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Fundamental absorption edge of $SrTiO_3$ at high temperatures

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Transmission measurements on single-crystal $SrTiO_3$ between room temperature and 1200 °C are reported. Urbach broadening of the absorption edge is observed at all temperatures. Below 200 °C the broadening is typical of the lowest indirect band gap. Above 400 °C the dominating broadening is due to the lowest direct gap located at 3.5 eV. This transition from indirect to direct broadening is related to the proximity of the direct and indirect gaps and should be observed in other narrow-band indirect-gap materials. The small temperature dependence of the band gaps is ascribed to the small magnitude of both the implicit and explicit electron-phonon contributions rather than to accidental cancellation of both terms as has been suggested by Redfield and Burke. We argue that, in indirect narrow-band materials, the explicit term of the direct gap may be small owing to intervalley scattering that compensates for the regular intravalley scattering.

I. INTRODUCTION

The absorption edge of $SrTiO_3$ at low temperatures and the nature of interband transition attracted much attention in the past two decades. Capizzi and Frova[1] (CF) have shown that between 80 and 160 K the absorption edge is indirect and composed of three thresholds which are phonon and impurity assisted. They assigned their 3.27-eV band gap to a $\Gamma_{15} \rightarrow X_3$ transition assisted by a single 51 meV longitudinal optical (LO) phonon. Precise measurements by Redfield and Burke[2] (RB) down to 6 K confirmed the indirect nature of the transition. They have, however, found that the transition strengths of the impurity and phonon-absorption thresholds have a very strong temperature (T) dependence, equivalent to a marked broadening even at very low temperatures. Various theoretical calculations of the band structure of $SrTiO_3$ (Ref. 3) as well as other perovskites[4] exist that support either the indirect[3(a)] or direct[4(a)] (e.g., at Γ) nature of the band gap. These differ by method of calculation, degree of self-consistency achieved and approximations made. Consequently, they disagree on the size of the gap, on the width of bands, or even on the ordering of valence bands. Under these circumstances, theoretical predictions of the nature of band gap and type of transition do not seem very useful. One feature is, however, common to these calculations;[4] that is, while the position of the valence-band maximum varies among the perovskites considered (e.g., it is at the Γ, M, or R point), the location of the conduction-band minimum at $\Gamma_{25'}$ does not, suggesting that the former feature is sensitive to details of the crystal potential. It is therefore possible that an improved calculation in $SrTiO_3$ will move the valence-band maximum away from the zone center in which case the transition becomes indirect and CF's assignment invalid.

The issue of direct versus indirect gap in $SrTiO_3$ is quite controversial and, besides the absorption edge measurements, has been addressed by many transport and other optical methods. These include magnetoresistance measurements[5] where similar results have been interpreted by two groups who arrived at opposing conclusions, Shubnikov—de Haas[6(a)] and de Haas—van Alphen[6(b)] effects that best fit to an indirect and direct gap, respectively, and superconductivity[7] which was interpreted in terms of an indirect gap. It should be noted that even if the conduction-band minimum is at the Γ point, this does not rule out an indirect transition as was mentioned above. Thus transport measurements are not conclusive in determining this question. Another experiment[8] on $KTaO_3$—a material with supposedly similar band structure[4(a)]—utilized resonant Raman scattering to conclude a direct gap at 3.4—3.5 eV. It cannot, however, be interpreted unambiguously owing to the low absorption coefficient at these energies (i.e., less than 10 cm^{-1}) and to lots of optical evidence for a direct gap at 3.7 eV or higher.[9] Evidently, the origin of this direct versus indirect dilemma lies in the large electronic effective mass; that is, in materials where bands are quite flat the energies of the indirect and direct gap fall closely together. Besides, low-symmetry effects such as doubling of the primitive cell (that occurs in the low-T tetragonal phase) and effects of high electron concentration, under which conditions most of these experiments were taken, complicate their analysis even further. A possible source of confusion can, however, be ruled out: Indirect transitions at low T (i.e., when the unit cell is doubled) cannot become direct at high T. Thus we conclude that none of these experiments convincingly proves the direct nature of the band gap, whereas absorption edge measurements (Refs. 1 and 2) strongly support indirect transition.

Above 160 K and at absorption coefficient $\alpha < 1000$

cm^{-1} CF and RB reported an Urbach broadening of the absorption edge, i.e., an exponential dependence of the form

$$\alpha = \alpha_0(T)\exp[\sigma(E - E_0)/kT] , \quad (1)$$

where E is the photon energy, k is Boltzmann's constant, and σ is a slope parameter of the order of unity. CF have, at times, associated E_0 with the three indirect thresholds and shown that $\alpha_0(T)$ contains contributions from the corresponding indirect transition strengths and is therefore T dependent. Thus, extrapolations of the exponential edges at various temperatures do not intersect at a single energy that would otherwise correspond to the band gap at zero temperature (see Sec. III).[1] CF's calculation is still valid at much higher temperatures, since recent infrared[10] and Raman[11] measurements show that LO-phonon frequencies are hardly T dependent. In fact, the 470 cm^{-1} (58.3 meV) and 172 cm^{-1} (21.3 meV) LO phonon frequencies have slight but opposing T dependences up to temperatures as high as 1200 K.

Two points in these results deserve further attention. The first, as RB have pointed out, is that the indirect thresholds are insensitive to temperature variations below 160 K (a similar result is implicit in CF's analysis). This is remarkable since most materials have a relatively strong T dependence of the band gap at elevated temperatures. It should be noted, however, that in SrTiO$_3$ the temperature range where indirect behavior is clearly observed in quite restricted (i.e., up to about $0.15\Theta_D$, where Θ_D is the Debye temperature) and that a small T dependence of the band gap is to be expected in this range. Nevertheless, they interpreted the lack of temperature sensitivity as an accidental cancellation of the explicit and implicit terms in the electron-phonon ($e\phi$) interaction which, we think, is unlikely (see Sec. III). The second point is a shoulder in the reflectivity observed at a higher energy (3.45–3.50 eV).[1] CF interpreted this as the onset of direct transitions at the X point.[12] RB, on the other hand, suggest that this shoulder is merely a result of saturation in the phonon-assisted process and does not reflect a direct gap. Since, as was mentioned above, the indirect and direct gap lie close together, it seems that, based on results in only a limited T range, it would be hard to tell which approach is correct.

We report here on absorption edge measurements between room temperature (RT) and 1200 °C. The results are described well by an exponential edge at all temperatures. We interpret our results in terms of Urbach broadening of the indirect edge at temperatures up to 200 °C in accordance with CF's results. Above 400 °C broadening of a direct edge located at 3.5 eV dominates the absorption edge. Our absorption edge and reflectivity results together with refractive index data reflect small sensitivity of the band gaps to temperature variations. We interpret this as due to the small magnitude of both the implicit and explicit $e\phi$ contributions to the temperature derivative of the direct band gap. We argue that the explicit term is small owing to compensation of the regular intravalley scattering term by an intervalley term that may be quite large and of the opposite sign in narrow band materials.

II. EXPERIMENT

The optical system was a conventional home-made double-beam spectrometer. The monochromatic light source consisted of a high pressure 1000-W xenon lamp, a high-intensity monochromator, a wavelength drive unit (all made by Kratos), a glass or sapphire beam splitter, a chopper, an optical furnace, two photodiodes (EG&G HUV-4000B with an integrated preamplifier), an infrared blocking filter (to protect the sample photodiode from thermal emission) and a lock-in amplifier. The slit width was 1 mm corresponding to a bandwidth of 40 Å. The scan speed was 10 nm/min which did not limit the spectral resolution (concluded by comparing RT spectra to those obtained on a Cary 17 spectrometer). The signals were collected and wavelength scan controlled directly by a Minc 11 mini computer (Digital Equipment Corporation) in order to ease data manipulations. Transmission measurements were performed in the sample-in—sample-out configuration.

The box-shaped furnace measures about 11 cm on a side. The sample was held inside a metal holder which was inserted between the parallel plates of two heating elements and attached to two sapphire rods suspending from one element. These elements were obtained on a special order from Lindberg and included an optical slot at the center. The surrounding walls were made from ZAL 45 insulating plates (made by Zircar), capable of retaining an external temperature in the range of 100—150 °C at the highest operating temperature. The temperature was monitored by a chromel-alumel thermocouple inserted into a hole in the sample holder very close to the sample. With power supplied by a Variac, the temperature was stable to within 1 °C during each measurement. At the highest temperatures (above 900 °C), we faced some contamination problems originating from the sample's metal holder. We first tried Inconel holders which resulted in large contamination. We then used Kanthal A1 holders which gave much less contamination. The residual contamination, which could be removed by repolishing the samples, did not decrease the average subgap transmission by more than 10%. This had but little effect on our final results as explained in the next section. We used two samples of thicknesses 0.117 and 1.070 mm which were cut at a random orientation from crystals grown by the Crystal Physics Laboratory at the Massachusetts Institute of Technology (MIT). They were polished with diamond pastes down to a particle size of 0.1 μm

III. RESULTS AND DISCUSSION

The transmission spectra of the thin sample at various temperatures are shown in Fig. 1. Up to temperatures of ~900 °C the subgap transmission "saturates" at a value of ~0.70 determined by reflection losses corresponding to a refractive index of 2.4. At higher temperatures, the curves tend to saturate at lower values, corresponding in part to the contamination problem mentioned in the previous section. We did not attempt to correct our results for this contamination since it would not affect much the lower transmission portion of each spectrum which was utilized in the analysis. For instance, in the most contam-

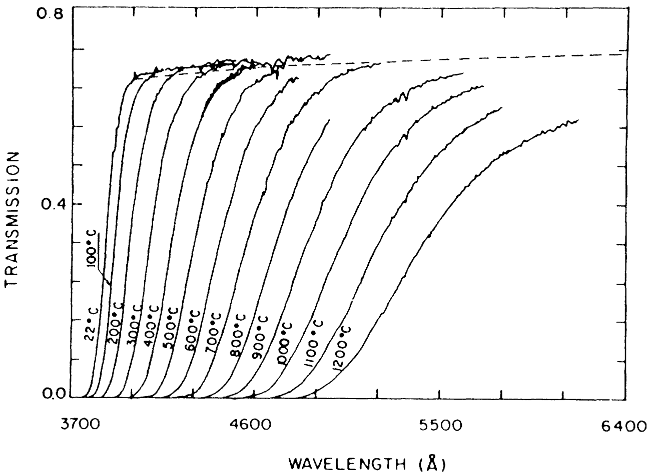

FIG. 1. As-measured transmission spectra of the thin sample (0.0117 cm) at various temperatures. Dashed curve presents reflection losses calculated from Cardona's refractive index.

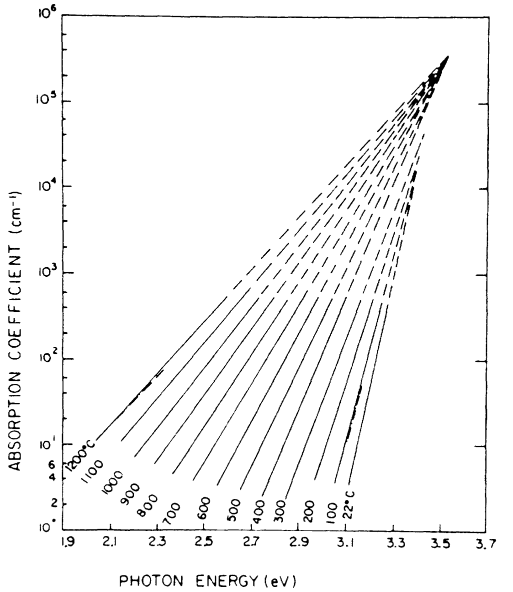

FIG. 2. Absorption spectra at various temperatures. Note that at $T > 400\,^{\circ}\mathrm{C}$ all lines intersect at a single point (at $E = 3.525$ eV) corresponding to the direct gap. The dashed-dotted lines at 100 and 1200 °C correspond to differences between both samples which are a measure for experimental error in the absolute transmission value.

inated 1200 °C spectrum, we only utilized the portion of the curve lying below 37% transmission ignoring the upper portion. In other curves, larger transmission ranges could be utilized. Such a procedure is justified since at the onset of strong absorption the contamination is only a small perturbation. We also did not make exact corrections for reflection losses, e.g., by measuring the actual reflectance of our samples.[2] Instead we applied the RT refractive index dispersion as was measured by Cardona.[13] The resulting reflection limited transmission is shown as a dashed curve that fits our data quite well at the saturation regime. Another limitation, imposed by zero offset and drift of the signal and by the noise level, resulted in ignoring transmission data below 0.5% at all temperatures. The absorption coefficient was evaluated using the usual transmission formula and allowing for multiple reflections. Our absorption spectra are presented in Fig. 2. The solid lines are the as-measured results of the thin sample. In the region of overlap ($\alpha < 50\ \mathrm{cm}^{-1}$) they fit well the results of the thick sample. (Slight differences between both samples that still exist—shown in the most extreme cases, i.e., at 100 and 1200 °C by the dashed-dotted lines—can be attributed to errors in measured value of absolute transmission.) The fact that both samples follow the same exponential dependence as given by Eq. (1), validates the approximations made in the data analysis. Our above RT results agree well with those of CF. For instance, our slope parameter σ is about 5% lower than theirs at 200 °C. This difference reflects presumably an experimental error since RT results of CF and of RB differ by a similar amount.

An interesting feature in Fig. 2 is that below 200 °C the extrapolated absorption spectra do not intersect at a single point. The same result has been reported by CF. As discussed in the Introduction, this is typical to broadening of an indirect threshold—where the α_0 term is T dependent owing to a similar dependence of the indirect transition strength—provided that the threshold does not contain nonlinear terms at these temperatures. Above 400 °C the extrapolated absorption edges at various temperatures do intersect at a single energy $E_0(0) = 3.525$ eV corresponding to $\alpha_0' = 3.6 \times 10^5\ \mathrm{cm}^{-1}$. We interpret this as an Urbach broadening of a direct threshold (since it does not have a T-dependent α_0 term) occurring in the vicinity of this energy. This would mean that the reflectivity shoulder at ~ 3.5 eV is due to the lowest direct transition. By this we adopt CF's rather than RB's interpretation (the latter assumed the threshold to be due to saturation of the indirect transition strength). However, CF's band model and assignment probably have to be altered; for instance, if the valence-band maximum moves to the X point, (see Introduction), the indirect gap will correspond to the $X_{5'} \rightarrow \Gamma_{25'}$ while the direct gap to the $X_{5'} \rightarrow X_3$ transitions. The change over from indirect to direct broadening is related to the small separation between both gaps. Since the direct edge pivots at various temperatures around an α_0' which is much larger than the corresponding indirect value, it supersedes the indirect edge at some elevated temperature. Thus, this changeover should be typical to narrow band indirect gap materials but, as far as we know, has not been reported previously.

Referring to the T dependence of the band gaps, it is rather hard to tell what its magnitude is, based on our data. This limitation is inherent to an Urbach edge if we suppose that $E_0(T) = E_0(0) - \beta T$, where $E_0(0)$ is the extrapolated band gap at 0 K. Then Eq. (1) is replaced by

$$\alpha = \alpha_0' \exp\{\sigma[E - E_0(0)]/kT\}\ , \qquad (1')$$

where $\alpha_0' = \alpha_0 \exp(\sigma\beta/k)$, i.e., β is absorbed into the preexponential and cannot be obtained separately unless estimates for the value of α_0 are available. To this end, let us choose $\alpha_0 = 3\times10^4$ cm^{-1}, which is the actual absorption coefficient at 3.5 eV obtained from reflectivity data.[13,14] Then, above 400 °C—where σ is a constant $(=0.89\pm0.01)$—one obtains $\beta = 2.4\times10^{-4}$ eV/K which is a rather small value. Moreover, the value of α_0 derived in this way is probably underestimated since broadening effects tend to lower the actual value of the absorption coefficient at high energies. Thus, the above value of β is probably an upper limit.

An alternative approach would be to assign an effective band gap to each curve in Fig. 2. The easiest way is probably to postulate some value of α for which $E_\alpha(T)$ (that is, the energy corresponding to that α at a given temperature) yields the effective band gap. In BaTiO$_3$ Wemple[15] has proposed the α value where the absorption edge starts to level off from exponential behavior, i.e., at 3000 cm^{-1}. In SrTiO$_3$ (Refs. 1 and 2) as well as in KTaO$_3$ (Ref. 9) this α is probably closer to 1000 cm^{-1}. In Fig. 3 are shown three effective gaps defined for $\alpha = 500$, 1000, and 2000 cm^{-1}, as determined from the extrapolated curves of Fig. 2, together with low T results of CF. If we define the effective value of β as $\beta_{\rm eff} = -dE_\alpha/dT$, we obtain for these values of α that the effective direct gap varies linearly with T like $\beta_{\rm eff} = 5.7\times10^{-4}$ eV/K$\pm$12%. This value could be derived directly from Eq. (1′) by substituting E_α for E, eliminating T, and taking the derivative with respect to T; assuming that α_0 and σ are independent of T above 400 °C, one obtains $\beta_{\rm eff} = (k/\sigma)\ln(\alpha_0'/\alpha)$, and the above result is obtained. At lower temperatures, where these parameters become T dependent, $\beta_{\rm eff}$ decreases $(<3\times10^{-4}$ eV/K). The difference between the high- and low-T values of $\beta_{\rm eff}$ together with the difference in the α_0 value of, and the separation between, the direct and indirect gaps (0.2—0.25 eV), account for the appearance of the direct edge only above 400 °C.

Again we would like to emphasize that the value of $\beta_{\rm eff}$ derived for the direct edge does not possibly reflect the actual value of β, since, if it did then

$$\alpha_0 = \alpha_0' \exp(-\sigma\beta_{\rm eff}/k) \cong 1000 \text{ cm}^{-1} .$$

This value is rather small and is unlikely to represent an absorption coefficient corresponding to a direct gap.

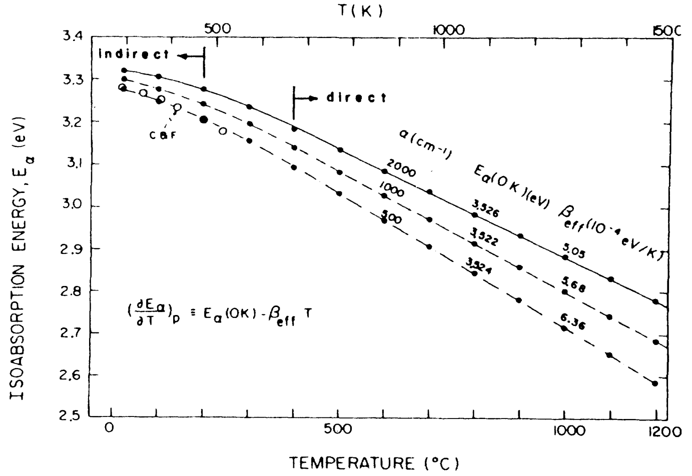

FIG. 3. Temperature variation of the effective band gap. Note that the straight portions of the curves extrapolate to the direct gap. Open circles present results of CF (Ref. 1).

There are two other optical measurements that give evidence for a small β value. The first is reflectivity. In BaTiO$_3$, a closely related perovskite, Cardona reported[13] that up to 200 °C no significant changes in the reflection spectrum were observed. We performed preliminary reflection measurements on SrTiO$_3$ around the ~4 eV peak at temperatures up to 500 °C. No definite change in peak position could be observed, particularly not a shift to lower energy with increasing temperature. The second evidence is reflected in recent refractive index measurements on SrTiO$_3$ by Toyoda and Yabe between RT and 400 °C.[16] Their measurements show a large *negative* temperature coefficient of the long-wavelength refractive index n_∞, i.e., $dn_\infty/dT = -1\times10^{-5}$ K^{-1} at 400 °C. n_∞ may be related to the fundamental ϵ_2 spectrum by a single oscillator equation

$$n_\infty^2 - 1 = \frac{E_p^2}{E_{\rm Penn}^2} = M_{-1} \tag{2}$$

where E_p is the valence electrons' plasma energy, $E_{\rm Penn}$ is the Penn gap, and $M_{-1} \propto \int_{E_0}^{\infty} \epsilon_2(E)dE/E$ is a moment of ϵ_2. Since E_p^2 is proportional to electron density, $d\ln Ep^2/dT = -\gamma = -2.7\times10^{-5}$ K^{-1}. Thus, $dE_{\rm Penn}/dT = -0.5\times10^{-4}$ eV/K. This value is about an order of magnitude smaller than regular band-gap derivatives in many other materials. Moreover, since M_{-1} decreases with temperature this may imply even a slight increase of the direct threshold with temperature, (e.g., owing to the E^{-1} term which gives ϵ_2 a heavier weight near E_0 than much above it, and assuming that ϵ_2 does not decrease with temperature). We conclude that β is possibly rather small in SrTiO$_3$. In what follows we give an argument for this anomaly, that applies to narrow conduction-band indirect gap materials.

The T dependence of the band gap (E_g) can be separated into an explicit $e\phi$ term (i.e., at constant volume) and to an implicit term (i.e., due to change in lattice constant). RB suggested that at low temperatures an accidental cancellation of these terms occurs, that is,

$$\left[\frac{\partial E_g}{\partial T}\right]_P = \left[\frac{\partial E_g}{\partial T}\right]_V - \frac{\gamma}{\kappa}\left[\frac{\partial E_g}{\partial T}\right]_T \cong 0 , \tag{3}$$

where P and V are pressure and volume, respectively, γ is the volume thermal expansion coefficient, and κ the isothermal compressibility. Cancellation would imply equality of both terms over a large temperature range. In the implicit term the dominant temperature dependence is due to the γ/κ term [i.e., assuming that $(\partial E_g/\partial P)_T$ is only weakly T dependent] which resembles that of the specific heat,[17] that is, this term would increase by at least 2 orders of magnitude between cryogenic and RT. In the conventional electron phonon theory the explicit term does not increase that much.[18] Thus, cancellation of these terms seems unlikely.

Alternatively, we propose that the implicit term is very small in this material [less than 10^{-5} eV/K if the value of $(\partial E_g/\partial P)_T = -5\times 10^{-7}$ eV/bar of $BaTiO_3$ (Ref. 19)—which probably is overestimated due to its evaluation at $\alpha = 75$ cm^{-1}—could be employed]. It is more difficult to rationalize a small explicit term particularly due to the relatively strong $e\phi$ coupling in $SrTiO_3$. Note, however, that in indirect narrow-band materials the conduction-band valley corresponding to the direct gap lies close in energy and above the valley of the indirect gap.[20] Thus for the direct gap, apart from virtual $e\phi$ transitions to intravalley intermediate states with higher energy (that is, the regular Fan terms), there is a possibility of intervalley down jumps to the conduction-band minimum, i.e., with intermediate electron energy *lower* than the initial state. This will result in a positive denominator in the second-order perturbation term and a positive contribution to the explicit term which compensates at least in part for the intravalley term. Thus the explicit term of the direct gap may be quite small.

In summary, the small-temperature sensitivity of the band gaps in $SrTiO_3$ at high temperatures is reflected in both our absorption edge and reflectivity results, and in refractive index data. It may be attributed to a small explicit $e\phi$ term (owing to compensation of regular intravalley scattering processes by intervalley processes) and a small implicit term, rather than to accidental cancellation of both terms.

Somewhat puzzling in this context are our recent high-temperature transport results on an alloy closely related to $SrTiO_3$.[21] The zero T extrapolated thermal gap coincided with the indirect gap. On the other hand, in order to interpret our high-T transport results, we had to assume that the thermal gap varies with temperature like the effective direct gap. Thus, it is not clear to which optical gap, if any, the electrical gap corresponds at high T. Moreover, ignoring the temperature dependence of the *effective* gap in the analysis of the thermoelectric power data would yield unreasonably small transport constants, whereas the *actual* optical gap—as we have seen—is not as sensitive to temperature as is the effective gap. Now, thermally, electrons are excited between states. Thus any T variation of an electrical gap should reflect variation in the density of states. On the other hand, in the theory of Dow and Redfield,[22] Urbach broadening is attributed to either matrix element effects (via tunneling through the Coulomb well) or to density-of-states effects (via introduction of new low-energy states) both of which are caused by internal microfields. It might thus be argued that, since the thermal gap varies in the same way as the effective gap defined by the Urbach broadening, the origin of both these variations is the microfields induced new subgap states, that is, a density of states rather than a matrix element effect.

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