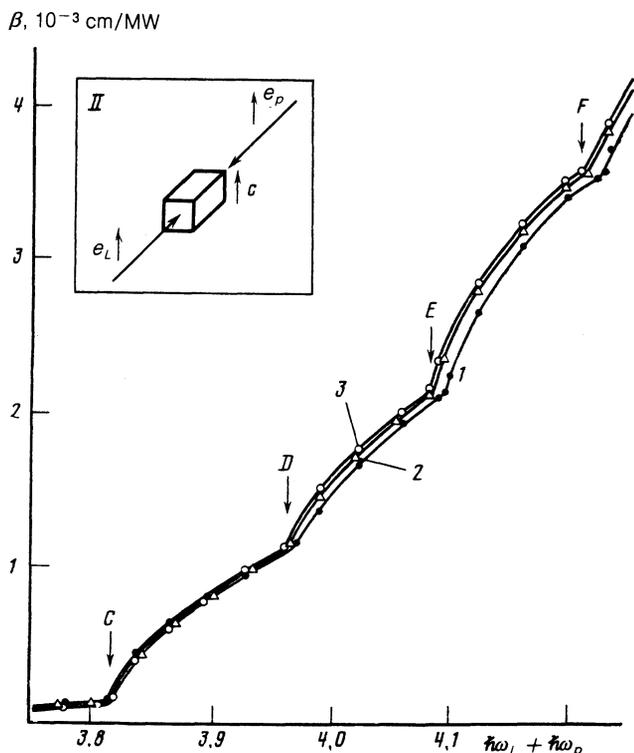


FIG. 3. Change in the two-photon absorption spectra of SrTiO₃ in the structural transformation (105.5 K) for temperatures *T*: 1) 126 K; 2) 100 K; 3) 83 K. *C*, *D*, *E*, and *F* are the energies of the direct edges. The inset shows polarization configuration II ($e_L \parallel e_p \parallel c$).

the thresholds of *E* and *F* are shifted by a greater amount than that of *D*.

It must be noted that spectra 2 and 3 of Fig. 3 and spectra 4 and 5 of Fig. 1 were obtained for the polarization configuration II shown in the inset of Fig. 3. In this configuration the polarization unit vectors of the laser beam (e_L) and of the lamp (e_p) and the tetragonal axis *c*, are all mutually parallel. The β spectra for the polarization configuration I (not shown in Fig. 3), for which the polarization vectors of the laser, e_L and of the lamp e_p are parallel to each other but perpendicular to the *c* axis are identical to spectra 2 and 3 of Fig. 3 and spectra 4 and 5 of Fig. 1 to within experimental error. The observed coincidence of the spectra for the two polarization configurations I and II indicate the absence of dichroism of the intrinsic two-photon absorption in the tetragonal phase of SrTiO₃.

In Fig. 4 the temperature dependences are plotted of the threshold energies E_i of transitions *A*, *B*, *C*, *D*, *E*, and *F*. It can be clearly seen from Fig. 4 that in the cubic phase the gaps between the bands of the two-photon transitions *A*, *B*, *C*, *D*, *E*, and *F* increase linearly with decreasing temperature. Upon reaching the temperature of the phase transition (105.5 K) there is a smooth decrease in the threshold energies of transitions *D*, *E*, and *F*, without the appearance of polarization dichroism. The energies of the indirect transitions *A* and *B* and that of the first direct transition *C* are essentially unchanged by the phase transition (that is, they vary in accordance with the temperature dependences of these transitions in the cubic phase).

We determined that when the temperature is raised from 83 to 140 K the temperature dependences of the thresholds of *A*, *B*, *C*, *D*, *E*, and *F* have no hysteresis (i.e., they correspond to the dependences shown in Fig. 4, which were obtained at the lower temperature), a result that corresponds, as is well known, to second order phase transitions.

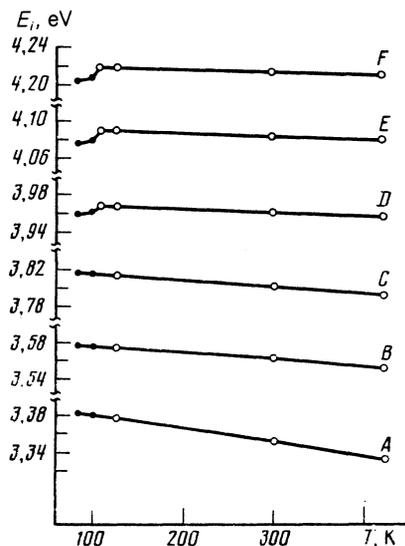


FIG. 4. Temperature dependences of the energies of the transitions *A*, *B*, *C*, *D*, *E*, and *F* of the SrTiO₃ crystal in the cubic and tetragonal phases. ●—polarization configuration II ($e_L \parallel e_p \parallel [001]$), ○—polarization configuration I ($e_L \parallel e_p \parallel c$).

DISCUSSION OF THE RESULTS

In our previous articles^{4-6,11,12} we studied in detail the spectral, polarization, and temperature dependences of the two-photon absorption of the perovskites BaTiO₃, SrTiO₃, and KTaO₃. Analysis of these dependences enabled us to determine the edge structure of the energy bands of these materials in the cubic phase and the changes in the band structure of BaTiO₃ in the ferroelectric transition (120 °C). It was determined that the band structures of BaTiO₃ and SrTiO₃ are very similar in the region of the direct transitions and differ only in the magnitudes of the corresponding gaps between the bands of the transitions *C*, *D*, *E*, and *F*, these gaps being somewhat greater for SrTiO₃ than for BaTiO₃ at the same temperatures. The structure determined for the band edges of SrTiO₃ in the cubic phase is shown in Fig. 5 by the solid lines. According to this diagram, the two-photon absorption edge is determined by the two indirect transitions *A* and *B* associated with the extrema of the valence band at the points *R* and *M* and with the conduction-band minimum at the Γ point. The first direct transition *C* is between the extrema of the valence band and the conduction band at the Γ point. The deeper direct transitions *D*, *E*, and *F* are located at the *X* point and are transitions from the three valence subbands *D*, *E*, and *F* to the extremum of the conduction band. As we have noted previously, in the ferroelectric transition in BaTiO₃ there is a splitting of the conduction band at the Γ and *X* points. This splitting produces in the two-photon absorption a polarization dichroism manifested by a jumpwise shift of the two-photon absorption spectrum towards higher energy without any change of shape in the phase transition when the polarization of the beams is parallel the tetragonal *c* axis (configuration II). The β spectrum

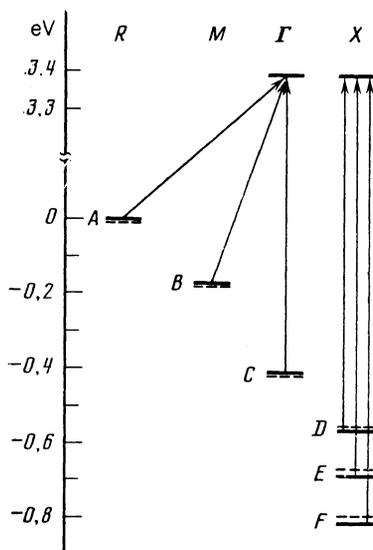


FIG. 5. Diagram of the energy band edges of the SrTiO₃ crystal. *A*, *B*, *C*, *D*, *E*, and *F* are the band states associated with the corresponding two-photon transitions. *R*, *M*, Γ , and *X* are the high-symmetry points in the Brillouin zone. The solid lines show the energy levels of SrTiO₃ in the cubic phase at 108 K. The dashed lines show the locations of the levels in the tetragonal phase at 83 K.

for light-beam polarization perpendicular to the tetragonal axis (configuration I) is essentially unchanged compared with the spectrum in the cubic phase. The splittings that are produced in the transitions *D*, *E*, and *F* by a shift in the same conduction band are equal. This same behavior is also observed in the two-photon spectra of SrTiO₃ when a strong electric field is applied in the [001] direction.⁶ In this case SrTiO₃ becomes similar to BaTiO₃ in the ferroelectric phase. Under the action of the electric field the Ti ion shifts relative to the center of the oxygen octahedron, polarization is induced and the conduction band is split. A small dichroism of the two-photon absorption is then produced and is qualitatively similar to the dichroism in the ferroelectric phase of the BaTiO₃.⁶

Therefore, our experimental results, which show an absence of polarization dichroism of two-photon absorption in the tetragonal phase of SrTiO₃ and different energy shifts of the thresholds of *C*, *D*, *E*, and *F*, indicate that the minimum of the conduction band is not split either at the Γ point or the *X* point of the Brillouin zone as a result of the phase transition. Moreover, there are practically no changes in the energy positions of the extrema of the valence band at the *R*, *M* and Γ points in the transition to the tetragonal phase of SrTiO₃, and as a result there are no changes in the β spectra in the region of the indirect two-photon absorption edges (transitions *A* and *B* in Fig. 4) or in the segment of the first direct transition *C*. Consequently, the phase transition in SrTiO₃ changes only the energy positions of the valence subbands *D*, *E*, and *F*, located at the *X* point of the Brillouin zone, as shown in Fig. 5 by the dashed lines.

It should be noted that no additional thresholds of the direct transitions of Figs. 1 and 3 arise in the tetragonal phase. Consequently, the valence subbands *D*, *E*, and *F* either are not split, which means that they are nondegenerate, or else their splittings are too small.

From these conclusions we can understand the results of a number of single-photon optical investigations of edge absorption in the region of the SrTiO₃ phase transition.⁸⁻¹⁰ The authors of these articles did not see, in the phase transition, in the behavior of the edge absorption, any changes attributable to a change in the edge structure of the bands, because those experiments were carried out in the energy range 3.2–3.4 eV, which corresponds to the indirect transitions between the extrema of the band edges, and according to our results, these edges do not change energy in the phase transition in SrTiO₃.

The simplified theoretical calculation⁷ of the change in the band structure of SrTiO₃ in the phase transition, which predicts a substantial dichroism in the edge absorption (the order of 35 meV at 80 K), is evidently wrong, since the predicted conduction band splitting is not observed in the two-photon spectroscopy experiments.

The principal changes in the phase transition in SrTiO₃ are experienced by the deep direct transitions *D*, *E*, and *F* of energies 3.96, 4.077, and 4.205 eV, respectively, at 83 K. This energy region has been studied by modulation reflection spectroscopy.¹³ However, no changes associated with the phase transition were observed in the spectra. It would

appear that this result is a consequence of the insufficient sensitivity of the modulation reflection spectra to small changes in the energy position of closely lying bands.

It has previously been established^{5,6} that a displacement of the central Ti ion in the [001] direction relative to the center of the oxygen octahedron leads only to a splitting of the minima of the conduction band at the Γ and X points, and to polarization dichroism of the two-photon absorption spectra. Here the β spectrum for parallel orientation II shifts towards higher energies without change of shape.^{5,6} Rotation of the TiO_6 oxygen octahedron without change of the position of the Ti ion within it causes unequal energy shifts of the subbands D , E and F in the valence band and a shift of the corresponding segments (D , E , and F) of the direct transitions in the two-photon absorption spectrum to lower energies, without the appearance of polarization dichroism.

In summary, we have found a correlation between the type of phase transitions, i.e., the structural changes in the positions of the atoms in the unit cell of the crystal, and the character of the splittings of the edge bands that are observed in two-photon absorption spectra. This correlation may be used as a means of identifying the type of phase transition in complex perovskites.

This investigation clearly shows the broad potential and the advantages of the two-photon spectroscopy method

compared to single-photon methods in studying the complex energy spectra of the ferroelectrics. The actual results obtained for the SrTiO_3 band structure and its changes incurred in the phase transition may serve as the basis for more accurate theoretical calculations.

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Translated by J. R. Anderson