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PHYSICAL REVIEW B

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Fundamental Absorption Edge of SrTiO₃

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Detailed measurements of the fundamental absorption edge of SrTiO₃ between 6 and 300 K are reported. Because these results provide the first detailed data below 82 K, several new properties of this material have been observed. The energies of the fundamental transitions are found to have unusually small temperature dependence. It is also observed that the strengths of the phonon-emission and impurity-induced absorption processes are more strongly temperature dependent than is found in other materials. In addition, we propose a different explanation for the prominent shoulder in the absorption at 3.40 eV: that it is merely the saturation of the phonon-assisted transitions.

I. INTRODUCTION

Among the many interesting properties of SrTiO₃, optical phenomena such as luminescence¹ and photochromicity² have gained much recent interest. It has been found that a full understanding of these phenomena depends upon a knowledge of the fundamental absorption process of the crystal on which we report here. In addition, detailed information on the fundamental optical transitions should aid in the elucidation of the electronic energy band structure of the material, which is not well established.

In SrTiO₃ the Kahn-Leyendecker band-structure calculation³ indicates that the lowest energy gap may be indirect from Γ_{15} to X_3 . Baer⁴ has concluded from his interband Faraday rotation data, however, that the transition is direct and most probably at the Γ point. DiDomenico and Wemple⁵ concluded from their high-temperature results in BaTiO₃ that the absorption edge is direct from X'_5 to X_3 and the lower-energy phonon-assisted $\Gamma_{15} \rightarrow X_3$ process is masked by the stronger direct transition. They expected that, because of the similarity of BaTiO₃ and SrTiO₃, these latter conclusions should apply for SrTiO₃. Capizzi and Frova⁶ concluded from their absorption measurements that the absorption edge is the $\Gamma_{15} \rightarrow X_3$

phonon-assisted process and that the shoulder at 3.40 eV is the direct $X'_5 \rightarrow X_3$ transition.

Past experimental data on the fundamental absorption edge of SrTiO₃ have been limited. The first transmission measurements⁷ of the absorption edge reported exponential spectral shapes whose temperature dependence was claimed to follow Urbach's rule.⁸ However, Capizzi and Frova's measurement⁶ between 300 and 82 K showed a change from exponential shape at room temperature to a structured edge characteristic of single phonon-assisted transitions.

The present paper reports similar transmission measurements, but carried to much lower temperatures and to higher precision. These features of the experiments have revealed several unexpected properties of the temperature dependence of the absorption edge and confirmed its phonon-assisted nature. These properties are: (i) The threshold energies of the different components of the edge are essentially temperature independent; (ii) the energy at which the absorption saturates (near 5000 cm⁻¹) is similarly insensitive to temperature; (iii) the strengths of the electronic transitions assisted by phonon emission and by impurities are more strongly temperature dependent than in any other known case.

II. EXPERIMENTAL PROCEDURES

The measurements reported here were all performed by direct optical transmission methods. The principal features worthy of comment are the extremely low level of stray light in the optical system and the accurate control of sample temperature during a series of measurements.

The low level of stray light was achieved by use of a double monochromator (Spex model No. 1400) of the type used in Raman spectroscopy. The samples were located in the monochromatic beam and a second small monochromator between the sample and the final detector was used to eliminate possible fluorescence radiation. The high intensity of the lamp (150-W xenon arc) combined with the good signal-to-noise ratio of the small cathode photomultiplier (EMI-6256S) permitted the use of narrow slits (0.1 mm) on the double monochromator resulting in typical spectral bandwidths of $\frac{1}{2}$ Å ($\sim \frac{1}{2}$ meV). The monochromatic beam was split by a fused silica plate located before the sample so that a portion of the incident light could be continuously monitored. This is necessary for accurate measurements because of instabilities in the arc lamp.

The temperature of the samples was controlled by a variable-temperature liquid-helium Dewar (Janis Super Varitemp) which permits sustained operation at any temperature from ~ 2 to 300 K. (The lowest temperature used here was 6 K.) The sample was always in contact with helium gas at 1 atm pressure; sample temperatures were taken to be the same as the immediately adjacent gas temperature as measured by calibrated Ge or Pt resistance thermometers. We believe the quoted temperatures were accurate and stable within $\sim 1\%$.

Samples were cut from several crystals of the highest available purity purchased from National Lead Co. They are easily polished to obtain very smooth surfaces having reflection losses very close to the theoretical values calculated from Cardona's measured refractive indices.⁹ Chemical etching (phosphoric acid) did not alter the absorption edge on the one sample treated this way. Sample thicknesses between 0.018 and 2.0 mm were used and excellent agreement was found in the overlapping spectral regions where samples of different thicknesses were measured.

To obtain reliable values of absorption coefficients, accurate corrections must be made for reflection losses. Unfortunately, the values of reflectivity R reported by Cohen and Blunt⁷ are several percent lower than the corresponding values computed from Cardona's formula fitted to his refractive index data. It happens, however, that the two sets of values of R have nearly the same spectral dependence in the range of our measurements,

3.0–3.4 eV. Therefore, we have consistently used the calculated *shape* from Cardona's formula but adjusted the *level* of the reflectivity correction to fit our transmission results in the nearby non-absorbing region for each measurement. In other respects, the transmission data were treated in the customary way (including allowance for multiple reflections).

III. EXPERIMENTAL RESULTS AND DISCUSSION

SrTiO₃ undergoes at least one phase transition at low temperature.¹⁰ It is well known that the cubic-perovskite structure at room temperature transforms to a tetragonal structure at approximately 105 K. This transition involves a doubling of the unit cell and a corresponding halving of the Brillouin zone. Therefore, some change in the lowest fundamental optical absorption might be expected. The absorption-edge spectrum was carefully measured at several fixed temperatures somewhat above and below 105 K and the temperature dependence of the absorption at several fixed photon energies was measured by scanning the temperature from 130 to 70 K. In neither case was there any observable change in the behavior of the edge which could be attributed to the phase transition. Blazey has claimed to have seen optical evidence of the phase transition in wavelength-modulation measurements of the absorption edge.¹¹ That interpretation is contrary to the present results and to those of Ref. 6; it has been refuted by the present authors who proposed an alternative one which is consistent with these and other experimental results and is independent of the phase transition.¹² Müller *et al.*¹³ have observed a dichroism of 3 meV in the absorption edge of a monodomain sample below 110 K. This measurement was stated to have been made in the "... Urbach tail ..." which we now know does not exist at temperatures below T_c . Thus it is not known at what temperature or at what photon energy this measurement was made. The measurements reported here as well as those reported in Refs. 6 and 11 were made on multidomain samples in which cases the dichroism would not be observable.

The absorption edge was measured at a number of temperatures between 6 and 80 K as well as between 80 and 300 K for comparison with Ref. 6. A summary of these measurements is shown in Fig. 1. Only three temperatures are shown here but they illustrate the results to be discussed in more detail later. At all temperatures the absorption is a monotonically increasing function of photon energy up to a shoulder in the range of 5000–7000 cm⁻¹ near 3.40 eV. The values of absorption coefficient near this energy increase somewhat with decreasing temperature although

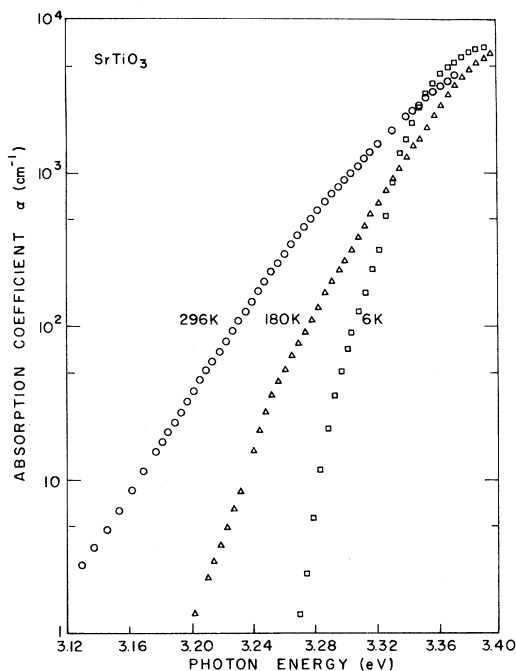


FIG. 1. Absorption edges of SrTiO₃ at several representative temperatures.

the energy at which this shoulder occurs is essentially temperature independent. This latter fact is quite remarkable and will be noted again as the data are discussed in more detail. The crossings of the absorption spectra for different temperatures are always present and are clearly related to the invariance of the spectral position of the shoulder.

The gradual transition observed from an exponential absorption spectrum at high temperatures to a structured energy dependence at low temperatures has been observed in many other materials. CdS,¹⁴ CdTe,¹⁵ and ZnO,¹⁶ among others, display such a transition even though in each case the lowest fundamental transition is a direct process with the structure arising from low- q phonon assistance in the direct transition.¹⁷ There are, of course, also the well-known cases of Ge and Si where the fundamental transitions are indirect and are allowed only with phonon assistance. The silver halides also have this property and display the transition from Urbach's rule at high temperatures to a structured edge at low temperatures.¹⁸ Many theoretical discussions of these phenomena have been given, the most general by Dow and Redfield.¹⁹

In Ref. 6 it was shown that the spectral dependence of the absorption coefficient α between 80 and 120 K followed the formula for indirect interband transitions. The edge was found to break naturally into three components,

$$\alpha = K_1(\omega - E_1)^2 + K_2(\omega - E_2)^2 + K_3(\omega - E_3)^2, \quad (1)$$

where each term contributes only above its threshold energy E_i and $E_3 > E_2 > E_1$. The coefficients K_i contain the interband electric-dipole matrix element, the electron-phonon-interaction matrix element, and the appropriate Bose factor. Sections I and III of Eq. (1) were associated with transitions assisted by the absorption and emission, respectively, of a ~ 50 -meV phonon. Section II, whose threshold occurs at the energy gap defined by sections I and III, was attributed to impurity-assisted transitions.

The present results for temperatures below 150 K are in accord with this interpretation. Figure 2 shows the data for 6 K plotted according to Eq. (1) and displaying only those components (labeled II and III) which remain when phonon absorption processes are frozen out.

If excitonic effects are important, a deviation from the square-law spectral dependence is expected at the onset of a new contribution to the absorption.²⁰ The inset in Fig. 2 shows on an expanded scale a detailed study at one such point. The near absence of any observable deviation from

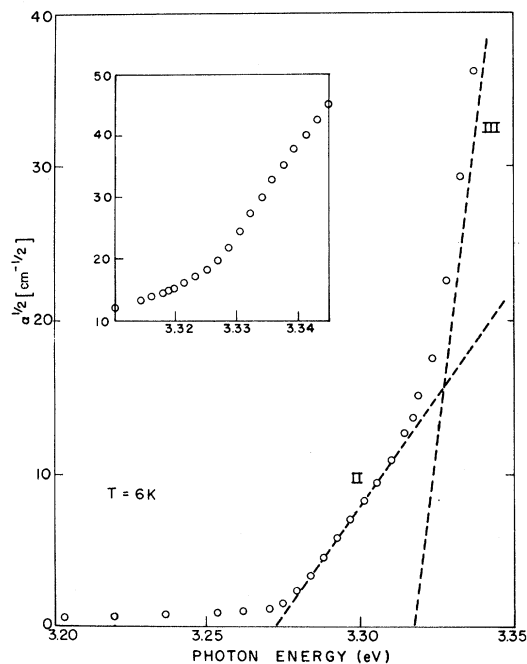


FIG. 2. Display of the linear relation between $\alpha^{1/2}$ and photon energy in accord with the theory of indirect optical transitions at 6 K. The data points have been decomposed into two linear segments shown by the dotted lines whose sum equals the measured values as in Eq. (1). Phonon absorption processes [section I of Eq. (1)] are absent at low temperatures. Inset with detail near the threshold at 3.32 eV shows the near absence of excitonic curvature.

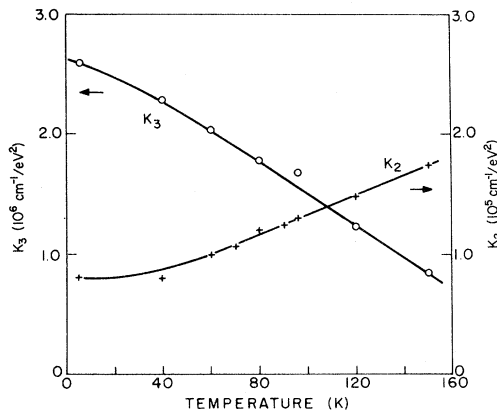


FIG. 3. Temperature dependence of the coefficients K_2 and K_3 of Eq. (1).

the square-law dependence indicates that exciton effects are not significant in SrTiO₃. This is the only material having a fairly strong electron-phonon coupling²¹ for which this is established and we interpret the effective absence of excitons as being due to the very large static-dielectric constant ($\epsilon_0 \approx 300$ at 300 K to $\epsilon_0 \approx 18\,000$ at 4 K).²²

The analysis discussed above for Fig. 2 was also carried out at a number of other temperatures between 6 and 150 K. In all cases, the intercepts were found to occur at $E_2 = 3.270 \pm 0.005$ eV and $E_3 = 3.320 \pm 0.005$ eV and at the higher temperatures a third intercept at $E_1 = 3.215 \pm 0.005$ eV. The energies at which the intercepts occurred were, within the errors cited, *independent of temperature*. This result is in marked contrast to other materials where there is a pronounced temperature dependence to the energy gap. It is clear that the temperature independence of these thresholds is closely related to the observed temperature independence of the spectral position of the shoulder near 3.40 eV.

Examination of the data such as that shown in Fig. 2 indicates that these results are the most clear-cut of any compound yet reported. That is, there is almost complete freedom from extra structure and curvature of the edge at low temperatures and remarkably good fits to the linear plots as shown. Only Ge²³ and Si²⁴ display more accurately the theoretically predicted behavior. For this reason, we have extended the analysis beyond previous limits by determining the explicit temperature dependence of the coefficients K_2 and K_3 . The results, shown in Fig. 3, were quite unexpected since the theory referred to above contains no explicit temperature variation of the extent found. For example, the change in K_3 between 6 and 150 K should be due only to the change in the Bose factor for phonon emission ($N_s + 1$), which amounts to an increase of 2% for a 50-meV

phonon. Yet the observed value decreases by about a factor of 3. This is equivalent to a considerable broadening of the highest portion of the curves.

For comparison with these results we have examined nearly all of the detailed measurements of low-temperature absorption edges in the literature (Refs. 14–16, 18, and others). Although no analyses of temperature dependences of these coefficients were presented explicitly, we find that qualitative broadening of the highest portions of the absorption spectra is very common. Furthermore, it generally appears to occur even at quite low temperatures (e.g., 50 K) as we found for K_3 . (These observations do not apply to the published curves for Ge and Si.)

In all other cases, broadening of the edge is accompanied by a shift to lower energies of the onset of absorption. In SrTiO₃ there is no shift in the edge within the experimental error of $\sim \pm 5$ meV.

This type of broadening has not been discussed in connection with any of the structure in low-temperature absorption edges in spite of its widespread occurrence. One possible explanation lies in the analysis by Mahr of the detailed shape of the smooth absorption edge of KCl:KI down to 77 K.²⁵ The central point of relevance here is the proposal that acoustic phonons dominate the low-energy components of the broadening at low temperatures. This would account for both the lack of structure associated with this broadening and its onset at very low temperatures.

Section II of Eq. (1), having an intercept at the energy gap, should ideally not appear in a pure material.²⁶ It persists to the lowest temperatures and has the same type of spectral dependence as the other two segments, but since the intercept is at the gap energy, it must arise from an indirect but not phonon-assisted transition. Capizzi and Frova attributed this absorption to an impurity-induced indirect transition such as has been observed by Joesten and Brown in the silver halides.¹⁸ The impurity rather than the lattice phonons scatters the electron to conserve momentum. As a result of the dimensionality of the phase space involved in such transitions, this process would have the same spectral dependence as the phonon-assisted process. Although we see no plausible alternative to this explanation, it has several difficulties. The concentration of impurities in nominally pure SrTiO₃ as received from National Lead Co. is on the order of 100 ppm. Recent measurements of ionic conductivity in these samples indicate that the oxygen vacancy concentration is comparable in magnitude to the impurity level cited above.²⁷ The samples used by Joesten and Brown had impurity concentrations

several orders of magnitude larger than those used here and their results show a strong dependence of K_2 on that concentration, suggesting that impurity-assisted processes should be exceedingly weak at our concentrations. The magnitude of the effect measured here is at least an order of magnitude stronger than would be expected from such a comparison with the silver halides. In addition, there is a surprising agreement of the strength of K_2 among the various SrTiO₃ samples reported here and in Ref. 6.

An additional difficulty with the proposed explanation of section II of Eq. (1) arises from the large temperature dependence of K_2 as shown in in Fig. 3. The simple qualitative picture predicts *no* temperature dependence to the magnitude of K_2 if only impurity-induced effects are responsible.

The opposite sense of the temperature dependence of K_2 —a steepening of the curve at higher temperatures—is a new and interesting feature of these results. We regard this observation as presently unexplained and contrary to the interpretation of an impurity-assisted transition.

The temperature dependence of the energy gap of a material has been shown to be separable into two contributions, the lattice-dilatation term and a term arising from the electron-phonon interaction.²⁸ The lack of a temperature dependence of the measured gap in SrTiO₃ could be explained in this framework by an accidental cancellation of these two contributions.

Recent work on the optical properties of BaTiO₃ and other perovskites has suggested that, in these materials, shifts in the band-edge position can also arise from polarization fluctuations δP associated with the soft TO mode.²⁹ The magnitude of this shift ΔE is

$$\Delta E = \beta \langle \delta P^2 \rangle = \beta kT \epsilon_0 / V_c ,$$

where β is the polarization potential, analogous to a deformation potential, and V_c is a volume over which the correlation occurs. For SrTiO₃ (assuming the same value of β as for BaTiO₃) the band-edge shift expected between 40 and 140 K is ~ 3 meV. The accuracy of the measurements presented here ($\sim \pm 0.005$ eV) is not sufficient to identify shifts of this order.

Finally, we consider the application of these results to the determination of the band structure of SrTiO₃. The data presented here and in Ref. 6 clearly show that the onset of absorption is attributable to indirect transitions, most likely from Γ to X as suggested by the band-structure calculation.³ Previously, the saturation in the absorption, the shoulder at 3.40 eV, has been attributed to a direct transition at either the Γ point⁴ or the X point.^{5,6} Recent calculations of Mattheiss³⁰ suggest that the conduction-band minimum in SrTiO₃ is at the zone center and that the fundamental absorption edge is a zone-center direct transition. The results of these measurements are clearly contrary to the suggestion that the edge is direct regardless of where in the zone the direct gap lies. While the origin of section II of the absorption edge [Eq. (1)] is not completely understood at this time, its spectral dependence appears to rule out the possibility that it represents a direct transition.

We interpret the shoulder near 3.40 eV as merely the saturation of the phonon-assisted processes, with the lowest direct transition at the strong 4.00-eV peak seen in reflectivity.⁹ The reasons for this are: (i) The electron-phonon coupling coefficient is quite strong in SrTiO₃, consistent with the observed occurrence of phonon-assisted absorption of $> 10^3$ cm⁻¹. (ii) The phonon-emission segment of the absorption edge [section III of Eq. (1)] obeys the $\alpha \propto (E)^{1/2}$ relation up to absorption coefficients of several thousand cm⁻¹ as seen in Fig. 2 and saturates at values slightly greater than this. Any direct transition should rise steeply above such indirect processes. (iii) Examination of reflectivity data shows the 4.00-eV peak to be 50 times stronger than the shoulder at 3.40 eV.⁹ (iv) The strength of the absorption at the shoulder (5000 to 7000 cm⁻¹) is too low for a direct allowed transition. Conversely, the sharp rise to $\sim 5 \times 10^5$ cm⁻¹ at 4.00 eV is characteristic of such direct processes.

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Brillouin Scattering in Anisotropic Media: Calcite

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We have used comparative Brillouin scattering (reference scatterer: toluene) to measure the nine photoelastic tensor elements of calcite (eight elastically symmetric, one elastically antisymmetric) in both magnitude and sign. Our measurement of the recently predicted antisymmetric component agrees in magnitude to 5% with that theoretically predicted. By adopting the theoretical sign for this component, the signs of all other components are determined from the data. The 5% agreement gives a measure of the *absolute* accuracy of the results. The presence of the antisymmetric component causes p_{2323} and p_{2332} , previously believed to be equal, to differ by more than a factor of 10. The formulas needed to analyze Brillouin scattering in anisotropic media are derived using a new constitutive relation and a new Green's function for radiation in an anisotropic medium. Inclusion of boundary effects (solid angle expansion, scattering-volume demagnification, etc.) makes the formulas valid *outside* the scattering medium. The convenience of comparative Brillouin scattering for the numerical determination of the photoelastic tensor components, particularly in low-symmetry crystals, is emphasized.

I. INTRODUCTION

We report here measurements of the photoelastic tensor elements of calcite made by comparative Brillouin scattering using toluene as a reference scatterer. All nine elements (eight symmetric upon interchange of the tensor indices associated with the measure of elastic deformation; one antisymmetric upon the interchange) were measured in both magnitude and sign using Brillouin scattering alone.

The purposes of this work are fivefold: (i) to measure the recently predicted^{1,2} *antisymmetric* tensor element that arises from the coupling of *rotations* (in contrast to strains) to the scattering process (we find agreement between the predicted and measured magnitudes of this element to within 5%); (ii) to demonstrate that the algebraic *signs*

of all the tensor elements can be determined from the theoretically known sign of the antisymmetric tensor element; (iii) to point out that measurement of the antisymmetric tensor element can be used to determine the *absolute* calibration of the scattered light intensity; (iv) to show that comparative Brillouin scattering is a method as accurate in determining absolute values of photoelastic tensor elements as acousto-optic diffraction or static-load-induced birefringence and is more convenient for low-symmetry crystals; and (v) to present Brillouin-scattering formulas valid for crystals of any symmetry and of any optical or acoustic anisotropy in any orientation, for any angle of scattering, and for rather general orientations of the exit surface. A derivation of the latter is presented that is based on a new constitutive relation derived by an *ab initio* calculation^{2,3} and on a new Green's