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Optical Properties and Band Structure of $SrTiO_3$ and $BaTiO_3$[†]

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The normal-incidence reflectance spectra of $SrTiO_3$ and $BaTiO_3$ and the optical constants derived by the Kramers-Kronig method are reported. These spectra are very similar to those of rutile. The strongest optical transitions (A) occur at about 4.4 eV: They are responsible for the dispersion observed below the fundamental absorption edge (3.2 eV). A tentative interpretation of these spectra in terms of the energy band structure of the materials is offered. The A peak seems due to transitions between $2p$ levels of oxygen and $3s$ levels of titanium at the X point of the Brillouin zone. The splitting of the A peak is assigned to the splitting of the $2p$ levels of the oxygen in the cubic field. Transitions between $2p$ oxygen and $4s$ titanium levels, between $2s$ oxygen and $3d$ titanium levels, and between $2s$ oxygen and $5s$ titanium or $6s$ barium levels are also observed. Plasma oscillations are seen around 21 eV.

INTRODUCTION

STRONTIUM titanate crystallizes at room temperature in the simple cubic perovskite structure (O_h^1).[1] Barium titanate has the same structure at temperatures above the ferroelectric Curie point (120°C) while below this temperature a slight tetragonal distortion (C^1_{4v}) modifies the perovskite structure. The difference between the lattice constant of $BaTiO_3$ along the c (tetragonal) and the a axis is only 1% at room temperature. These materials have an oxygen-titanium coordination (a titanium ion surrounded by six oxygen ions) typical of many transition-metal oxides. Because of their simple crystal structure they offer a natural starting point for the study of the electronic structure of materials with this coordination. Considerable interest in these materials has been triggered recently by their superconducting properties at high doping levels.[2]

$SrTiO_3$ has a fundamental absorption edge at 3.22 eV at room temperature.[3] The fundamental edge of $BaTiO_3$[4] occurs at about the same energy (3.15 eV at room temperature) as that of $SrTiO_3$, however, this edge is slightly dichroic[5] for $BaTiO_3$ due to the tetragonal structure of this crystal. Correspondingly $BaTiO_3$ shows a small long-wavelength birefringence[6] below the Curie temperature. The fundamental edge of rutile[7] (4.0 eV at room temperature), a material with the same Ti-O coordination as $SrTiO_3$ and $BaTiO_3$, is also close to that of $SrTiO_3$ and $BaTiO_3$. In spite of large deviations from the cubic crystal structure, the absorption edge of rutile also shows little dichroism. The noncubic structure of rutile produces, however, a strong long-wavelength birefringence.[8] The closeness of the absorption edge of $SrTiO_3$, $BaTiO_3$, and TiO_2 indicates that this edge is due to transitions between states with little admixture of Sr or Ba wave functions. It is generally agreed that this absorption edge is due to transitions between predominantly $2p$ oxygen states and $3d$ titanium states.

Very little additional experimental information about the band structure of these materials is available. The presence of superconductivity in $SrTiO_3$ indicates conduction-band minima off $\mathbf{k}=0$. The effect of uniaxial stress on the superconducting critical temperature seems to indicate conduction-band minima in the [100] direction.[9] However, this conclusion is not supported by piezoresistance measurements.[10] Kahn and Leyendeker[1] have reported a band-structure calculation for $SrTiO_3$. They use as wave functions linear combinations of atomic orbitals and they vary the ionicity of the oxygen and titanium atoms so as to fit the direct gap at $\mathbf{k}=0$ to the observed value of the fundamental absorption edge. There is some question[11] about the method used to estimate the O ($2p$)-Ti ($3d$) gap at $\mathbf{k}=0$ and hence about the ionicity of the material. While Kahn and Leyendeker neglected the change in the ionization potentials of the oxygen and titanium ions with the degree of ionicity, Šimanek and Šroubek show that this change is compensated by the effect of the polarizability of the oxygen ion, also neglected in the calculation of Ref. 1. Hence this calculation probably represents well the qualitative behavior of the O ($2p$) and Ti ($3d$) bands of $SrTiO_3$ and $BaTiO_3$.

Considerable information about the energy bands of solids can be obtained by means of ultraviolet reflectance studies.[12] This method is particularly useful when various related materials with the same or similar crystal structure are measured and when some rough idea of the energy band structure is already available. In this paper we report the normal incidence reflectance

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[†] Supported by the Advanced Research Projects Agency and the National Science Foundation.

[1] A. H. Kahn and A. J. Leyendeker, Phys. Rev. **135**, A1321 (1964).

[2] M. H. Cohen, Phys. Rev. **134**, A511 (1964).

[3] T. A. Noland, Phys. Rev. **94**, 724 (1954).

[4] R. C. Casella and S. P. Keller, Phys. Rev. **116**, 1463 (1959).

[5] D. Meyerhofer, Phys. Rev. **112**, 413 (1958).

[6] R. Hoffmann, Helv. Phys. Acta **35**, 532 (1962).

[7] P. Moch, M. Balkanski, and P. Aigrain, Compt. Rend. **251**, 1373 (1960).

[8] J. R. Devore, J. Opt. Soc. Am. **51**, 416 (1961).

[9] J. Schooley, W. Hosler, M. H. Cohen, and C. Koonce (private communication).

[10] O. N. Tufte and E. L. Stelzer, Bull. Am. Phys. Soc. **10**, 304 (1965).

[11] E. Šimanek and Z. Šroubek, Phys. Status Solidi **8**, K47 (1965).

[12] M. Cardona, in *Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 181.

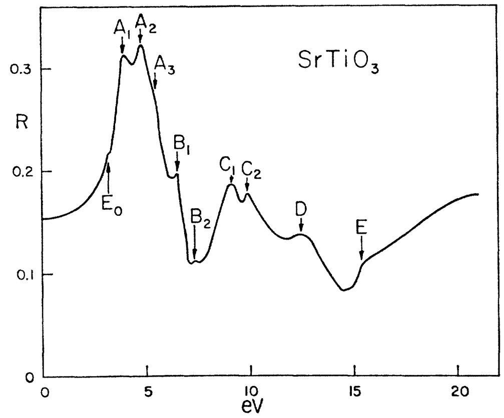

FIG. 1. Reflectivity spectrum of strontium titanate at room temperature.

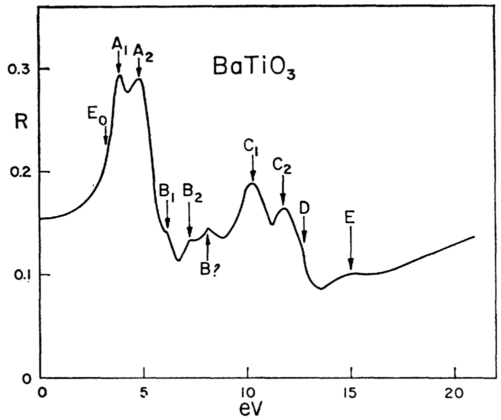

FIG. 3. Reflectivity spectrum of barium titanate at room temperature.

spectra of $SrTiO_3$ and $BaTiO_3$. An attempt is made at identifying several peaks observed in these spectra in terms of the calculations of Ref. 1.

Several of the high photon-energy peaks are asisgned to transitions beyond the scope of Kahn and Leyendeker's calculations (O $(2p)\to$ Ti $(3d)$) such as O $(2p)\to$ Ti $(4s)$, O $(2p)\to$ Sr $(5s)$ or Ba $(6s)$, and O $(2s)\to$ Ti $(3d)$.

MEASUREMENTS

We have measured the reflectivity of several $BaTiO_3$ and $SrTiO_3$ crystals for photon energies between 2 and 22 eV. The method used has been described earlier.[13] A 1-m Macpherson monochromator of the Seya-Namioka type with a Tanaka lamp as a light source was used. In order to cover the whole spectral range between 2 and 22 eV, the lamp was operated with several gases (H_2, A, Ne, and He). Both ac excitation and a spark-gap-triggered condenser discharge were used as modes of excitation for the lamp. A flat $SrTiO_3$ sample for reflectivity measurements and a prism for angle-of-minimum-deviation determinations were cut out of a boule supplied by Semi-Elements.[14] The samples were polished with Buehler Al_2O_3 (0.05-micron grit) and etched with either HF or a mixture of HCl and HNO_3. Reflectivity measurements were also performed on the as-grown surfaces of $BaTiO_3$ platelets obtained from Semi-Elements and from the Tyco Laboratories.[15] After measuring it, the as-grown surface was polished with Buehler Al_2O_3 and remeasured. The sample was then etched with either HF or a mixture of HNO_3 and HCl and measured again. In an attempt to observe the effect of the ferroelectric transition on the reflection spectrum of $BaTiO_3$, a little heater was attached to the sample holder and measurements were taken with the sample heated above the Curie temperature.

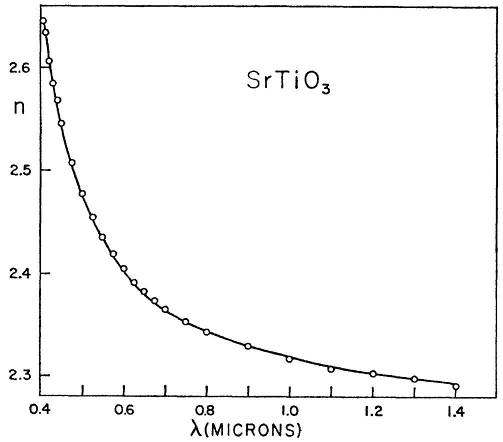

FIG. 2. Refractive index of strontium titanate at room temperature. The full curve has been calculated with Eq. 1.

RESULTS

The reflection spectrum of a polished and etched $SrTiO_3$ sample at room temperature is shown in Fig. 1. The points below 3 eV were not measured directly since some inaccuracy was introduced in this region by reflections from the back of the sample. Instead these points were calculated from the refractive-index values determined by the angle-of-minimum-deviation method. The values of the refractive index of $SrTiO_3$ measured at room temperature for wavelengths between 4000 and 11 000 Å are plotted in Fig. 2. They are in agreement with the data reported by Levin *et al.*,[16] for wavelengths between 4000 and 7000 Å. The reflectivities measured at and above 3 eV were renormalized so as to match the reflectivity calculated from the refractive index at 3 eV. The main reflection peak, between 4 and 5 eV, is a doublet (A_1-A_2) with a splitting of 0.86 eV. This

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[13] M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963).

[14] Saxonburg, Pennsylvania.

[15] We are grateful to Dr. G. Rupprecht for supplying these samples.

[16] S. B. Levin, N. J. Field, F. M. Plock, and L. Merker, J. Opt. Soc. Am. **45**, 737 (1955).

TABLE I. Energy of the various reflection peaks observed in $SrTiO_3$, $BaTiO_3$, and rutile ($\mathbf{E}\perp c$) at room temperature.

	E_0	A_1	A_2	A_3	B_1	B_2	C_1	C_2	D	E
$SrTiO_3$	3.2	4.00	4.86	5.5	6.52	7.4	9.2	9.9	12.5	15.3
$BaTiO_3$	3.2	3.91	4.85		6.10	7.25	10.3	11.8	12.8	15
TiO_2 ($\mathbf{E}\perp c$)		3.97	5.52		6.50	7.64	8.53	9.24	11	14.1

peak seems to have a high-energy shoulder (A_3) at 5.5 eV. There is another somewhat less strong doublet (C_1-C_2) with about the same splitting, between 9 and 10 eV. One is tempted to call the weak B_1-B_2 lines around 7 eV another doublet since their splitting is also about 0.8 eV. The fundamental absorption edge E_0 produces slight structure in the reflection spectrum at 3.2 eV. Two other peaks (D and E) are seen at 12.5 and 15.5 eV, respectively. The reflection is still rising near the end of our photon energy range (22 eV) indicating additional structure at still higher photon energies.

The reflectivity spectrum of a polished and etched crystal of $BaTiO_3$ at room temperature is shown in Fig. 3. The measurements were taken with unpolarized light and the samples were not poled. An examination under crossed polarizers indicated a random orientation for the ferroelectric domains. Because of back reflection, the reflection coefficients below 3 eV could not be accurately determined. Since we did not have samples thick enough to prepare prisms, we assumed that the reflectivity below 3 eV was the same as that of $SrTiO_3$. This assumption is plausible in view of the discussion in the next section. Also, the average measured value of n in the region of transparency[17] ($n\approx 2.4$) agrees well

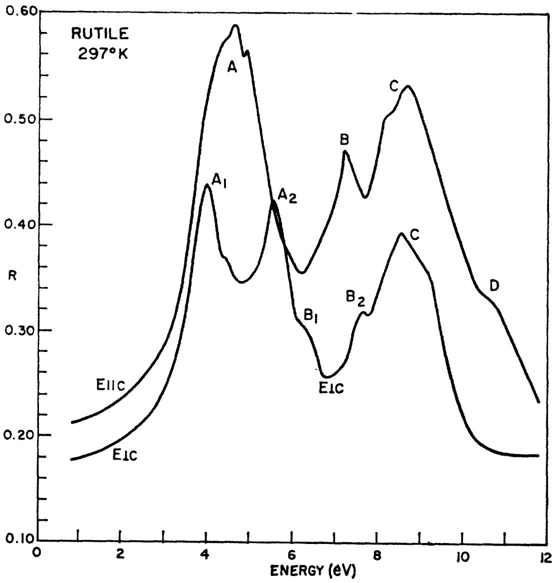

FIG. 4. Reflectivity spectrum of rutile (see Ref. 18).

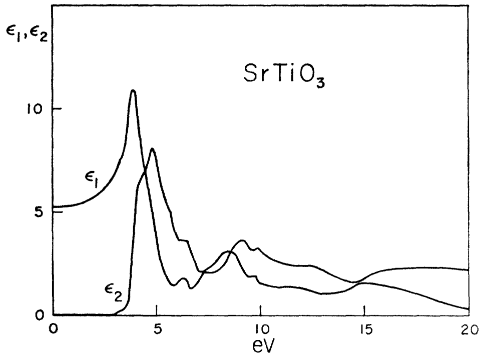

FIG. 5. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant of strontium titanate at room temperature.

with the average value for $SrTiO_3$. The structure in the reflection spectrum of $BaTiO_3$ (Fig. 3) is very similar to that observed for $SrTiO_3$ (Fig. 1). The A_1-A_2 doublet occurs at nearly the same energy as in $SrTiO_2$. The B_1-B_2 doublet is shifted towards slightly lower energies while the C_1-C_2 doublet is shifted towards higher energies. The E_0, D, and E structure is also observable and the reflectivity is still increasing at the end of our photon energy range. The positions of the reflection peaks of $SrTiO_3$ and $BaTiO_3$ are listed in Table I. The peaks observed in the reflection spectrum of rutile[18] for the electric vector of the light perpendicular to the tetragonal axis are also listed in Table I since this spectrum bears a striking similarity to that of $SrTiO_3$ and $BaTiO_3$. For the sake of comparison we have shown the reflection spectrum of rutile in Fig. 4.

The reflection spectrum of an as-grown surface of a $BaTiO_3$ platelet has also been measured. It looks nearly identical to that of Fig. 3; the only significant difference is a slight enhancement of the A_1 component of the A_1-A_2 doublet at the expense of the A_2 component which seems to be smaller than in the polished-etched sample. An attempt to see the effect of the ferroelectric transition on the ultraviolet reflection spectrum was made by heating the sample above the

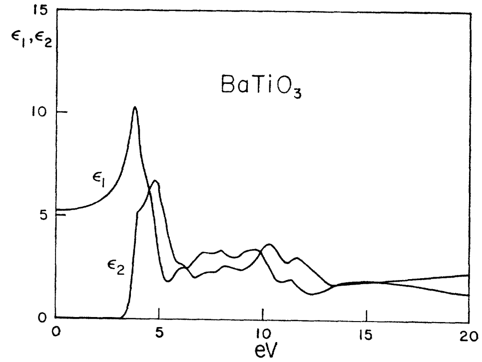

FIG. 6. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant of barium titanate at room temperature.

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[17] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

[18] M. Cardona and G. Harbeke, Phys. Rev. **137**, A1367 (1965).

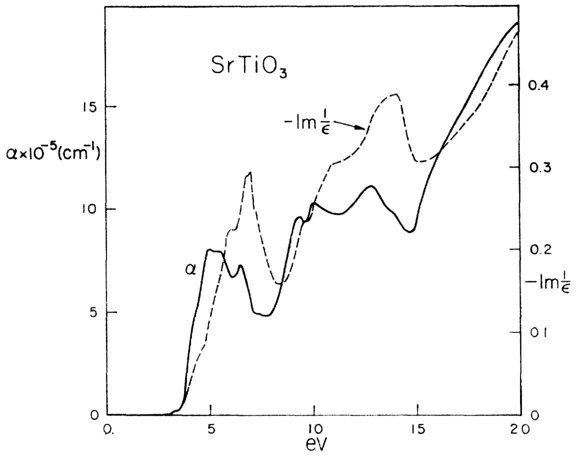

FIG. 7. Absorption coefficient α and energy-loss function $-\mathrm{Im}(1/\epsilon)$ of strontium titanate at room temperature.

Curie temperature. Measurements to temperatures as high as 200°C indicated no significant change in the reflection spectrum. The shift in the reflection peaks was too small to be detected. We believe that this observation makes measurements with polarized light in the tetragonal phase unnecessary.

Figures 5 and 6 show the real and imaginary parts of the dielectric constant (ϵ_1 and ϵ_2) of SrTiO$_3$ and BaTiO$_3$ derived by the Kramers-Kronig analysis of the data of Figs. 1 and 3 extrapolated beyond the region of measurement by using the expression[19] $R = AE^{-\beta}$ where E is the photon energy, A and β are constants. Whenever the reflectivity has already become quite small at the end of the available spectral region, β is approximately equal to 4. This is obviously not the case for the data of Figs. 1 and 3, and β has to be adjusted *ad hoc* until reasonably small values for the absorption coefficient in the region of transparency are obtained. In this way we obtained $\beta = 2.9$ for SrTiO$_3$ and $\beta = 1.5$ for BaTiO$_3$.

Figures 7 and 8 show the absorption coefficient α and the energy-loss function $-\mathrm{Im}(1/\epsilon)$ obtained for SrTiO$_3$ and BaTiO$_3$ from the data of Figs. 5 and 6. The energy-loss function peaks strongly at the energies at which collective plasma resonances ocur.[20]

DISCUSSION

Figure 9 shows the band structure of SrTiO$_3$ calculated by Kahn and Leyendeker. The Δ point is a general point along the [100] direction in the simple cubic Brillouin zone (B.Z.). The X point is the center of the faces of the B.Z., the M point is the midpoint of an edge of the B.Z., and the R point a corner of the B.Z. The bands in Fig. 9 were calculated using as wave functions linear combinations of O^{-2} ($2p$) and Ti^{+3} ($3d$) orbitals. The energy separation (gap) between the valence and conduction band was estimated from the difference in the ionization potentials of the O^{-2} and Ti^{+3} ions and the Madelung energy for the perovskite lattice. It was found that for a lattice with two negative charges in the oxygen sites, three positive charges in the titanium sites, and two positive charges in the strontium sites the energy gap at $\mathbf{k}=0$ would be about 16 eV. In order to fit this gap to the observed fundamental absorption edge (3.2 eV) negative charge was transferred from the O^{-2} to the Ti^{+3} ions. Agreement with the fundamental absorption edge was obtained for a negative charge of 1.7 in the oxygen sites (the smallest direct energy gap is indeed at $\mathbf{k}=0$ in the bands of Fig. 9; this gap is allowed for optical transitions). This procedure has been recently criticized by Šimanek and Šroubek on the grounds that it neglects the change in the ionization energies of the Sr, Ti, and O with ionicity. It turns out[11] that this change almost completely cancels the effect of the change in Madelung energy. The proper energy gap is obtained, however, if the polarization energy of the Ti-O in the strong electric fields produced by the ionicity is taken into account.[11] A charge of -1.8 is then required for the oxygen ions, close to the value assumed by Kahn and Leyendeker. Hence, in spite of the apparently incorrect method used to fit the experimental energy gap, we believe that the bands of Fig. 9 represent the qualitative behavior of the energy bands in SrTiO$_3$. The $2s$ levels of the oxygen ion, not taken into account in these calculations, will give bands approximately 11 eV below the $2p$ bands (estimated from the atomic energy levels of neutral Ne).[21] Other levels of possible importance in the ultraviolet region not taken into account in the calculations of Fig. 9 are the $4s$ levels of Ti^{+2} and the $5s$ levels of Sr^{+1}. They lie about 13 and 17 eV above the O^{-2} ($2p$) levels, respectively.

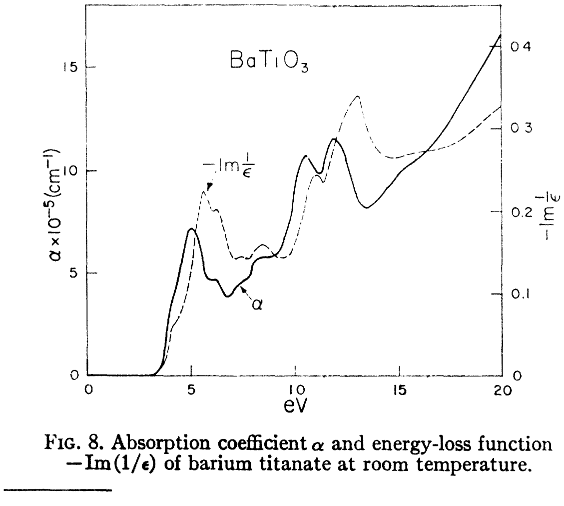

FIG. 8. Absorption coefficient α and energy-loss function $-\mathrm{Im}(1/\epsilon)$ of barium titanate at room temperature.

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[19] M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

[20] H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).

[21] C. E. Moore, *Atomic Energy Levels* (U. S. National Bureau of Standards, Washington, D. C. 1949, 1952), Vols. I, II.

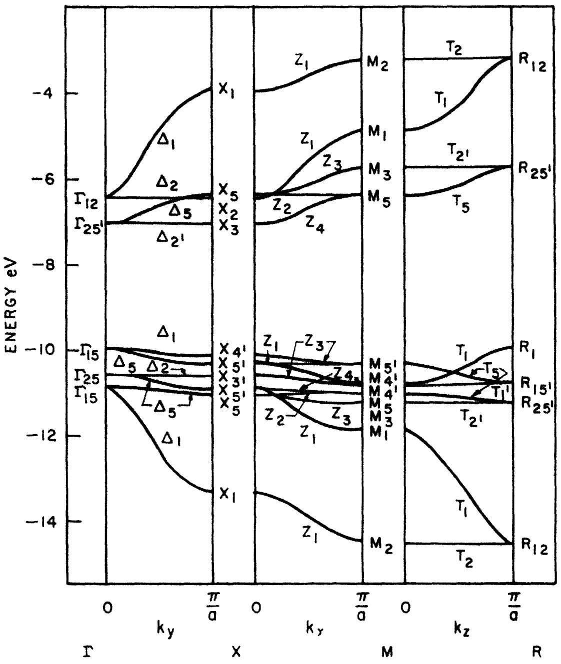

FIG. 9. Calculated energy bands of strontium titanate (see Ref. 1).

The three O^{-2} ions per unit cell produce three triply degenerate levels at $\mathbf{k}=0$ (Γ_{15}, Γ_{25}, and Γ_{15}) separated by energies of 0.6 ($\Gamma_{15}-\Gamma_{25}$) and 0.3 eV ($\Gamma_{25}-\Gamma_{15}$). This splitting is produced by the crystal field and the electrostatic interaction between O^{-2} ($2p$) ionic orbitals. This splitting is quite close to the A_1-A_2, the B_1-B_2, and the C_1-C_2 splittings observed in the reflection spectrum of $SrTiO_3$ (see Fig. 1). Hence it seems reasonable to try to interpret the observed optical structure in terms of transitions between O^{-2} ($2p$) levels and the various conduction bands. A series of levels with a width roughly the same as the O^{-2} ($2p$) splitting at $\mathbf{k}=0$ is seen at the X point ($X_{4'},X_{5'},X_{3'},X_{5'}$) and at the M point ($M_{5'},M_{4'},M_{4'},M_{5'},M_3$). As usual we shall assume that the structure in the reflection spectrum is due to transitions at high symmetry points or lines, at which $\nabla_{\mathbf{k}}(E_c-E_v)=0$ (E_c and E_v are the energies of the conduction and valence bands involved in the transitions). In Fig. 3 this condition does not seem fulfilled for any point inside the B.Z. other than Γ. The same thing applies to other high symmetry directions[1] not shown in Fig. 1. Parity arguments forbid all transitions between valence and conduction bands at the R point. Transitions at $\Gamma(\Gamma_{15}\rightarrow\Gamma_{25'})$ seem responsible for the fundamental absorption edge E_0. Transitions at X and M, stronger than transitions at Γ from the density-of-states point of view, appear as possible candidates for the strong reflection structure above E_0. Parity and other group-theoretical selection rules must be respected at X and M. If one takes the energy bands of Fig. 9 literally, one would probably attribute the A_1 peak to $X_{4'}$ or $X_{5'}\rightarrow X_5$ transitions (3.8 eV) and the A_2 peak to $X_{5'}\rightarrow X_5$ transitions (4.5 eV). The large separation between the X_5 level and the Sr^+ ($5s$) levels explains the small shift of the (A_1-A_2) peak when strontium is replaced by barium. A number of candidates are likely for the A_3 structure but a closer indentification is not possible. The B_1-B_2 doublet is affected considerably when replacing strontium by barium and hence must correspond to transitions to a fairly high conduction-band level. Likely candidates are $X_{5'}\rightarrow X_1$ (6.3 eV) and $X_{5'}\rightarrow X_1$ (7.0 eV). The large shift in the C_1-C_2 doublet position between $SrTiO_3$ and $BaTiO_3$ suggests transitions to Sr^{+1} ($5s$) levels [Ba^{+1} ($6s$) for $BaTiO_3$]. The $SrTiO_3$-$BaTiO_3$ shift of the C_1-C_2 peak is quite close to the difference in the ionization energies of Sr^{+1} and Ba^{+1} (1 eV).[21] These levels are going to be heavily mixed with Ti^{+2} ($4s$) levels. Similar transitions, and possibly also transitions from O^{-2} ($2s$) levels are responsible for the rest of the structure at higher energies.

Figure 1 shows that the maximum intensity for the optical transitions in $SrTiO_3$ occurs near 4.4 eV. We have fitted the refractive index measured at photon energies below the fundamental edge (see Fig. 2) with a dispersion formula corresponding to a single oscillator at 4.4 eV ($\lambda_0=0.28\ \mu$):

$$n^2=5.197+0.160/(\lambda^2-\lambda_0^2)\quad(\lambda \text{ in microns}). \qquad (1)$$

Equation (1) is shown as a full curve in Fig. 2 and fits the experimental points quite well. Hence the dispersion below the fundamental absorption edge E_0 is produced mainly by the A_1, A_2 virtual transitions and not by virtual transitions at E_0.

The existence of plasma oscillations slightly beyond the end of our photon energy range can be inferred from the plots of the energy-loss function $-\mathrm{Im}(1/\epsilon)$ from Figs. 7 and 8. Such oscillations are expected to occur at the plasma frequency of the valence electrons, which is 24 eV.

ACKNOWLEDGMENTS

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