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Optical Absorption in Single-Domain Ferroelectric Barium Titanate

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The optical-absorption coefficients for polarized light have been measured for single-domain crystals of *n*-type $BaTiO_3$. The measurements were made over a wavelength range from approximately 0.4 to 12 μ, and over a temperature range from 26 to 130°C. This temperature range includes both the cubic and the ferroelectric tetragonal states. The most significant feature of the measurements is a broad peak in the optical-absorption coefficient α centered near a photon energy of 0.6 eV; the absorption exhibits a threshold at a photon energy of approximately 0.2 eV. In addition, a large anisotropy, comparable to that observed in the transport behavior, is noted in the infrared values of α in the tetragonal state. It is shown that a consistent explanation of the optical-absorption properties is that most of the absorption in the visible and near infrared is the result of optical excitation of electrons in impurity states approximately 0.2 to 0.3 eV below the conduction-band minimum, superimposed on a free-carrier and lattice-absorption background. The deep impurity states are probably associated with oxygen vacancies.

I. INTRODUCTION

THE perovskite-type semiconductors $BaTiO_3$ and $SrTiO_3$ are of considerable interest not only because of their ferroelectric properties, but also because there is very strong electron-phonon coupling in these materials. This strong coupling should have unique effects on both dc transport and free-carrier absorption properties, and it should be possible from measurements of these properties to gain a great deal of information on the effects of strong electron-phonon interactions in solids and to test the applicability of present theoretical models such as that of the small polaron.

Although recent transport measurements of $BaTiO_3$[1] can be consistently interpreted without invoking a small-polaron picture, Gerthsen *et al.*[2] point out that free-carrier absorption is a more decisive measurement to determine the contribution of small polarons than dc transport measurements. However, there are some conflicting features in the interpretations of such absorption in the literature. Barker,[3] in his analysis of reduced $SrTiO_3$ reflectivity data between 3 and 30 μ, showed that there is a rather broad-absorption peak centered near 5 μ, in addition to the expected classical free-carrier absorption, which he discusses in terms of polaron effects. However, Baer[4] later measured optical absorption in reduced $SrTiO_3$ between 0.4 and 5 μ, and showed that the high-energy tail of this additional absorption has a power-law dependence similar to free-carrier absorption rather than an exponential dependence on the photon energy as required by small-polaron theory.[5] He also noted that the absorption is over an order of magnitude larger than expected from free-carrier absorption theories.[4] Small-polaron theory has also been invoked to explain the peculiar infrared reflectivity of $BaTiO_3$,[2] but the measurements and their interpretation are not definitive since the temperature dependence of the reflectivity was not measured and polarized light was not used.

One other interpretation of some of the infrared and visible optical properties of reduced perovskite semiconductors involves energy levels within the forbidden energy gap which may be associated with oxygen vacancies.[6–10] The two visible absorption peaks near 2.1 and 2.6 eV have been described and interpreted by Coufova and Arend and others[7,8] in terms of *F*-center absorption, and it has been suggested that the broad infrared absorption peak centered near 2 μ in $BaTiO_3$ may be due to optical excitation of electrons in relatively deep states.[8,9] Such a mechanism may also be responsible for the infrared peak near 5 μ in $SrTiO_3$.[3,4]

The purpose of the present work is to take advantage of the temperature-dependent tetragonality of $BaTiO_3$ in its ferroelectric state to determine the absorption mechanisms which are dominant in the visible and infrared. The optical-absorption coefficient of reduced, single-domain $BaTiO_3$ for polarized light is presented and interpreted over a wavelength range from approximately 0.4 to 12 μ, and over a temperature range from 26 to 130°C. Since this temperature range includes both the cubic and ferroelectric tetragonal states of $BaTiO_3$, (the cubic-tetragonal phase transition occurs at 126°C in the measured samples) a more detailed interpretation of the data can be made than if only the cubic state were included, and more definite conclusions can be drawn concerning the mechanism responsible

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[1] C. N. Berglund and W. S. Baer, Phys. Rev. **157**, 358 (1967).

[2] P. Gerthsen, P. Groth, K. H. Hordtl, D. Reese, and H. G. Reik, Solid State Commun. **3**, 165 (1965).

[3] A. S. Barker, Jr., in *Optical Properties and Electronic Structure of Metal and Alloys*, edited by F. Abeles (North-Holland Publishing Company, Amsterdam, 1966), 452.

[4] W. S. Baer, Phys. Rev. **144**, 734 (1966).

[5] H. G. Reik, Solid State Commun. **1**, 68 (1963).

[6] M. Di Domenico, Jr., and S. H. Wemple (to be published).

[7] P. Coufova and H. Arend, Czech. J. Phys. **B11**, 416 (1961); V. Dvorak, *ibid.* **B11**, 253 (1961).

[8] H. Arend, in *Proceedings of the International Meeting on Ferroelectricity* (Czechoslovak Academy of Science, Prague, 1966), Vol. II, 231.

[9] S. Ikegami, I. Ueda, and Y. Ise, J. Phys. Soc. Japan **16**, 572 (1961); S. Ikegami and I. Ueda, *ibid.* **19**, 159 (1964).

[10] See, for instance, D. C. Cronemeyer, Phys. Rev. **113**, 1222 (1959); H. W. Gandy, *ibid.* **113**, 795 (1959).

for the 2-μ absorption peak. In Sec. II the experimental methods and the measured data are described. In Sec. III the data are discussed in terms of classical free-carrier, small-polaron, and optical-excitation-from-deep-impurity theories, with particular emphasis on the broad infrared absorption peak centered near 2 μ.

II. EXPERIMENTAL

A. Measurement Techniques

The single-domain $BaTiO_3$ samples studied were cut from the same slices as those used in previous transport measurements.[1] A previously described hydrogen reduction treatment was made on the samples prior to cutting to introduce donors which give rise to electron-carrier concentrations of the order of 10^{18} cm^{-3}. The sample thicknesses varied from 0.004 to 0.05 cm.

Figure 1 shows the experimental arrangement for the measurements. A conventional sample-in–sample-out technique was used with a tungsten-lamp, Glan-Thompson polarizer, and a PbS detector from the visible to approximately 3μ in the infrared. A globar, Perkin-Elmer wire grid polarizer, and a thermocouple detector were used beyond 3μ. The free-carrier concentrations were determined from dc conductivity measurements and the mobility data of Berglund and Baer.[1]

The experimental data were reduced using the expression for transmission T taking account of multiple reflections in the sample:

$$T=(1-R)^2e^{-\alpha d}/(1-R^2e^{-2\alpha d}), \qquad (1)$$

where α is the absorption coefficient, d is the sample thickness, and R is the reflectivity. In all cases α was determined either by measurements of two thicknesses of the same sample or by using published reflectivity values for insulating $BaTiO_3$.[2] A computer reduction and plotting program was written so that very closely spaced data points could be taken, the data in Figs. 2–4 being taken every 20 Å in the visible increasing to $\approx$160 Å in the 8–12-μ range, with ever closer spacings used at the band edge.

B. Optical-Absorption Data

The optical-absorption coefficient of two reduced, single-domain samples of $BaTiO_3$ were measured over a wavelength range from 0.4 to approximately 12 μ, and at temperatures of 26, 50, 70, 90, 110, and 130°C. Since the cubic-tetragonal phase transition occurs in the measured samples at 126°C, only the data at 130°C is on cubic $BaTiO_3$.

Figure 2 shows the absorption coefficient for one of the samples at 26°C for light polarized parallel to and perpendicular to the tetragonal c axis. Also shown is the (isotropic) absorption coefficient of cubic $BaTiO_3$ at 130°C. Data from the other sample showed essentially identical features. The more detailed temperature variations of the absorption are shown in Figs. 3 and 4.

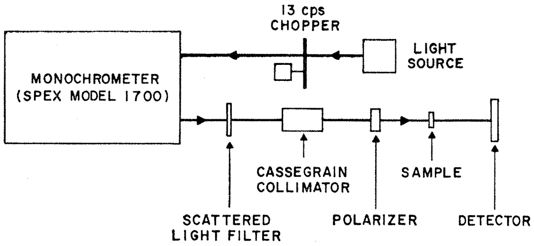

FIG. 1. Experimental arrangement for optical-absorption coefficient measurements.

At photon energies below approximately 0.18 eV, several sharp peaks appear in the optical absorption, the amplitudes of which exhibit little or no anisotropy. These peaks are probably due to multiple-phonon absorption processes, some of which have been previously described by Hilsum.[11] The large increase in absorption with increasing wavelength near a photon energy of 0.1 eV is also due to lattice absorption.

At photon energies between 0.18 and 2 eV, there is a broad, structureless absorption peak. The center of the peak is near 0.6 eV, although it varies depending on the polarization of the light and the temperature from 0.45 to over 0.65 eV.

The relative amplitude of the two absorption peaks near 2.1 and 2.6 eV was found to vary for both polarizations of light depending on the thickness of the sample. For the thicker samples, it was found that $\alpha_\perp$ was larger than $\alpha_{||}$ over the entire wavelength range measured. However, when the samples were lapped and polished to smaller thicknesses, $\alpha_\perp$ was smaller than $\alpha_{||}$ in the vicinity of the 2.6-eV peak. These observations are in reasonable agreement with those of Coufova and Arend,[7] although the origins of the two peaks and their peculiar behavior with sample thickness have not been explained in detail.

The band-edge absorption at photon energies near 3 eV appears exponential over a considerable range of α, exhibiting Urbach-rule behavior for both light polarizations.[12] However, the absorption occurs at somewhat higher photon energies, and increases more rapidly with photon energy than the experimental data of Casella and Keller.[13] (A detailed presentation of the band-edge absorption in $BaTiO_3$ is given in a recent paper by Di Domenico and Wemple.[6]) The anisotropy in the band-edge absorption is very large and in the same direction as that observed by Casella and Keller, and both absorption edges tend to lower photon energies with increasing temperature.

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[11] C. Hilsum, J. Opt. Soc. Am. **45**, 771 (1955).

[12] F. Urbach, Phys. Rev. **92**, 1324 (1953).

[13] R. C. Casella and S. P. Keller, Phys. Rev. **116**, 1469 (1959).

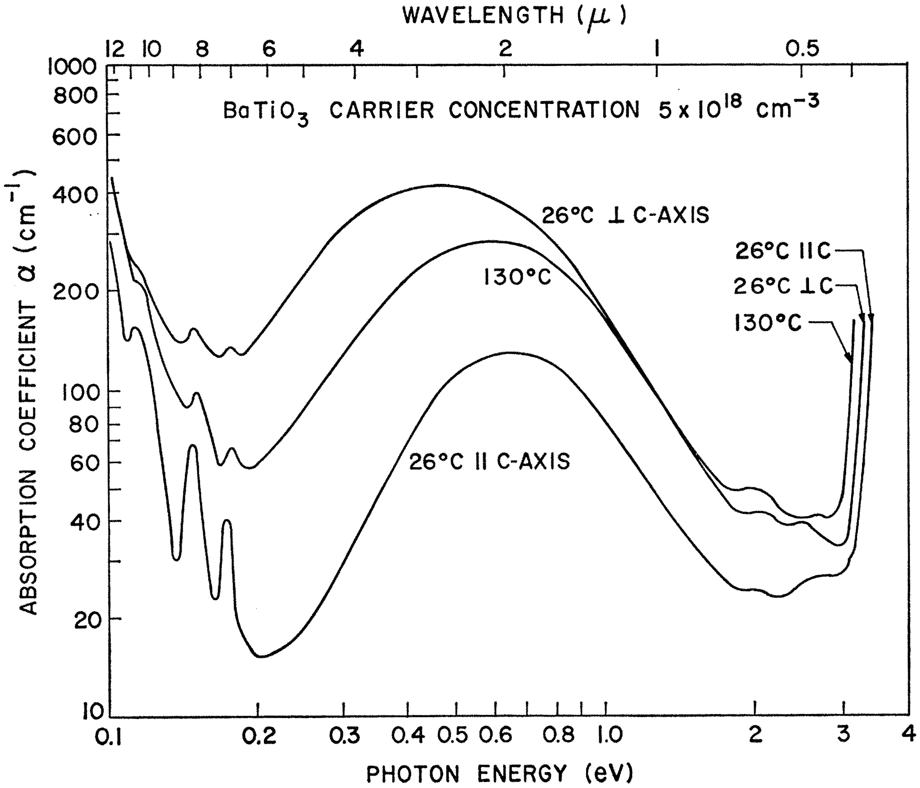

FIG. 2. Absorption coefficients for cubic and tetragonal $BaTiO_3$.

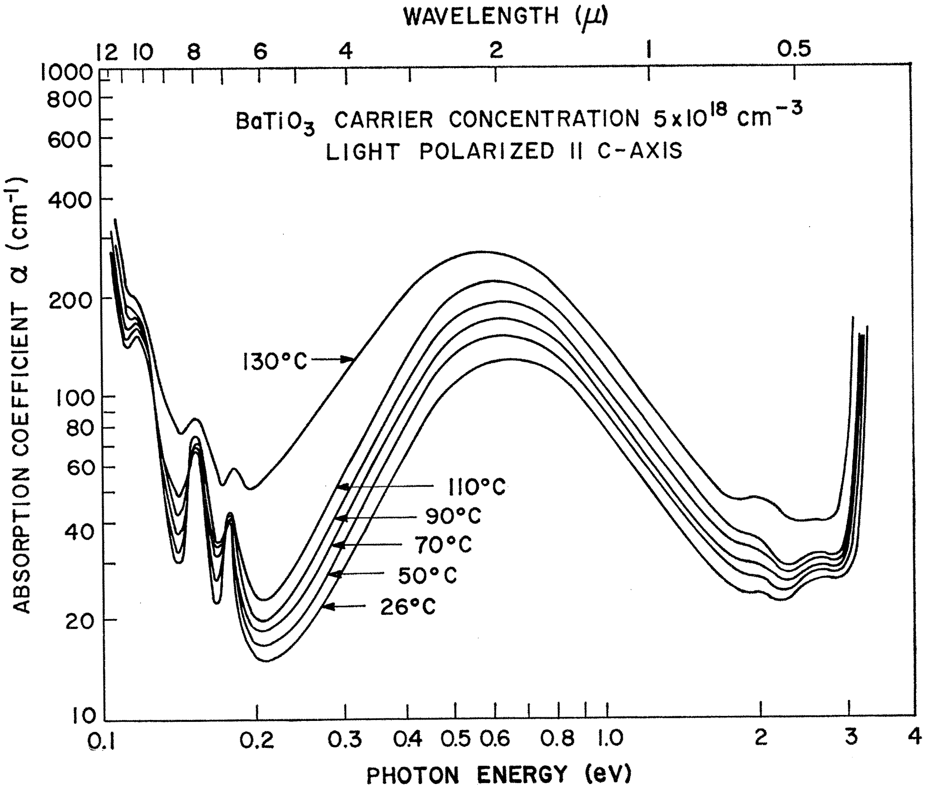

FIG. 3. $BaTiO_3$ absorption coefficients for light polarized parallel to the tetragonal *c* axis as a function of temperature.

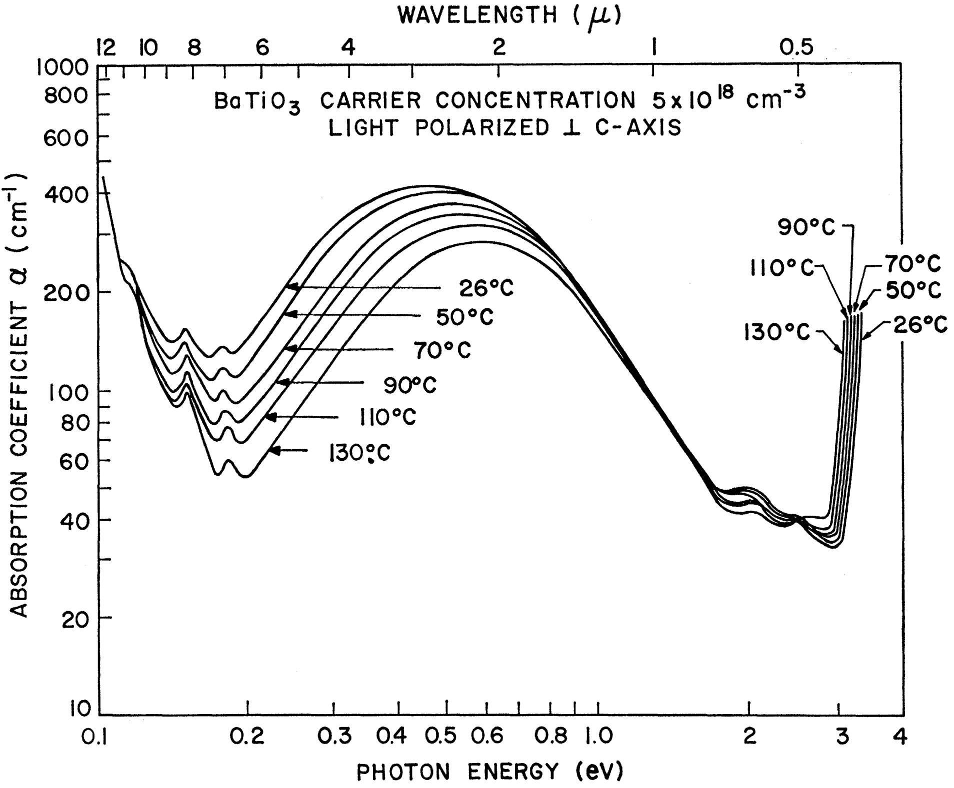

FIG. 4. $BaTiO_3$ absorption coefficients for light polarized perpendicular to the tetragonal c axis as a function of temperature.

III. DISCUSSION OF RESULTS

A. Free-Carrier Absorption

1. Classical and Large Polaron Effects

The wavelength dependence of free-carrier absorption in semiconductors has been extensively studied, since it may be useful in determining the free-carrier scattering mechanisms dominant at a given temperature. At frequencies considerably larger than the reciprocal of the carrier scattering time constant, the classical Drude theory predicts a λ^2 dependence of the absorption coefficient, while treatments of electron scattering from acoustical phonons,[14] longitudinal optical phonons,[15,16] and ionized impurities[16] give free-carrier absorptions varying as $\lambda^{1.5-2}$, $\lambda^{2.5}$, and λ^3, respectively. Since the optical absorption in $BaTiO_3$ in the visible exhibits similar power-law behavior, and since the absorption appears to scale with the carrier concentration, it is tempting to try to explain the present results in terms of free-carrier absorption.

The experimental data for $BaTiO_3$ shown in Figs. 2–4 at photon energies between 0.9 and 1.8 eV can be fit quite well by an expression of the form

$$\alpha \propto \lambda^{\beta}, \qquad (2)$$

where β is 2.5 ± 0.2, the variation representing the change is β over the measured temperature range. This result is nearly the same as that obtained by Baer on $SrTiO_3$,[4] and is in reasonable agreement with the theory of Gurevich, Lang, and Firsov for scattering from longitudinal optical phonons.[15]

$$\alpha(\omega)=\frac{8\pi N_c e^2 a}{3ncm^*\omega_l}\left(\frac{\omega_l}{\omega}\right)^{2.5}\left(1-\frac{\omega_l}{\omega}\right)^{1/2} \qquad \omega_l<\omega, \qquad (3)$$

where a is the electron-longitudinal optical-phonon coupling constant, n is the refractive index at light frequency ω, c is the velocity of light, m^* is the optical or bare-band effective mass, N_c is the carrier density, and ω_l is the frequency of the longitudinal optical phonon. However, the experimentally determined wavelength dependence of the absorption in the photon-energy range from 0.1 to 0.9 eV is not in agreement with that predicted by Eq. (3) using the known value of ω_l. In addition, an estimate of the magnitude of the absorption at 130°C using Eq. (3) is more than a factor of 40 smaller than the measured absorption over the photon-energy range from 0.9 to 1.6 eV. For this estimate, the values $a=2.06\,(m^*/m)^{1/2}$,[17] $m^*=1.5m_0$,[1] $n=2.4$, and $\hbar\omega=0.087$ eV [16] were used. The use of the measured-conductivity effective mass, $m^*\approx 1.5m_0$, for the optical effective mass should not introduce enough error to significantly alter this result.

For the reasons described above, it is unlikely that

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[14] H. J. G. Meyer, Phys. Rev. **112**, 298 (1958); R. Rosenberg and M. Lax, *ibid.* **112**, 843 (1958).

[15] V. L. Gurevich, I. G. Lang, and Yu. A. Firsov, Fiz. Tverd. Tela **4**, 1252 (1962) [English transl.: Soviet Phys.—Solid State **4**, 918 (1962)].

[16] S. Visvanathan, Phys. Rev. **120**, 376 (1960); **120**, 379 (1960).

[17] A. S. Barker, Jr., Phys. Rev. **145**, 391 (1966).

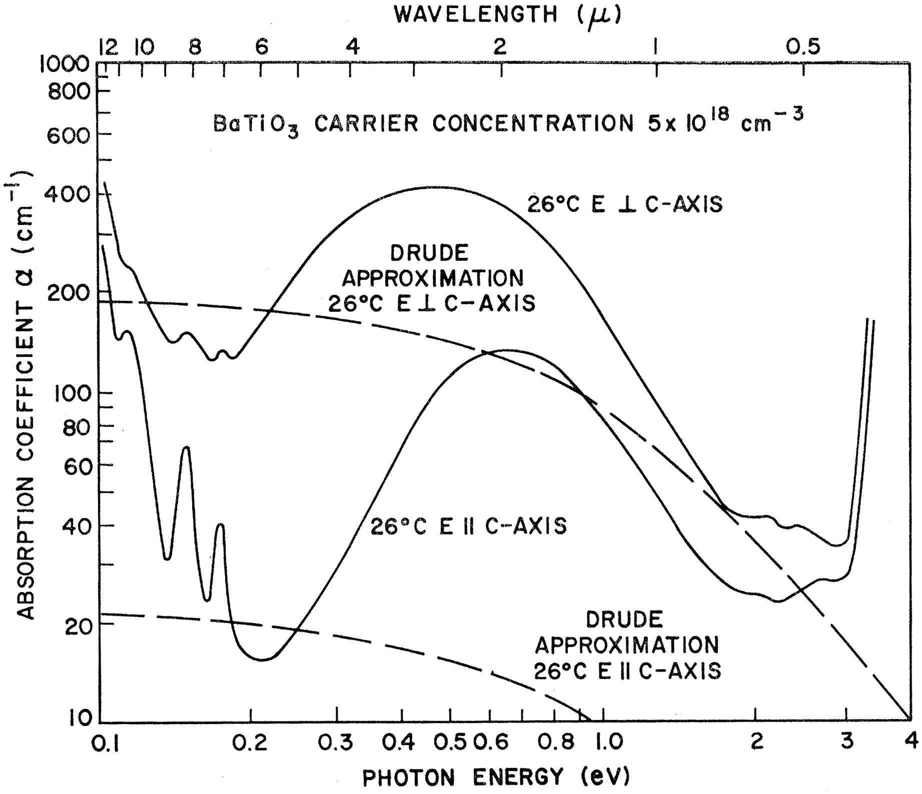

FIG. 5. Illustration of the Drude free-carrier contribution to the optical absorption in BaTiO$_3$ at 26°C.

the large infrared absorption peak can be explained by free-carrier absorption. However, it is of interest to obtain a crude estimate of the absorption due to free carriers, since they must make some contribution to the observed results. For lack of more detailed knowledge the simple Drude theory will be used here for this purpose, since in principle all of the necessary parameters can be experimentally determined.

Using the Drude model,

$$\alpha(\omega) = (\sigma_0/nc\epsilon_0)\omega_0^2/(\omega_0^2+\omega^2), \qquad (4)$$

where σ_0 is the dc conductivity, ϵ_0 is the permittivity of free space, and ω_0 is the reciprocal of the free-carrier scattering time constant. The dc conductivity was determined from a conductivity measurement at 130°C and the mobility data of Berglund and Baer,[1] and the scattering time constant was estimated to be 6×10^{-16} sec using their measured mobility and effective masses. The index of refraction was calculated from reflectivity measurements on insulating BaTiO$_3$,[2] since in the photon energy range of interest the additional absorption reported here does not make a significant contribution to n.

Figure 5 provides a comparison between the experimentally observed absorption coefficient and the free-carrier contribution to the absorption given by Eq. (4) at 26°C. Similar results are obtained at other temperatures. Although it is apparent that the Drude contribution has been slightly overestimated since it is greater than the measured total absorption at photon energies near 0.2 eV, it seems reasonable to conclude that a major contribution to the infrared absorption coefficient of reduced BaTiO$_3$ is by free-carrier absorption. This fact is further verified by Fig. 6, which compares the temperature dependencies of the experimental absorption coefficients and their anisotropy at the infrared minimum near 0.2 eV with the normalized dc conductivities measured on the same samples. The good

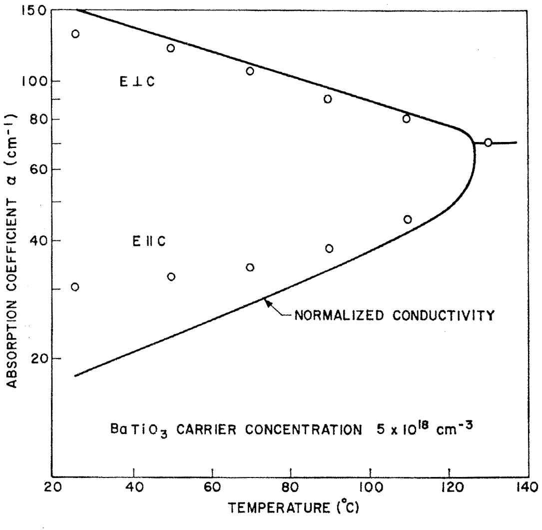

FIG. 6. Absorption coefficients at the infrared minimum near 0.2 eV plotted versus temperature. Also shown is the conductivity versus temperature on the same sample arbitrarily normalized for best fit.

agreement suggests that nearly all of the optical absorption at photon energies near 0.2 eV, except in $\alpha_{||}$ at the lower temperatures where the lattice absorption is significant, is due to free carriers. It is also clear that an additional absorption mechanism similar to that found in $SrTiO_3$ by Barker[3] exists in $BaTiO_3$. This absorption exhibits a threshold near 0.2 eV, a broad peak centered near 0.6 eV, and an absorption coefficient which falls off as $\lambda^{2.5\pm0.2}$ in the visible region of the spectrum.

2. *Small-Polaron Effects*

It has been proposed by Gerthsen *et al.* that small-polaron theory may be applicable to *n*-type $BaTiO_3$, since such a theory is in reasonable agreement with measured reflectivity at one temperature.[2] Barker has also discussed the applicability of small-polaron theory to his data on $SrTiO_3$.[3] The expression for small-polaron absorption derived by Reik, within the appropriate range of validity, is[5]

$$\alpha(\omega)=\frac{\sigma_0}{nc\epsilon_0}\,\frac{\sinh(\hbar\omega/2kT)}{\hbar\omega/2kT}\exp(-\omega^2\tau^2), \qquad (5)$$

where σ_0 is the real part of the low-frequency conductivity, T is the temperature, k is Boltzmann's constant, and τ is a scattering time which depends on the phonon frequencies which couple with the electrons. Barker found for $SrTiO_3$ that Eq. (5) provides a reasonable approximation to his measurements at a single temperature provided σ_0 and τ are treated as parameters to be adjusted for best fit.[3] However, he points out that the temperature dependence of the absorption is not in agreement with that expected from small-polaron theory, and Baer shows that the high-frequency falloff of the absorption is power-law rather than exponential.[4] The present results for $BaTiO_3$ allow conclusions to be drawn about the applicability of small-polaron theory with considerably less ambiguity than in the case of $SrTiO_3$. First, the peak in the $BaTiO_3$ absorption occurs at a photon energy of approximately 0.6 eV compared to a photon energy of approximately 0.2 eV in $SrTiO_3$. Hence, Eq. (5) does not provide reasonable agreement with the experimental results even when τ and σ_0 are treated as adjustable parameters. Second, the anisotropy in the tetragonal state provides two different sets of absorption data for the two polarizations of light. When $\omega\tau\ll1$, Eq. (5) indicates that the two sets of data should differ only by a multiplicative constant. Such behavior is not observed. All of the results suggest that present small-polaron theory is not applicable to the experimental observations.

B. Optical Absorption from Deep Impurity States

1. *Oxygen Vacancies*

One other possible explanation of much of the optical absorption in reduced $BaTiO_3$ is optical excitation of electrons from deep impurity states.[6–10] Such an explanation is intuitively reasonable since the spectral variation of α in $BaTiO_3$ shown in Figs. 2–4 is very similar to that of the photo-ionization cross sections for impurity states in Si,[18] Ge,[19] and GaAs.[20] It will be shown later that the observed broad optical absorption peak centered near a photon energy of 0.6 eV can be consistently explained if an impurity level is located 0.2 to 0.3 eV below the conduction-band edge. Such a level may also be used to account for the two optical-absorption peaks at photon energies of 2.1 and 2.6 eV. Although the experimental data does not provide sufficient information to precisely identify the deep level, it is of interest to examine the possibility that it is associated with the oxygen vacancy since such an explanation has been previously proposed.[7–9]

Experimentally, it has been found that the observed optical absorption can be eliminated by heating the samples in an oxidizing atmosphere and reintroduced by subsequent hydrogen reduction, and that the magnitude of the measured absorption coefficient appears to scale with the free-carrier concentration similar to the behavior in $SrTiO_3$.[4] Since Berglund and Baer show that the free carriers in reduced $BaTiO_3$ are donated by a relatively shallow, fully ionized level,[1] it can be concluded that the deep level responsible for much of the optical absorption and the shallow donor level responsible for the free carriers are associated with the same impurity. For this reason, a simple oxygen vacancy with a first ionization energy less than 0.025 eV [1] and a second ionization energy of approximately 0.2 to 0.3 eV is a possible model for the impurity. It should be emphasized, however, that the reduction process in $BaTiO_3$ is not well understood and that alternate and equally consistent explanations for both the deep and shallow levels may exist.

2. *Absorption Coefficient*

The optical-absorption peaks near 2.1 and 2.6 eV in Figs. 2–4, including the peculiar variation in the relative strengths of the two peaks with sample thickness, have been described by others,[7,8] and will not be discussed. However, the broad infrared peak near 0.6 eV has not previously been compared to theoretically expected absorption, and is the subject of major interest here.

There are a number of factors which may prevent an accurate analysis of optical absorption from a deep level to the conduction-band continuum. The band structure of the perovskites and the wave functions of electrons in deep states are not well known, and it may not be possible to apply simple first-order perturbation theory to the problem. The impurity responsible for

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[18] E. Burstein *et al.*, in *Photoconductivity Conference*, edited by R. G. Breckinridge, B. R. Russell, and E. E. Hahn (John Wiley & Sons, Inc., New York, 1956); p. 353; E. Burstein *et al.*, J. Phys. Chem. Solids **1**, 65 (1956); R. Newman, Phys. Rev. **99**, 465 (1955).

[19] R. A. Chapman and W. G. Hutchinson, Phys. Rev. (to be published).

[20] R. A. Chapman and W. G. Hutchinson, Phys. Rev. Letters **18**, 443 (1967).

the absorption may distort the lattice and the band structure in its vicinity in different ways depending on its charge state. Since the mean time between scattering events for electrons in the conduction band determined from mobility measurements is shorter than or comparable to the reciprocal of the light frequencies of interest,[1] electron-phonon interactions may be so large that phonon-assisted transitions must not be ignored. In addition, it has been pointed out to the authors that when $BaTiO_3$ is in its ferroelectric state oxygen vacancies can have two different kinds of nearest-neighbor configurations.[21] In one the vacancy is located between two titanium ions lying along the c axis, and in the other the vacancy is located between two titanium ions lying perpendicular to the c axis. Hence, for every energy level associated with oxygen vacancies in cubic $BaTiO_3$, there may be two in tetragonal $BaTiO_3$.

Many of the major features of absorption from a deep level to the conduction-band continuum can be estimated from simple sum-rule considerations and symmetry arguments. However, it may be more useful to calculate the absorption coefficient using first-order perturbation theory and making certain simplifying assumptions. Such an analysis, while not expected to be accurate in detail for the reasons described above, will provide an estimate of the magnitude of the absorption and of the anisotropy expected in tetragonal $BaTiO_3$ as well as verifying the conclusions that would be obtained from simpler considerations.

The Koster and Slater model for the wave function of the impurity state will be used,[22] with the energy level of the impurity treated as an adjustable parameter. In this model, the wave function of the impurity state is expanded in a series of the unperturbed Bloch functions $u_{n,\mathbf{k}}(\mathbf{r})$ of the crystal.

$$\Psi(r)=\sum(n,\mathbf{k}')\,f_n(\mathbf{k}')\,u_{n,\mathbf{k}'}(\mathbf{r}),\tag{6}$$

where n is a band index and $f_n(\mathbf{k}')$ is a weighting coefficient. From perturbation theory $f_n(\mathbf{k}')$ is given by

$$f_n(\mathbf{k}')+\sum(m,\mathbf{R}_i,\mathbf{R}_j,\mathbf{k})\,\frac{\exp(-ik'\cdot R_i)\,V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)}{[E_n(\mathbf{k}')-E]N}\times\exp(i\mathbf{k}\cdot\mathbf{R}_j)\,f_m(\mathbf{k})=0,\tag{7}$$

where N is the total number of unit cells in the crystal, E is the energy at the impurity level, $E_n(\mathbf{k}')$ is the energy eigenvalue corresponding to the Bloch wave $u_{n,\mathbf{k}'}(\mathbf{r})$, and $\mathbf{R}_i$ and $\mathbf{R}_j$ are primitive translation vectors of the crystal. The potential function $V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)$ is defined by the equation

$$V_{m,n}(\mathbf{k},\mathbf{k}')=N^{-1}\sum(\mathbf{R}_i,\mathbf{R}_j)\,V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)\times\exp(-i\mathbf{k}'\cdot\mathbf{R}_i)\exp(i\mathbf{k}\cdot\mathbf{R}_j),\tag{8}$$

where

$$V_{m,n}(\mathbf{k},\mathbf{k}')=\int_V u^*_{m,\mathbf{k}}(\mathbf{r})\,H_I u_{n,\mathbf{k}'}(\mathbf{r})\,d^3r\tag{9}$$

and H_I is the perturbation Hamiltonian for the impurity site. The integration is performed over the volume V of the crystal.

An assumption will be made here concerning the potential function $V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)$. Since consideration will be limited to relatively deep impurity states (energy$\approx$0.2 to 0.3 eV), and since the perovskite semiconductors have an extremely large dielectric constant, it seems reasonable to assume that the potential function $V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)$ is only large within a few lattice constants of the impurity. In fact, it will be assumed that

$$V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)\approx V_{m,n}(0,\mathbf{R}_j).\tag{10}$$

In this case, Eq. (7) becomes

$$f_n(\mathbf{k}')=A_n/[E_n(\mathbf{k}')-E],\tag{11}$$

where A_n is a constant for each band given by

$$A_n=-N^{-1}\sum(m,\mathbf{R}_j,\mathbf{k})\,V_{m,n}(0,\mathbf{R}_j)\exp(i\mathbf{k}\cdot\mathbf{R}_j)\,f_m(\mathbf{k}).\tag{12}$$

Such an assumption has been used by Koster and Slater with the additional assumption of a single, parabolic band of effective mass m^* to show that the effective "radius" of an electron in such a state is given by[22]

$$r=\hbar^2/(2m^*E_D)^{1/2},\tag{13}$$

where E_D is the binding energy of the state. Using values appropriate for $BaTiO_3$, $m^*=1.5m_0$ and $E_D\approx$ 0.3 eV, the effective radius is 2.5 Å. Hence the approximation represented by Eq. (10) is probably reasonable for $BaTiO_3$.

The optical-absorption coefficient due to a density N_D of electrons in the deep states is given by

$$\alpha(\omega)=\frac{\pi e^2N_D}{\omega m_0^2nc\epsilon_0}\sum_{\text{B.Z.}}(k)\,|P|^2\delta(E_c-E-\hbar\omega),\tag{14}$$

where ω is the angular frequency, E_c is the energy of the final state in the conduction band, and the sum is over all states in the Brillouin zone. The momentum matrix element P joining the initial and final states is

$$P=\int_V u^*_{c,\mathbf{k}}(\mathbf{r})\,(-i\hbar\mathbf{a}_0\cdot\nabla)\psi(\mathbf{r})\,d^3r,\tag{15}$$

where $\mathbf{a}_0$ is a unit polarization vector, the subscript c refers to the final state in the conduction band, and the integration is over the volume of the crystal. Using

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[21] J. Brews (private communication).

[22] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

Eqs. (6) and (11),

$$P=\sum(n,\mathbf{k}')\,\frac{A_n}{E_n(\mathbf{k}')-E}\int_V u^*_{c,\mathbf{k}}(\mathbf{r})\times(-i\hbar\mathbf{a}_0\cdot\nabla)u_{n,\mathbf{k}'}(\mathbf{r})d^3r. \quad (16)$$

Making the usual assumption that phonon-assisted transitions are negligible at photon energies where direction transitions not requiring phonon assistance are allowed, the integral in Eq. (16) is nonzero only when $\mathbf{k}=\mathbf{k}'$. Hence

$$P=\sum(n)\,\frac{A_nP_{cn}(\mathbf{k})}{E_n(\mathbf{k})-E}, \quad (17)$$

where $P_{cn}(\mathbf{k})$ is the conventional momentum matrix element between Bloch states in bands n and c. One of the components in the sum of Eq. (17), $P_{cc}(\mathbf{k})/(E_c(\mathbf{k})-E)$, is easily evaluated, since $P_{cc}(\mathbf{k})$ is the definition of the component of the momentum of the state in the polarization direction

$$P_{cc}(k)=m_0\mathbf{a}_0\cdot\langle\mathbf{v}_g\rangle, \quad (18)$$

where $\langle\mathbf{v}_g\rangle$ is the group velocity of the Bloch state, and $E_c(k)-E$ is confined by conservation of energy to the photon energy. Using Eq. (18), Eq. (17) becomes

$$P=\frac{A_cm_0\mathbf{a}_0\cdot\langle\mathbf{v}_g\rangle}{\hbar\omega}+\sum(n\neq c)\,\frac{A_nP_{cn}(\mathbf{k})}{E_n(\mathbf{k})-E}. \quad (19)$$

From Eq. (19) it is evident that the solution of the problem of optical absorption from a deep impurity, even with simplifying assumptions, requires a knowledge of all the energy bands in the unperturbed crystal. However, in many cases it might be expected that one of the terms in Eq. (19) will dominate in certain photon energy ranges. For $\mathrm{BaTiO_3}$ it is found that reasonable agreement with the 0.6-eV absorption peak results if only the first term in Eq. (19) is retained. This is not unexpected, since the impurity level is much closer to the lowest conduction band in $\mathrm{BaTiO_3}$ than to any other band. It will be assumed here, as a first approximation, that only the first term of Eq. (19) is important. The effects of other terms will be discussed later.

Under this assumption, Eq. (14) becomes

$$\alpha(\omega)=\frac{e^2\pi N_DA_c^2\hbar}{nc\epsilon_0(\hbar\omega)^3}\sum_{\mathrm{B.Z.}}(k)\,|\,\mathbf{a}_0\cdot\langle\mathbf{v}_g\rangle\,|^2\delta(E_c-E-\hbar\omega). \quad (20)$$

From Eq. (20) alone, many of the general features of optical absorption from a deep state become apparent. The absorption will exhibit a threshold at a photon energy equal to the binding energy. It will increase to a peak at a photon energy somewhat greater than that corresponding to the threshold energy. Then it will decrease at higher photon energies as the reciprocal of the photon energy to some power probably near 3. The actual rate of decrease at higher photon energies and the photon energy at the absorption peak will depend strongly on the energy bands in the crystal, and on the relative contribution of other bands to the absorption. Density-of-states peaks in the conduction band due to symmetry points will tend to be suppressed, since the group velocity $\langle\mathbf{v}_g\rangle$ tends to zero at symmetry points in the zone. Hence, very little strong structure is expected in $\alpha(\omega)$.

Estimates of the magnitude of the absorption coefficient and the polarization dependence of the absorption near threshold in the tetragonal state can be obtained by evaluating Eq. (20), using a parabolic band approximation for the conduction band, since for these two features of the results such an approximation should be reasonable. Under this assumption and the additional assumption that the conduction band has s valleys characterized by the same effective masses, the constant A_c can be determined by normalizing Eq. (6) to unity over the volume of the crystal, and the integral in Eq. (20) can be evaluated, giving

$$\alpha(\omega)=\frac{8\hbar e^2N_D}{3nc\epsilon_0(\hbar\omega)^3}\sum_i\frac{(\hbar\omega-E_B^{(i)})^{3/2}}{m_{\|}^{(i)}}\left[\sum_j^s(E_B^{(j)})^{-1/2}\right]^{-1},\qquad \hbar\omega\geq E_B^{(i)} \quad (21)$$

where N_D is the density of filled impurity states, $E_B^{(i)}$ is the minimum energy separation between the ith valley and the impurity level, and $m_{\|}^{(i)}$ is the effective mass in the ith valley parallel to the polarization direction of the light. When the conduction band under study has only one minimum, or when the valleys are all located at the same energy (such as in cubic $\mathrm{BaTiO_3}$), Eq. (21) becomes

$$\alpha(\omega)=\frac{8\hbar e^2N_DE_B^{1/2}(\hbar\omega-E_B)^{3/2}}{3nc\epsilon_0m_c(\hbar\omega)^3}\qquad \hbar\omega\geq E_B, \quad (22)$$

where m_c corresponds to the conductivity effective mass in the direction of polarization of the light. This expression is similar to that derived by Lucovsky in a semiclassical calculation assuming a delta-function potential for the impurity,[23] and results in the same prediction that the optical-absorption peak will occur at a photon energy of 2 E_B. Note that Eqs. (21) and (22) will be strictly accurate only over an energy range $(\hbar\omega-E_B)$ for which the parabolic band approximation is reasonable. In $\mathrm{BaTiO_3}$, the energy separation between $\Gamma_{25'}$ and X_3 of the lowest conduction band is only 0.1 to 0.15 eV,[1,24,25] so that an effective-mass

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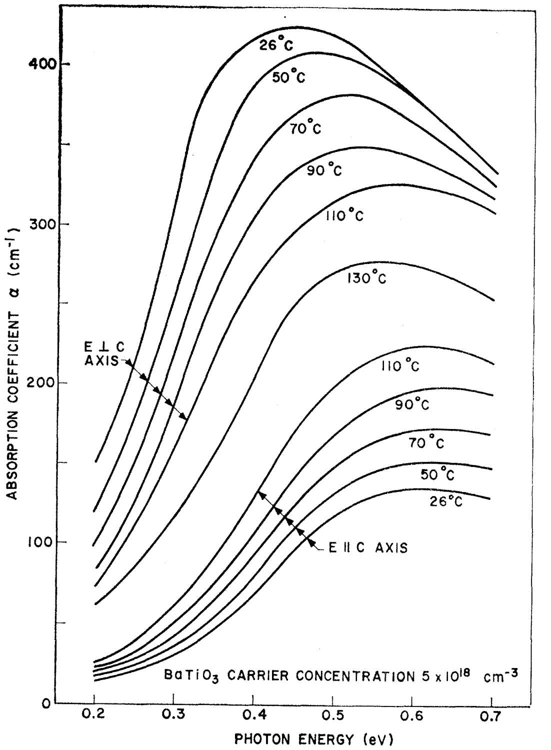

FIG. 7. Optical absorption near the threshold for deep impurity absorption on a linear plot to illustrate the polarization dependence.

characterization of the band along the ⟨100⟩ directions is probably not accurate over a photon-energy range of more than 0.1 eV. However, the energy separation between X_3 and M_5 of the lowest conduction band is slightly under 1 eV,[24,25] so that a characterization of the band by a transverse-effective mass at X_3 will be a good approximation for photon energies at least up to the optical absorption peak near 0.6 eV. Since Eqs. (21) and (22) show that the major absorption is to those regions of the conduction band characterized by the smallest effective mass in the light polarization direction, Eq. (22) may provide a reasonable estimate of the optical absorption up to photon energies in excess of 0.6 eV.

The polarization dependence of the deep impurity absorption near threshold in tetragonal $BaTiO_3$ can be seen in Fig. 7, where the absorption is plotted on a linear scale. Since the correction for free-carrier absorption is not accurately known, the best indication of the polarization dependence of the deep impurity absorption is its rate of increase with photon energy near the threshold ($\backsim$0.2 eV).

Berglund and Baer show that there are two possible conduction-band configurations which can explain their $BaTiO_3$ transport data.[1] In one, the conduction band is many-valleyed, with prolate ellipsoidal minima located at or near the Brillouin-zone edge along the ⟨100⟩ directions, and in the other, the conduction-band minimum is at $\Gamma_{25'}$, the center of the zone. Considering the many-valley model first, Berglund and Baer show that in the tetragonal state the two minima located along the c axis are at a somewhat lower energy than the four minima located along the a axes. At photon energies where only absorption to the two lower c-axis minima is occurring, Eq. (21) indicates that the absorption coefficient $\alpha_\perp$ should exhibit approximately five to ten times as rapid an increase near threshold as $\alpha_{||}$, since the longitudinal-to-transverse mass ratio in each minimum extracted from the transport data is between 5:1 and 10:1. As the photon energy is increased so that transitions to the four a-axis minima begin to contribute, the two absorption coefficients should tend to be more equal. Hence, the absorption peak in $\alpha_\perp$ should be slightly larger, and should occur at a slightly lower photon energy than that in $\alpha_{||}$. Ideally, two thresholds should be experimentally observed separated in energy by the energy difference between the c-axis minima and the a-axis minima. However, the narrowness of the conduction band along the ⟨100⟩ directions and any smoothing of the thresholds due to effects such as phonon-assisted transitions will tend to make their identification difficult, and results similar to those shown in Fig. 7 will be observed.

If the conduction-band minimum is at $k=0$, the band distortions indicated by the transport data[1] are also consistent with those expected from the impurity absorption hear threshold using Eq. (21). In this case, the model is more difficult to analyze in detail, but it can be concluded that both conduction-band configurations can be used to explain the experimental results and that there is no unambiguous experimental evidence supporting one model in preference to the other.

The magnitude of the absorption coefficient can be estimated from Eq. (22) assuming the concentration of deep impurities is equal to the free-carrier concentration. With this assumption, the absorption coefficient is in reasonable agreement with the experimental data. For example, using $E_B=0.3$ eV, $m_{||}=1.5\ m_0$, $n=2.0$, and $N_D=6\times10^{18}$ cm^{-3} in Eq. (22), the absorption coefficient at the 130°C absorption peak (0.6 eV) is estimated to be 160 cm^{-1} above the free-carrier background. This compares to an experimental value from Fig. 2 of approximately 220 cm^{-1}. Note, however, that because of the breakdown of the parabolic-band approximation in Eq. (22), it can only be concluded that the experimental absorption does not disagree in magnitude with that expected from deep-impurity absorption.

The experimental data and the above discussion indicate that a consistent explanation of the infrared absorption peak in $BaTiO_3$ is optical excitation from a deep level to the conduction band. In view of the unknown contribution of phonon-assisted transitions from such a level, which will influence the absorption particularly near threshold, the binding energy of the donor cannot be accurately determined. However, Lucovsky's result[23] that the binding energy is approximately one-half the photon energy at the absorption peak, and the clear threshold effects shown in Fig. 7, can be used to estimate that the binding energy is approximately 0.2 to 0.3 eV. The two absorption peaks in the visible at photon energies near 2.1 and 2.6 eV are probably due to transitions from this deep level to other excited states of the oxygen vacancy, or to absorption to other conduction bands which have been neglected in the derivation of Eqs. (20) and (21).

IV. CONCLUSIONS

The electron-transport properties of $BaTiO_3$ indicate that the scattering time for electrons in the conduction band is only about 10^{-15} sec, which corresponds to a mean-free path between scattering events of less than a lattice constant. For this reason, interpretations of both transport and optical-absorption data in terms of a conventional band picture must be treated with caution. However, the dc mobility of $BaTiO_3$ is considerably higher than might be expected from small-polaron theories. Further, both the transport data and the infrared absorption properties presented here can be consistently explained assuming a one-electron band model. Hence, it is unlikely that small-polaron effects make a significant contribution to the optical absorption properties of reduced $BaTiO_3$, particularly since the experimental data show several features which are inconsistent with present small-polaron theories. These conclusions are of particular significance since they provide experimental evidence which may aid in determining the range of validity, and the limitation, of the conventional one-electron band model.

The infrared and visible absorption properties of reduced $BaTiO_3$ can be explained as optical excitation of electrons in deep levels within the forbidden gap to the conduction-band continuum superimposed on a lattice and free-carrier absorption background. At photon energies below approximately 0.18 eV, the absorption is due primarily to lattice modes and free carriers. At photon energies near 0.18 eV, the absorption is due almost entirely to free-carrier absorption, and the anisotropy of the absorption coefficient in the tetragonal state, $\alpha_\perp$ much larger than $\alpha_{||}$, is in close agreement with the anisotropy in the dc conductivity (a factor of over 8:1 at 26°C). At photon energies between 0.2 and 2 eV there is a broad absorption peak centered near 0.6 eV which results from optical excitation of electrons in states 0.2 to 0.3 eV below the conduction-band minimum to the conduction-band continuum. This absorption is superimposed on the weaker free-carrier absorption, and it exhibits some anisotropy in the tetragonal state, the major features of which are expected from the known band-structure anisotropies in tetragonal $BaTiO_3$. At photon energies above approximately 0.3 eV, the free-carrier absorption is sufficiently weak compared to the deep impurity excitation that it is not possible to determine the free-carrier scattering mechanisms. In the visible region of the spectrum there are two absorption peaks at 2.1 and 2.6 eV which are probably due to excitation of electrons in the same deep states to higher lying bands or to excited states of the oxygen vacancy. They exhibit little anisotropy in tetragonal $BaTiO_3$. There is no evidence of strong small-polaron effects.

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