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Optical Gap of Strontium Titanate (Deviation from Urbach Tail Behavior)

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The absorption of $SrTiO_3$ below the fundamental edge shows, near liquid-nitrogen temperature, an oscillatory behavior, for which an explanation is proposed in terms of indirect transitions $\Gamma_{15} \rightarrow X_3$, centered around 3.27 eV and involving a 51-meV LO phonon. There is no evidence of excitonic effects. The first direct transition is probably $X_{5'} \rightarrow X_3$ and is located at ~3.46 eV. Broadening effects mask the indirect structure at higher temperatures where the absorption curves gradually evolve into normal Urbach tailing.

Studies of the optical threshold of perovskite-type ferroelectrics[1-6] always show the occurrence of Urbach tails,[7] except in impure crystals.[8,9] For this reason, although LCAO (linear combination of atomic orbitals) band-structure calculations[10] indicate, for $SrTiO_3$, a valence-band maximum at Γ and a conduction-band minimum at X, the latter feature being well established also by transport experiments,[11-16] the presence of indirect transitions has never been detected.

This Letter reports the first observation of fine structure in the absorption coefficient of $SrTiO_3$ near liquid-nitrogen (LN) temperature. The structure is absent at room and dry-ice temperatures (RT and DI), where Urbach behavior is exhibited over at least three decades, with saturation at high absorption levels.[17] This gives, to our knowledge, the first experimental evidence of indirect transitions in a ferroelectric perovskite. Somewhat similar behavior has been observed in other materials (e.g., AgBr,[18] CdTe,[19] and SnO_2[20]). The data allow a description of the optical band gap of $SrTiO_3$ which adds information to what is known from transport results. Measurements were taken on eleven samples of thickness 13 to 1300 μm, cut from two single-crystal boules provided by the National Lead Company at different times. One boule was specifically requested to be of high purity. Two monochromators were used, a double-pass glass-prism Perkin Elmer (Zürich) and a prism-plus-grating Cary 14 (Rome). In both cases energy calibration was accurate to within 3 meV and resolution better than 1 meV. These data were always reproducible within experimental errors; in particular, no significant discrepancies were found in samples from different boules. Experimental curves are shown in Fig. 1. The linear range of RT and DI data can be described by Urbach's equation

$$\alpha = \alpha_0 \exp[(h\nu - E_0)/kT^*], \quad (1)$$

where E_0 is related to the energy gap and T^* is

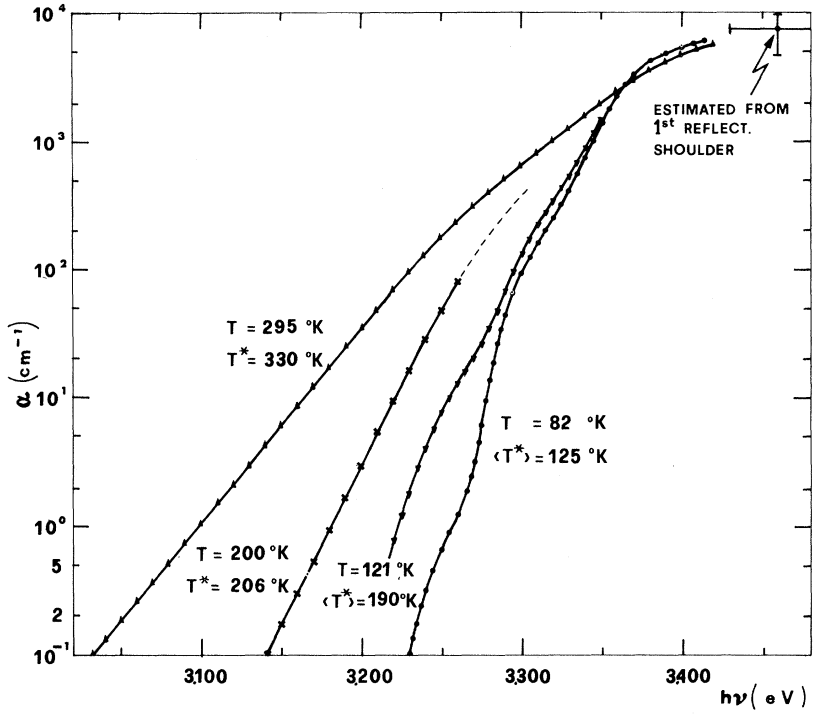

FIG. 1. Absorption coefficient α of $SrTiO_3$ at four different values of temperature T. For the meaning of T^* see Eq. (1). A value for α at 3.46 eV, as roughly estimated from the first shoulder observed in RT reflectance (Ref. 27, see also Ref. 4), is also given.

an effective temperature not too different from the actual temperature T. In this respect, $SrTiO_3$ differs substantially from $KTaO_3$ and $BaTiO_3$, where T^*-T is equal to $T_0 \sim 140°K$, independent of temperature.[2,6] A completely different behavior is shown at lower temperatures: The 82, 105 (not shown in figure), and 121°K curves exhibit oscillations around an average $\langle T^* \rangle$ much larger than T.[21,22]

We assume that this fine structure is an intrinsic behavior of the material and is not due to impurity effects, since no important differences were seen between the two kinds of samples used, and because of the type of temperature dependence shown [see discussion below at (i)]. In Fig. 2 we have replotted our 121°K data as $\alpha^{1/2}$ vs $h\nu$. The three ranges of linear behavior, as well as the relatively low absorption levels, suggest the presence of indirect-transition processes, without Coulomb interaction.[24] The solid line was calculated from the equation[25]

$$\alpha = \sum_{i=1}^{3} A_i (h\nu - E_i)^2, \tag{2}$$

where A_i is zero below its associated threshold E_i, while

$$A_i \propto \frac{|M_i|^2}{h\nu(\Delta E \pm E_{\mathrm{ph},i})^2} \tag{3}$$

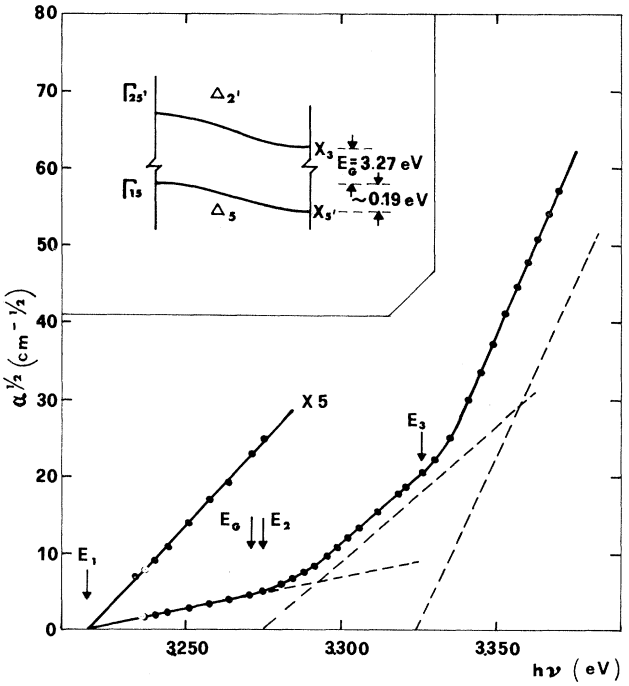

FIG. 2. Square root of absorption coefficient at 121°K versus phonon energy. Dots are experimental data; dashed lines are theoretical for indirect edges at E_1, E_2, and E_3; and the solid lines are given by their added contributions. The insert shows a schematic picture for the optical gap of $SrTiO_3$ in the Δ direction.

at and above the threshold. In Eq. (3) M_i is the matrix element of the electron-phonon interaction, ΔE is the width of the band where the electron is virtually phonon scattered, and $E_{\mathrm{ph},i}$ is the phonon energy taken with upper (lower) sign for phonon destruction (creation). Values for A_i, at $h\nu = E_i$, and $E_i (= E_G \mp E_{\mathrm{ph},i})$ that give best fitting to experiment are listed in Table I.

LN electroabsorption exhibits no induced dichroism for electric field applied along the (111) direction suggesting that the transition involved has X symmetry.[26] This implies that the photon process in the indirect transitions occurs at X and, from Eq. (3), that the valence band in the Δ direction is narrower than the conduction band, and/or that the joint density of states at X is much higher than at Γ. In all cases, it is conceivable to assume that, above the indirect structure, the first detectable direct transition is $X_5' \rightarrow X_3$, in agreement with the conclusions of DiDomenico and Wemple for $BaTiO_3$.[3] We locate this transition at 3.46 ± 0.03 eV (Fig. 1), where RT reflectance spectra exhibit a shoulder.[4,27] At high temperatures, broadening of this edge (and/or of the indirect thresholds) give rise to Urbach tailing. A discussion of the many theoretical models proposed for this behavior[28-30] is beyond the scope of this Letter.[31]

Close examination of the possible phonon mechanisms responsible for the observed structure leads us to conclude that the structure is in large part associated with a longitudinal optical phonon. We propose that E_1 and E_3, separated by 102 ± 2 meV, are due to destruction and creation, respectively, of a LO phonon of 51 meV at the zone boundary. This sets the gap E_G at 3.271 eV. Our picture is supported by the following arguments:

(i) A_1 increases with T approximately as the Bose function for a 51-meV phonon. Moreover, the ratio A_3/A_1 is nearly equal to the Boltzmann factor for this phonon at all temperatures shown in Table I.

(ii) At LN, a LO phonon of energy 55 meV at $k = 0$ has been observed by Raman scattering,[32] and of ~57 meV by infrared absorption,[33] photoluminescence,[34] and tunneling.[35]

(iii) This phonon has the correct symmetry to scatter an electron from Γ_{15} to X_5'. In constrast to our conclusions, Cowley[36] predicts, approximately at the correct energy, a LO phonon which in none of the models illustrated exhibits a dispersion curve bending down towards the zone edge. Other experiments[33,35,37] seem to be consistent with Cowley's results.

As to E_2, the constancy of A_2 (Table I) shows that it must not involve phonon destruction. However, on the basis of the available data, this does not necessarily imply phonon emission (e.g., a low-energy phonon, or the same phonon above with transition starting at a different energy). It is worthwhile mentioning that the above behavior is strikingly similar to what is observed in AgBr,[38] where addition of small quantities of AgCl induces a threshold precisely at the energy gap, due to impurity-assisted indirect transitions. A final comment should be made. If one attempts to explain the observed structure in terms of Dumke processes,[39] i.e., vertical phonon-assisted transitions, the temperature dependence suggests again that E_1 and E_3 have to be linked together in the manner discussed above, and E_2 would then be the actual direct edge. In such case, however, E_2 is expected to be by far the strongest process, contrary to observations.

In conclusion, a scheme for the optical gap can be suggested (insert of Fig. 2). The first direct transition at X (3.46 ± 0.03 eV) is preceded by indirect transitions $\Gamma_{15} \rightarrow X_3$, assisted by a 51-meV LO phonon and centered around 3.27 eV. The valence bandwidth is therefore 0.19 ± 0.03 eV, in agreement with theory.[10] The conduction band, unless the density of states at Γ is extremely weak, is not likely to be much narrower, giving an upper limit of $\sim 10 m_0$ for the longitudinal effective mass. This is consistent with transport and susceptibility results,[11-16] while being rather

Table I. Fitting parameters for Eq. (2) at three temperatures, with $E_1 = 3.220 \pm 0.002$, $E_2 = 3.275 \pm 0.002$, and $E_3 = 3.322 \pm 0.002$ eV. $F = (1 + f_B)/f_B$ is the Boltzmann factor, calculated for a 51-meV phonon.

T (°K)	$\langle T^* \rangle$ (°K)	A_1 ($\mathrm{cm}^{-1}\,\mathrm{eV}^{-2}$)	A_2	A_3	$(A_1/A_3)F$
82	~125	6.2×10^2	1×10^5	10×10^5	0.83
105	~160	3.2×10^3	1.3×10^5	7×10^5	1.3
121	~190	8×10^3	1.3×10^5	8×10^5	1.3

higher than the theoretical estimate of 0.02-0.05 eV.[10] Tunneling experiments by Sroubek[40] suggest an even wider conduction band. We suggest that careful reinvestigation of the absorption tail of other ferroelectrics, down to the lowest temperatures, is of great interest, as it should enable one to deduce a unified picture of the optical gap of solids having oxygen-octahedra structure.

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Thanks are due to K. A. Müller for bringing to the attention of the authors the problem of Brillouin zone changes at the transition temperature in connection with electronic transitions,[41] and to F. Bassani and H. P. R. Frederikse for a critical reading of the manuscript. A stimulating correspondence with D. Dunn is gratefully acknowledged.

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[22]It should be pointed out here that below ~110°K the sample is in its tetragonal-paraelectric phase. In single-domain crystals, this results in a small dichroism [about 3 meV displacement between the edges for light polarized parallel and perpendicular to the c axis; see K. A. Müller, W. Berlinger, M. Capizzi, and H. Gränicher, Solid State Commun. 8, 549 (1970); M. Capizzi and A. Frova, to be published]. In the present experiment unpolarized light has been used. No essential changes are found in going through the transition temperature even if folding of the Brillouin zone (BZ) suggests the possibility of "direct" (i.e., without phonons) Γ transitions approximately at the same energy of the $\Gamma_{15} \rightarrow X_3$ phonon-assisted threshold of the cubic phase [for the change in the BZ see, e.g., H. Unoki and T. Sakudo, J. Phys. Soc. Jap. 23, 546 (1967)]. It can be shown (Capizzi and Frova, *loc. cit.*), by perturbation theory arguments, that the phonon-assisted optical process is nearly unaffected by the phase transition, and the new "direct" process is proportional to the square of the distortion, being negligible for the very small deformation involved here [F. W. Lytle, J. Appl. Phys. 35, 2212 (1964)]. For the sake of simplicity, we shall use throughout the symmetry notations for the cubic phase, although this is strictly valid only for data above ~110°K.

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$M1$ Giant Resonance in ^{208}Pb From Threshold Photoneutron Measurements*

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From threshold photoneutron cross-section and angular-distribution measurements on ^{208}Pb, seven 1^+ states have been detected, which have a total $M1$ strength of 51 eV. This $M1$ strength, centered at an excitation energy of 7.9 MeV and spread over a range of 700 keV, constitutes at least half and perhaps all of the total $M1$ strength obtained from shell-model calculations.

In the measurements reported here, an exceptionally large concentration of ground-state $M1$ radiation strength (more than five Weisskopf units) has been detected in ^{208}Pb, centered at an excitation energy of 7.9 MeV. This strength is spread over seven resonances in the energy range from 7.40 to 8.25 MeV. Two of these resonances individually have widths in excess of one Weisskopf unit.

The $M1$ strength was detected in photoneutron cross-section measurements on ^{208}Pb by the threshold photoneutron technique, which has been described elsewhere.[1,2] This method, which makes use of electron bremsstrahlung, is applied near threshold where neutron time-of-flight techniques allow the measurement of (γ, n) cross sections with very high resolution.

The 135° (lab) differential photoneutron cross section is shown in Fig. 1, plotted as a function of both the detected neutron energy and the excitation energy in the compound system. The low-energy data (upper plot) were taken with an enriched sample of ^{208}Pb (with isotopic ratios ^{208}Pb:^{207}Pb:^{206}Pb = 99.75:0.05:0.20), using a neutron detector which operates by detecting a multiplicity of γ rays and neutrons from a fission event.[3,4] The high-energy data (lower plot) were taken with natural lead, using a proton-recoil neutron detector.[5] Both measurements were carried out with an end-point energy of 9.8 MeV. Additional measurements were performed at lower energies with each detector in order to identify both excited-state photoneutron transitions (designated by arrows in the upper plot) and, with the help of previous measurements on separated ^{207}Pb samples, resonances associated with contaminant isotopes (designated by arrows in the lower plot). The prominent peaks at 547, 620, 660, and 860 keV were shown definitely to be resonances in ^{208}Pb associated with ground-state transitions. No prominent peaks were observed between 860 and 1200 keV. The measured area A under a resonance is proportional to the ground-state radiation width $\Gamma_{\gamma 0}$ (since $\Gamma_{\gamma 0} \ll \Gamma_n \cong \Gamma$ here). Table I contains the laboratory neutron energy E_l (column 1) and a quantity proportional to A (column 2) for each prominent resonance in the Fig. 1.

The spins of most of these resonances were determined by comparing the data of Fig. 1 with that of similar measurements carried out at 90°, with the natural lead sample, for each neutron detector. The measurements which used the multiplicity detector covered the range from 10 to 1000 keV; those with the proton-recoil detector, from 130 to 1200 keV. The 90 and 135° data from the multiplicity-detector runs were normalized at the 40.8-keV resonance, a well-established 1^- state,[6] which de-excites with $l = 0$ neutrons and whose angular distribu-