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# Studies of the Optical Absorption Spectrum of Rutile Single Crystals

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**Studies of the Optical Absorption Spectrum of Rutile Single Crystals**

by

**Bernard H. Soffer**

**Laboratory for Insulation Research  
Massachusetts Institute of Technology  
Cambridge, Massachusetts**

**Contract AT (30-1)-1937**

**August, 1959**

STUDIES OF THE OPTICAL ABSORPTION SPECTRUM  
OF RUTILE SINGLE CRYSTALS \*

by

Bernard H. Soffer †

Laboratory for Insulation Research  
Massachusetts Institute of Technology  
Cambridge, Massachusetts

**Abstract:** The optical absorption of single crystals of synthetic rutile was investigated in the spectral range from 1200 to 25,000  $\text{cm}^{-1}$  and from room temperature to 1000°C.

The electronic absorption exhibits dichroic behavior. The edge moves toward lower energies as temperature is increased, with the shift depending upon the absorption coefficient; for a decadic absorption coefficient ( $\alpha'$ ) of 400  $\text{cm}^{-1}$  the shift is  $7.1 \times 10^{-4} \text{ ev}/^\circ\text{K}$ , while at 1  $\text{cm}^{-1}$  it is  $9.5 \times 10^{-4} \text{ ev}/^\circ\text{K}$ . The broad band in the region of 6850  $\text{cm}^{-1}$ , which occurs in reduced rutile, does not appear in fully oxidized rutile, even at high temperature.

At high temperatures an additional wavelength-independent absorption appears which, by applying the Drude-Zener theory of free carrier absorption, can be correlated with good agreement to d-c conductivity.

New bands in the 3300  $\text{cm}^{-1}$  region are shown to stem from O-H valence vibrations. The main bands are unusually sharp, with peaks at 3277 and 3322  $\text{cm}^{-1}$  and half-widths of 28 and 13  $\text{cm}^{-1}$ , respectively;

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\* Based in part on a thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science in Physics at the Massachusetts Institute of Technology.

† Present address: Hughes Aircraft Co., Culver City, Calif.

a satellite structure of combination and difference bands was also detected. Deuterium substitution causes an absorption at  $2442\text{ cm}^{-1}$ . The entire structure shows a marked dependence of the absorption on the polarization direction of the light. Some evidence is presented that these O-H groups cause a dielectric dispersion.

Changes in carrier density were detected in transmission measurements on a current-carrying crystal.

### Introduction

The Laboratory for Insulation Research is engaged in comprehensive research on charge-carrier mobilization and motion. The present investigation is part of this program and especially concerned with the effect of temperature on the electronic behavior of dielectric materials, as revealed by spectroscopy.

Rutile has been under scrutiny in the Laboratory for a number of years. Studies<sup>1-4)</sup> on the dielectric behavior of  $\text{TiO}_2$  ceramics and single crystals as a function of frequency, field, and temperature, and an investigation of the electrical and optical properties of single crystals<sup>5)</sup> have been published. Electrical evidence indicates that at higher temperatures a thermal transfer of electrons from  $\text{O}^{2-}$  to  $\text{Ti}^{4+}$  takes place if a purely ionic description is chosen. Electronic conductivity could then be explained by electron exchange between  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ , possibly accompanied by hole transfer in the oxygen structure of the

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- 1) A. von Hippel et al., NDRG Rep. VII, Aug., 1944, and Rep. XI, Oct., 1945, Lab. Ins. Res., Mass. Inst. Tech.
  - 2) A. von Hippel, R. G. Breckenridge, F. G. Chesley, and L. Tisza, Ind. Eng. Chem. 38, 1097 (1946).
  - 3) A. von Hippel, Revs. Mod. Phys. 22, 221 (1950).
  - 4) K. G. Srivastava, Tech. Rep. 127, June, 1958; Tech. Rep. 139, June, 1959; Progr. Rep. No. XXI, p. 12, Lab. Ins. Res., Mass. Inst. Tech.
  - 5) D. C. Cronmeyer, Phys. Rev. 87, 876 (1952).

lattice. The electronic transfer would be analogous to the well-known electron exchange between ferrous and ferric ions located on octahedral lattice sites in magnetite.<sup>6)</sup> In the case of rutile, enough of these carriers might be transferred at sufficiently high temperature to permit observation of transitions from these excited states and new absorptions. Simultaneously, the increased lattice vibrations should shift and broaden the whole system of original levels. It might also be possible to observe changes in absorption due to injected carriers.

It was found previously<sup>1, 2)</sup> that in order to explain the negative temperature coefficient of the dielectric constant as well as other properties, one had to assume that  $\text{TiO}_2$  is not purely ionic but a transition case between polar and nonpolar binding. A discussion of the crystal structure of rutile (tetragonal:  $P_2/mnm$ ) and a review of its optical properties have been presented by Cronemeyer.<sup>5)</sup> No adequate calculations of the electronic structure of the rutile lattice by band theory exist. Cronemeyer succeeded in correlating the low-temperature threshold of optical absorption at 3.03 eV with the activation energy of high-temperature conductivity and the maximum photoconductivity response. Certain absorptions attributed by him to impurities in the lattice appear to be spurious (i. e., they were probably caused by changes of prisms and instruments). In reduced rutile Cronemeyer correlated vacant oxygen sites with conductivity data and a broad band at about  $1.85 \mu$ , using a model of heliumlike atoms modified by the dielectric environment.

A temperature study of the eigenabsorption edge was made by Cronemeyer from 4000 to 5400 Å between  $4.2^\circ$  and  $775^\circ\text{K}$ . These data indicated a general shift of the band edge toward lower energies at the rate of  $6.3 \times 10^{-4} \text{ eV}/^\circ\text{K}$ , with an absorption coefficient of about  $30 \text{ cm}^{-1}$ , except for an anomalous shift toward longer wavelengths as the temperature was reduced to near  $4^\circ\text{K}$ . (The only

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6) E. J. W. Verwey et al., J. Chem. Phys. 15, 181 (1947).

other optical temperature study of rutile is Schröder's<sup>7)</sup> work on the decrease of the two refraction indices of natural red rutile crystals with increasing temperatures from 25° to 680°C in a wavelength range from 0.7 to 0.5  $\mu$ .)

A second long-range investigation of the Laboratory concerns dielectric relaxation spectra. Originally such spectra were analyzed according to Debye's<sup>8)</sup> model of dipoles rotating with high frictional damping. Frequently, however, dipole orientation by rotation is inconceivable while orientation by inversion might still occur, as for example in the shifting of hydrogen bonds or of polar molecular or atomic groups.<sup>9)</sup> In addition, a new kind of dipole, connected with crystalline lattice defects, has been invoked to explain dielectric spectra.<sup>10)</sup> Optical absorptions associated with lattice defects have been observed, for instance, in neutron-irradiated silicon.<sup>11)</sup> Dielectric-inversion spectra, due to polar centers of some kind, have been found in synthetic single crystals of  $\text{TiO}_2$  under certain conditions.<sup>4, 12)</sup> It appeared important to correlate these spectra with possible optical manifestations of such polar centers.

Our measurements, as here presented, cover a wavelength range from the electronic-absorption edge near  $24,000 \text{ cm}^{-1}$  to  $1200 \text{ cm}^{-1}$ , the tail of the highest infrared vibration band. Special attention was paid to the broad band in reduced rutile and to a region near  $3 \mu$ , because the activation energy of the

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7) A. Schröder, Z. Krist. 67, 485 (1928).

8) P. Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929, Chap. 5.

9) A. von Hippel, Progr. Rep. No. XXI, Lab. Ins. Res., Mass. Inst. Tech., p. 3.

10) R. G. Breckenridge, J. Chem. Phys. 18, 913 (1950).

11) M. Becker, H. Y. Fan, and K. Lark-Horovitz, Phys. Rev. 85, 730 (1952).

12) Y. L. Sandler, Progr. Rep. No. XVII, Lab. Ins. Res., Mass. Inst. Tech., p. 16.

dielectric dispersion suggested the possibility of finding an absorption there. The measurements in our investigation range from room temperature to 1000°C.

### Sample Preparation and Measurement Techniques

#### Sample preparation

Boules of rutile,<sup>\*</sup> grown by flame fusion, were oriented by back-reflection Laue X-ray pictures to within one degree and cut with a diamond saw into slabs of various sizes. The samples were polished by hand and specimens ranging in thickness from 18 mm to 30  $\mu$  prepared. With thick specimens the light between crossed polarizers could not be extinguished and the optical axis figure appeared biaxial. This strain was not discernible with X rays since the latter penetrate only a short distance into  $\text{TiO}_2$ .

One of the boules exhibited, in addition to strain birefringence, a doubling of the Laue spots on (100) faces (perpendicular to the a axis). For example, points (00 $\ell$ ) appeared as two parallel lines, indicating that this crystal was really not single but had a twinned structure with an angle of about 3°50'. This effect was not visible on (001) faces (perpendicular to the c axis).

Light scattering, caused by polishing marks and crystalline imperfections, can falsify the value of  $\alpha$  when the mismatch in index of refraction between material and imbedding medium is large. This is the case for rutile with its high anisotropic index of refraction (e.g.,  $n_{\perp} = 2.74$  and  $n_{\parallel} = 3.06$  at 0.48  $\mu$ ;  $\perp$  and  $\parallel$  refer to the orientation of the electric vector in reference to the optical axis). Hence, especially careful polishing is required.

During the course of the study it became necessary to oxidize and reduce rutile and at one time to introduce deuterium into it by heating the crystals to high temperatures in appropriate atmospheres. For this purpose the samples were placed in alumina boats in a Vycor tube and heated up to 1100°C. It is known

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\* Our boules courtesy of Dr. C. H. Moore of the National Lead Co., Titanium Division, South Amboy, N. J.; some others were purchased from Linde Air Products Co., Speedway Laboratories, Indianapolis, Ind.

that the reduction is nearly reversible, when not carried too far,<sup>5, 13)</sup> by heating in oxygen. Since rutile will reduce in vacuum or even in air at sufficiently high temperature, the partial pressure of oxygen had to be kept high. This may also be inferred from measurements<sup>14)</sup> of the conductivity as a function of oxygen pressure at elevated temperature in the range of  $> 30$  mm Hg where  $\sigma \propto P_{O_2}^{-1/\alpha}$ , with  $\alpha = 4.3$ .

### Instrumentation

Absorption spectra were investigated primarily with a Beckman IR-3 spectrophotometer using  $CaF_2$  prisms (spectral range 25,000 to ca. 1200  $cm^{-1}$ ). Line spectra of gases accurately measured on grating instruments<sup>15)</sup> served for calibration. To detect any drift in the instrument adjustment, the spectra of water, carbon dioxide, and mercury vapors were recorded as a secondary calibration. The use of a chopped light beam (10 cps) made it possible to measure the absorption of heated samples by eliminating thermal background radiation. The beam was chopped in front of the sample close to the light source. Stray light was negligible over the entire spectral range.

Three signal detectors of various spectral ranges were used: a Golay cell from 1000 to 14,000  $cm^{-1}$  in combination with a Nernst glower; a photomultiplier from 14,000  $cm^{-1}$  to 25,000  $cm^{-1}$  in conjunction with a tungsten lamp; and a PbS cell from 12,500 to 3600  $cm^{-1}$ , which gave increased sensitivity, especially when cooled with solid  $CO_2$ .

Some measurements were made with a Cary Model-12 spectrophotometer, which, as a quartz-prism double monochromator, affords more resolution than  $CaF_2$  in the region of 25,000  $cm^{-1}$ .

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13) N. Nasu, Science Repts. Tôhoku Imp. Univ. [1] 25, 510 (1936).

14) M. D. Earle, Phys. Rev. 61, 56 (1942).

15) A. R. Downie, M. C. Magoon, T. Purcell, and B. Crawford, Jr., J. Opt. Soc. Amer. 43, 941 (1953).

### Auxiliary equipment

The cell used in the high-temperature study is shown in Fig. 1. A small alumina tube wound with platinum heater wire is inserted in a water-cooled steel tube insulated with Sil-O-Cel; the furnace ends, made of Transite, support the alumina tube and the windows. The furnace is suspended from a steel plate by two hollow bolts that carry the electrical leads for the heater.

Thin samples were placed between two pre-crimped platinum foils cut out over a portion of the specimens' faces. The foil, serving both as holder and mask, was placed over the hole of an  $\text{Al}_2\text{O}_3$  plate and laced on with fine platinum wire. Large samples were mounted in tubular holders made from fire brick.

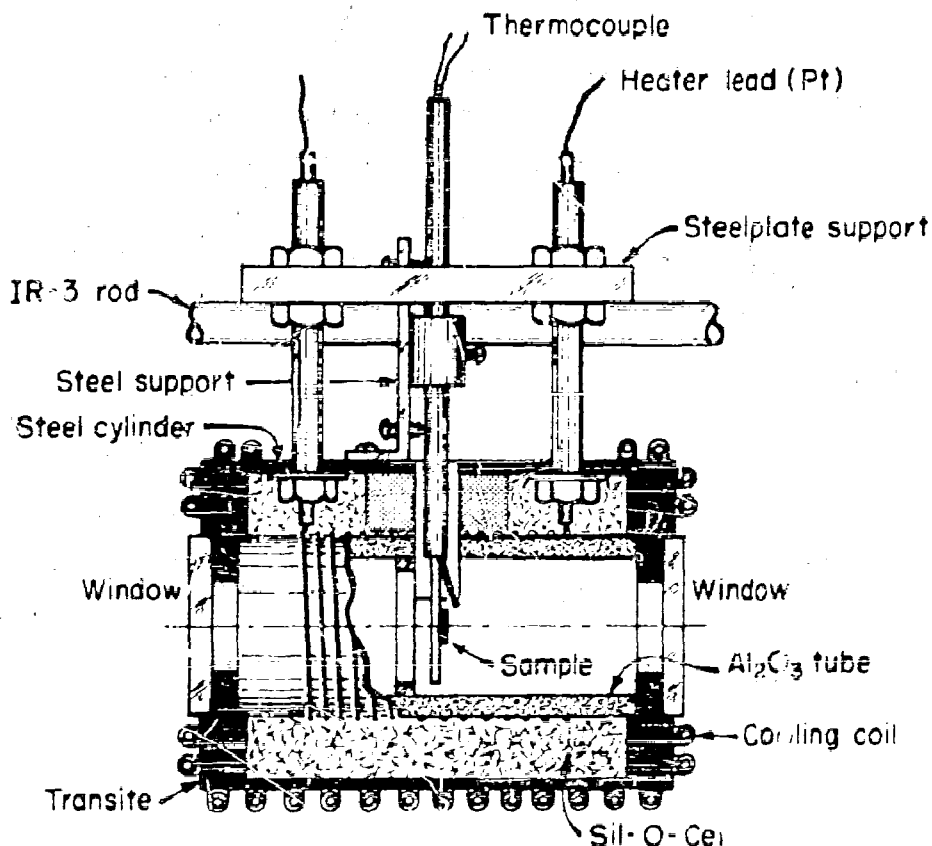


Fig. 1. Cross section of high-temperature optical absorption cell.

For simultaneous measurement of the dielectric and optical properties of a crystal, a special type of holder, shown in Fig. 2, was used. Before each run the cell was dried and outgassed at high temperature to avoid window contamination. Some measurements were made at liquid-nitrogen temperature in a Dewar cell previously described.<sup>16)</sup>

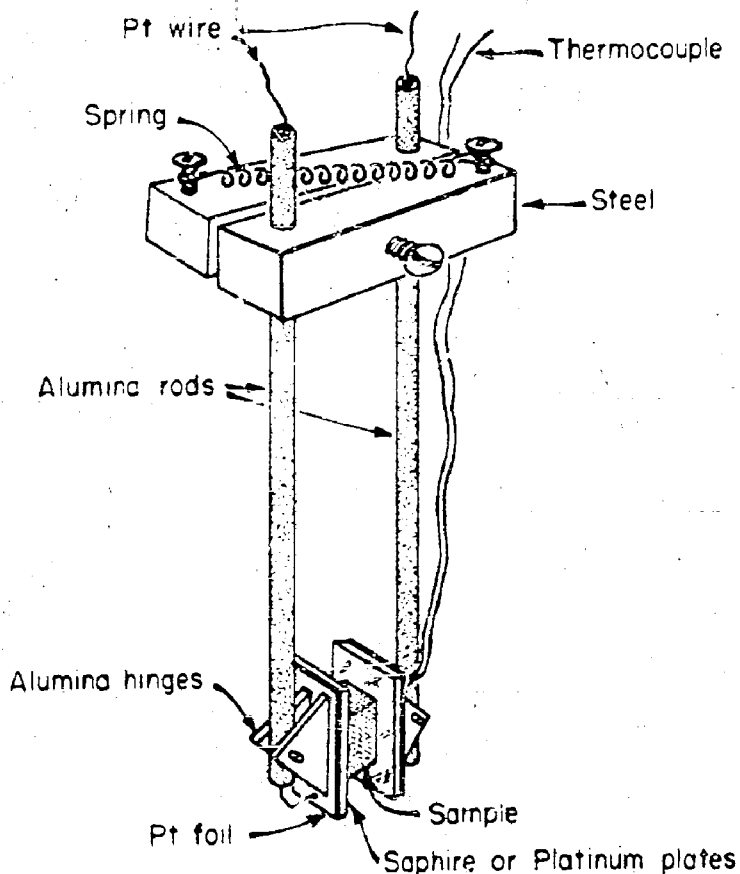


Fig. 2. High-temperature sample holder.

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16) J. T. Last, Phys. Rev. 105, 1740 (1957).

An external focusing optical system was employed in absorption and electro-optical experiments. This system (Fig. 3) permits optical masking of any portion of the sample and its surroundings, and thus allows correction for furnace-window contamination.

For polarization measurements in the visible region Polaroid disks and a Nicol prism were used. In the infrared, four sheets of AgCl at the Brewster angle provided 90 percent polarization.

### Representation of Data

The recording spectrophotometer measures the transmittance  $T$ , the ratio of transmitted to incident light intensity

$$T = \frac{I}{I_0} \cong \frac{(1 - R)^2 e^{-ad}}{1 - R^2 e^{-2ad}} \quad (1)$$

The equation holds for  $a < 10^3 \text{ cm}^{-1}$ ;  $R$  is the ratio of reflected to incident intensity; interference effects are neglected.<sup>17)</sup> The reflectivity  $R$  is:

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (2)$$

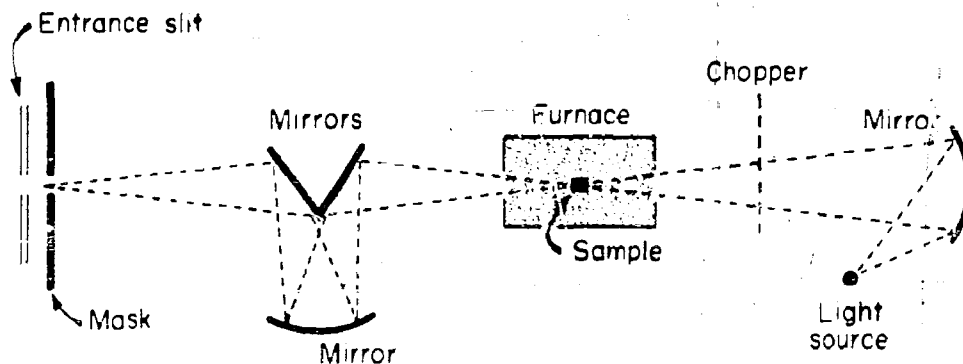


Fig. 3. External optical plan for high-temperature experimentation.

where  $k = \alpha\lambda/4\pi$ . For small ( $\alpha d$ ), Eq. (1) reduces to

$$T = \frac{1 - R}{1 + R} \quad (3)$$

and for large ( $\alpha d$ ), to

$$T \cong (1 - R)^2 e^{-\alpha d} \cong (1 - R)^2 10^{-\alpha' d} \quad (4)$$

Von Hippel and associates<sup>1, 2)</sup> made an analysis of the reflection data of Liebisch and Rubens<sup>18)</sup> to obtain the values of  $n$  and  $k$ . Cronmeyer<sup>5)</sup> correlated these values of  $n$  to values measured by others and extended their measurement with a small prism to 4359 Å. Thus, using Eqs. (1) to (4) one can calculate reflection loss and obtain the true absorption coefficient.

### Results

The general features of the absorption near the electronic edge of Sample 4 (thickness 18.32 mm, transmission || to c axis) are shown in the upper curve of Fig. 4.\* This spectrum corresponds in general to previously reported work, with a gradual rise in absorption before the sudden rise at the edge of the eigenabsorption. The tail can be explained by imperfections and may be due to indirect transitions.<sup>19)</sup>

Superimposed is a small residual absorption at 0.56  $\mu$  with a maximum decadic coefficient  $\alpha' < 0.01 \text{ cm}^{-1}$ . Replotting the upper curve of Fig. 4 logarithmically (Fig. 5) makes its shape independent of sample thickness. The curvature of this characteristic is a measure of the speed with which the absorption grows as the band is approached. Now an inflection point appears near  $19,000 \text{ cm}^{-1}$  and the existence of a band at  $17,900 \text{ cm}^{-1}$  seems doubtful.

A curve showing the theoretical reflection loss is also included in Fig. 5 for the region of small absorption; it is apparent that the absorption is higher

18) Th. Liebisch and H. Rubens, Sitzber. preuss. Akad. Wiss. 8, 211 (1921).

\* Before annealing in  $O_2$ , cf. p. 14.

19) L. H. Hall, J. Bardeen, and F. J. Blatt, Phys. Rev. 95, 559 (1954).

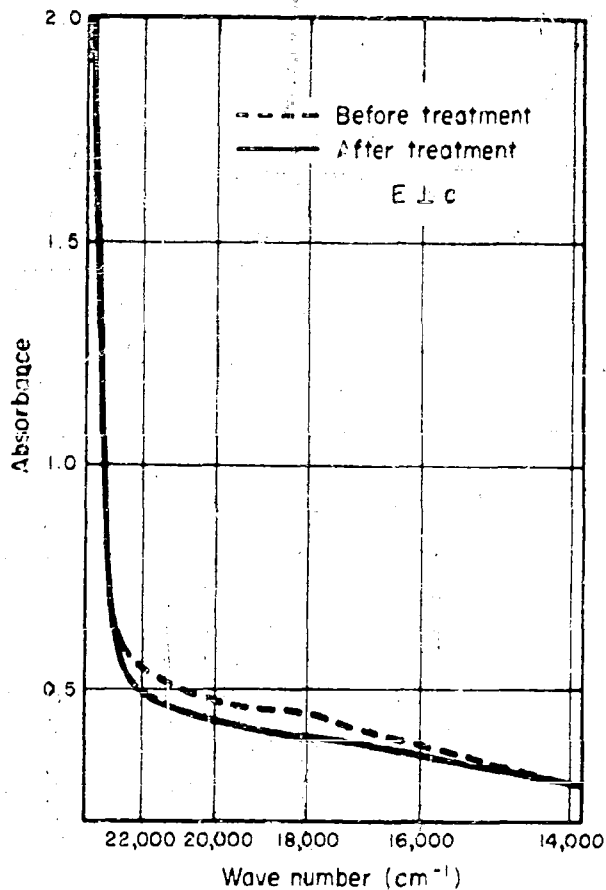


Fig. 4. Absorption of rutile Sample 4 (18.32 mm thick).

and rises faster than explained by reflection alone.

The spectrum as recorded on the IR-3 spectrophotometer from 14,000 to 1800  $\text{cm}^{-1}$  (Fig. 6) gives the absolute transmission assuming that outside of the absorption band the transmission is determined entirely by reflection loss. The tail of the first infrared vibration band makes its appearance at

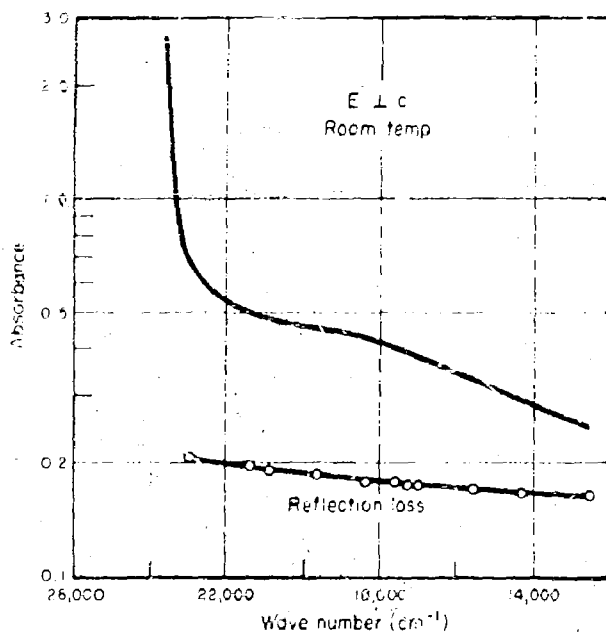
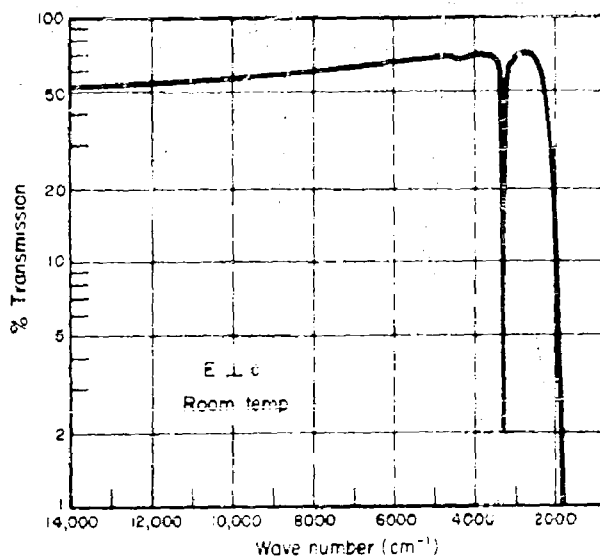


Fig. 5.

Logarithmic representation of the absorbance of Sample 4, showing theoretical reflection loss.

Fig. 6.  
Infrared spectrum  
of Sample 4.



2700  $\text{cm}^{-1}$ . The exciting feature is the very narrow absorption near 3300  $\text{cm}^{-1}$ , with its satellite structure, which includes the absorption at 4340  $\text{cm}^{-1}$ . The main absorption is shown in more detail in Fig. 7 (effective slit width  $< 7 \text{ cm}^{-1}$  through this region). There is a large peak with an absorption maximum at 3277  $\text{cm}^{-1}$  (peak absorption coefficient  $\alpha' = 0.78 \text{ cm}^{-1}$ ) and a sharp side band at 3322  $\text{cm}^{-1}$ . A graphical separation, assuming harmonic oscillator shape, gives 28  $\text{cm}^{-1}$  for the half-width of the former and 13  $\text{cm}^{-1}$  for that of the latter band.

The peak absorption  $\alpha'$  at 3322  $\text{cm}^{-1}$ , corrected for finite slit width, is about 0.43  $\text{cm}^{-1}$ . (It can be shown<sup>20, 21</sup>) that for a slit width equal to the true band width the measured absorption coefficient will be 0.7 of the true peak.)

There are two shoulders on the long wavelength tail, at 3070 and 3170  $\text{cm}^{-1}$ . On the short wavelength side structure may exist but the presence of atmospheric water bands begins to cause a residual distortion from about 3420 to 3950  $\text{cm}^{-1}$ , obscuring the detailed structure.

The 3300- $\text{cm}^{-1}$  region was also examined at the temperature of liquid

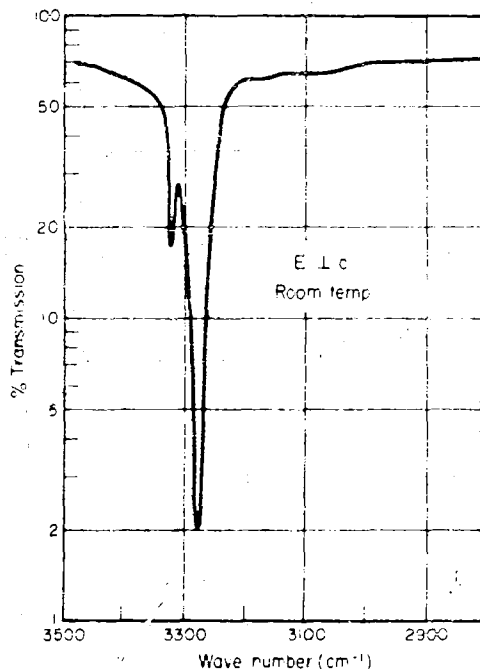


Fig. 7. Infrared spectrum of Sample 4 in the 3300  $\text{cm}^{-1}$  region.

20) X. S. Gibson, Nat'l. Bureau Standards: Circular 464, 1949.

21) D. A. Ramsay, J. Am. Chem. Soc. 74, 72 (1952).

nitrogen. The entire structure shifted to shorter wavelengths by  $12\text{ cm}^{-1}$ ; no new absorptions appeared but the old one was sharpened.

The absorption proved very sensitive to the direction of polarization. Because of the limited efficiency of the polarizer and the strains in the crystals, no absolute value of the effect can be given, but the entire structure, including the band at  $4340\text{ cm}^{-1}$ , behaves identically and the absorption coefficient is at least seven times greater for  $E \perp c$  than for  $E \parallel c$ .

An attempt was made to remove the band by heating in oxygen for thirty hours at  $1000^\circ\text{C}$ . No significant change resulted except for a slight drop in absorbance near the edge (cf. the lower curve of Fig. 4) including removal of the bump near  $0.56\text{ }\mu$ . Gronemeyer,<sup>5</sup> in contrast, found an increased absorbance near the edge in his crystal after similar treatment.

Certain atomic and molecular groups create characteristic bands in particular environments.<sup>22)</sup> The band in the region  $3300\text{ cm}^{-1}$  lies in the O-H stretching region and suggests the presence of O-H groups in the crystal. To test this hypothesis, deuterium was introduced in substitution for H. Heating in gaseous deuterium caused difficulties: the specimen reduced and a very broad, dense band appeared, completely obscuring the region of interest (Fig. 8). To substitute as much deuterium as possible without severe reduction, heating above  $900^\circ\text{C}$  for short times (less than 1 minute) was found necessary. Now a new absorption at  $2442\text{ cm}^{-1}$  appeared in these deuterated specimens. This is in the expected region and the bands were of the same shape as the previous ones. However, the over-all opacity caused by reduction made observation of the line structure impossible.

In the course of this study it was found that the O-H band in the  $3300\text{-cm}^{-1}$  region could be removed by strong reducing followed by re-oxidizing of the speci-

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22) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954.

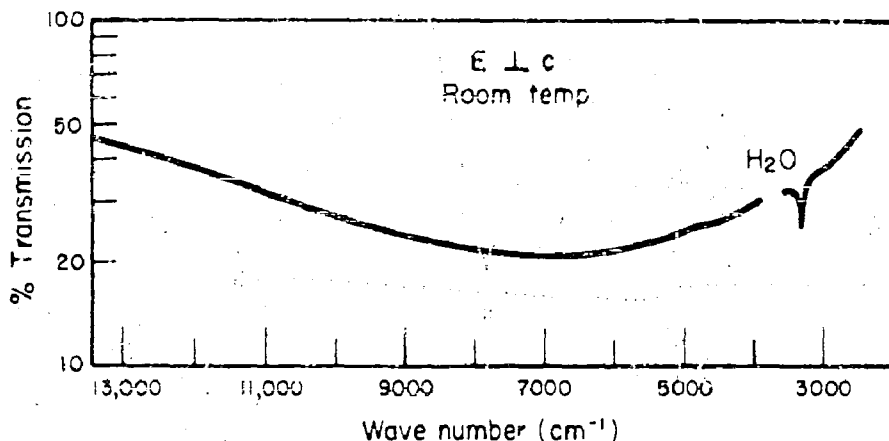


Fig. 8. Broad absorption caused by weak reduction of Sample 3, 0.52 mm thick.

men. Simply exposing a crystal to oxygen at high temperatures for long periods of time had no such effect.

The broad band appearing in weakly reduced  $\text{TiO}_2$  (cf. Fig. 8) extends from the nearest vibrational band to the electronic edge. In our case the minimum transmission occurs in the region of  $6850 \text{ cm}^{-1}$  ( $1.46 \mu$ ); Cronmeyer<sup>5</sup> reported a slightly different value,  $5405 \text{ cm}^{-1}$  ( $1.85 \mu$ ), for this sample.

In order to determine whether high temperature alone would produce such a band (or any new absorption) in fully oxidized rutile, high-temperature spectra were taken. Figure 9 refers to a sample of 0.52 mm between c faces. (The observed regions marked " $\text{H}_2\text{O}$ " and " $\text{CO}_2$ " were caused by vapors in the cell; at high temperatures their absorption modifies and broadens.) The transmittance values are not to be considered absolute because slight changes in equilibrium position of the high-index sample at the various temperatures, and differing degrees of window contamination occur. However, it is evident that no absorption corresponding to the reduction band appears.

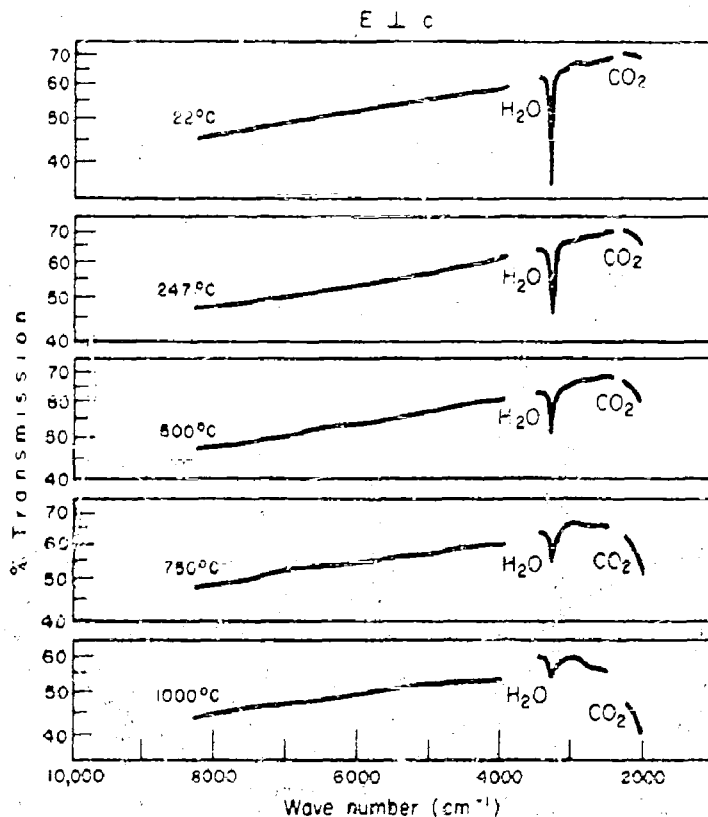


Fig. 9. Infrared absorption spectra of Sample 1 (0.52 mm thick).

Figure 10 shows the shift of the eigenabsorption edge for temperatures up to  $1000^{\circ}\text{C}$  for the case  $E \perp c$ ; the shift for  $E \parallel c$  is identical within the errors of the high-temperature experiment. The theoretical reflection loss is plotted as one curve only. As Schröder<sup>7)</sup> has shown, the indices of both the ordinary and extraordinary rays change only slightly with temperature. (According to his data, the reflection loss at  $5791\text{\AA}$  and  $600^{\circ}\text{C}$  produces 67.0 and 62.0 percent transmission for  $E \perp c$  and  $E \parallel c$ , respectively, whereas at room temperature 66.7 and 61.5 percent result.)

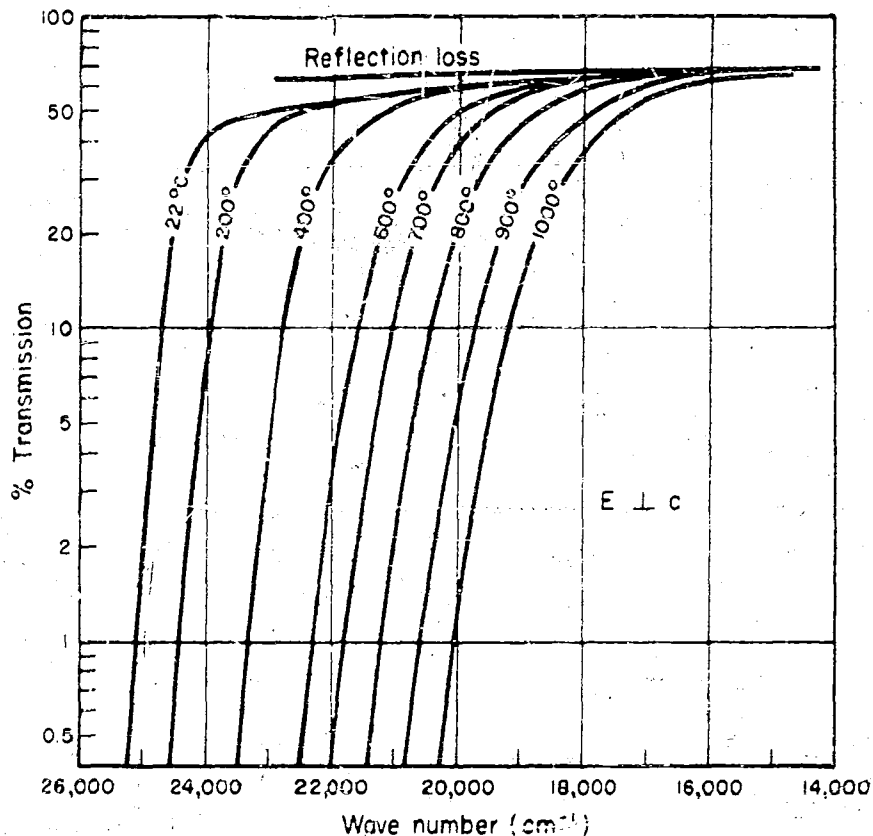


Fig. 10. Absorption spectrum of Sample 6 (29.5  $\mu$  thick) as function of temperature.

The spectra in Fig. 10 refer to a sample of 29.5- $\mu$  thickness. The rate of change of the edge position must be measured in the region of high absorption where the curves become almost parallel and the errors introduced by the vertical translations are negligible. At an absorption coefficient  $\alpha'$  of 400  $\text{cm}^{-1}$  the average shift for both  $E \perp c$  and  $E \parallel c$  is  $7.1 \times 10^{-4} \text{ eV}/^\circ\text{K}$  toward longer wavelength.

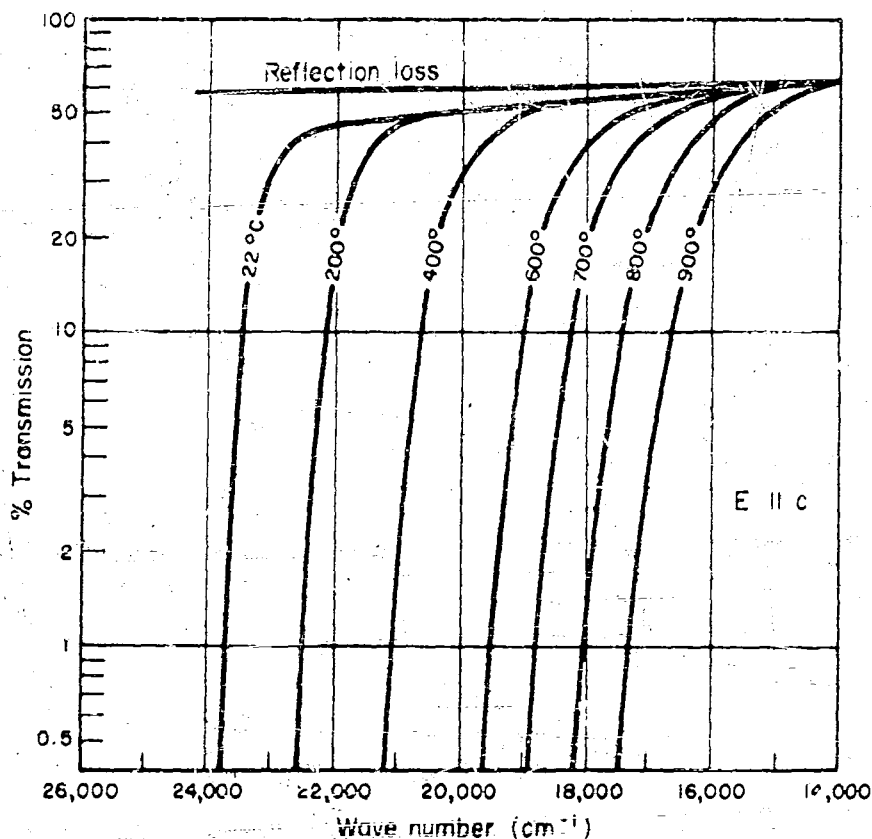


Fig. 11. Absorption spectrum of Sample 5 (11.94 mm thick) as function of temperature.

Figure 11, for a sample thickness of 11.94 mm ( $E \parallel c$ ), shows that at an absorption coefficient  $\alpha'$  of about  $1 \text{ cm}^{-1}$  the average rate of shifting of the edge is  $9.5 \times 10^{-4} \text{ eV/}^\circ\text{K}$ .

For absolute values of transmission at high temperatures in the infrared, the optical system of Fig. 3 was used. A portion of the results for the case  $E \parallel c$  is shown in Fig. 12. The general shape is that already shown in Fig. 9, but now a marked achromatic drop in transmission at  $1000^\circ\text{C}$  can be observed,

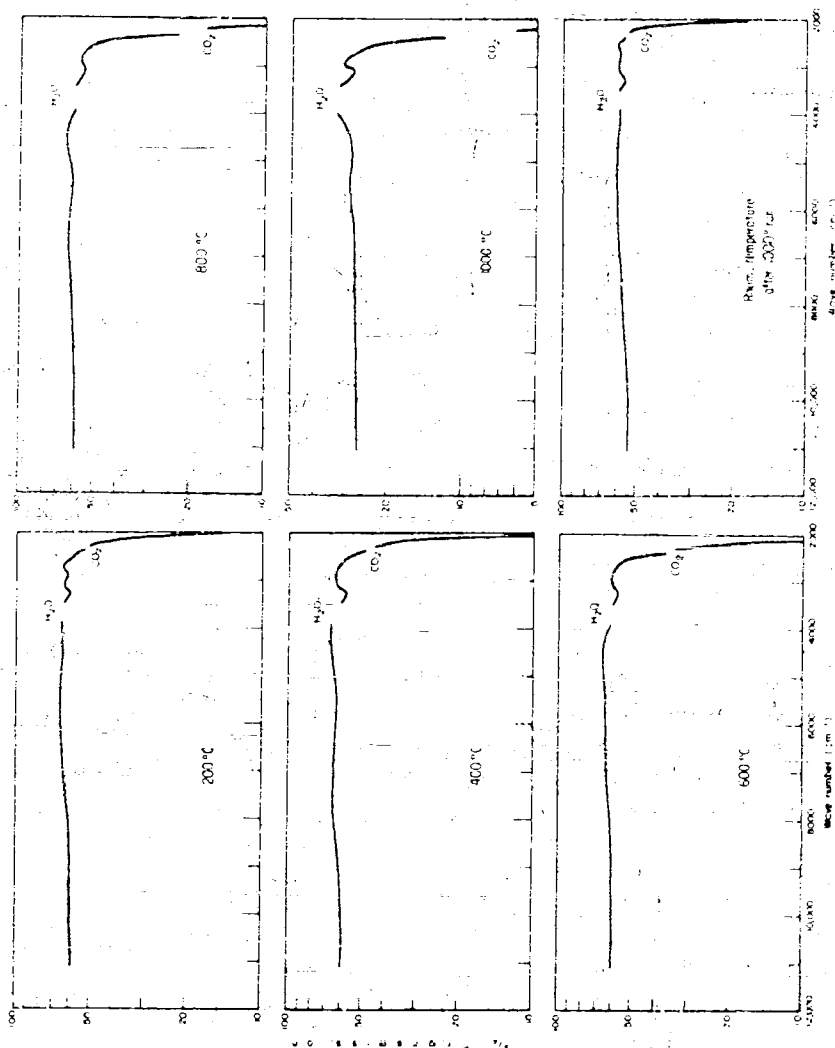


Fig. 12. Infrared absorption spectra for alumina-free rutile sample (path length 8.52 mm.) as function of temperature.

representing an increase of absorption coefficient;  $\Delta\alpha' = 0.42 \pm 0.02 \text{ cm}^{-1}$ . At  $800^\circ\text{C}$  there is already a slight increase of absorption coefficient;  $\Delta\alpha' = 0.03 \pm 0.02 \text{ cm}^{-1}$ . Re-examination after the heating experiment at room temperature revealed a slight over-all drop in transmission from the starting value:  $\Delta\alpha' = 0.05 \pm 0.02 \text{ cm}^{-1}$ , probably due to a slight contamination by Pt at elevated temperatures.

#### Miscellaneous observations

Dichroism of the electronic absorption edge has not been previously noted in the literature. Here we observed an effect as shown in Fig. 13. The edge for  $E \perp c$  occurs at an energy lower than for  $E \parallel c$ , when instrumental polarization effects are avoided. (A Nicol prism was used because it has a flat transmission characteristic in the region of interest; both sets of measurements were taken through a single pair of "a" faces to obviate effects of differing polish.)

Very preliminary measurements were made of the influence of electric current on

the optical transmission in an 8.5-mm crystal cube at

$1000^\circ\text{C}$  for several wavelengths. A variety of effects, superimposed on a general slow drift toward smaller transmission, were observed. Systematic studies of

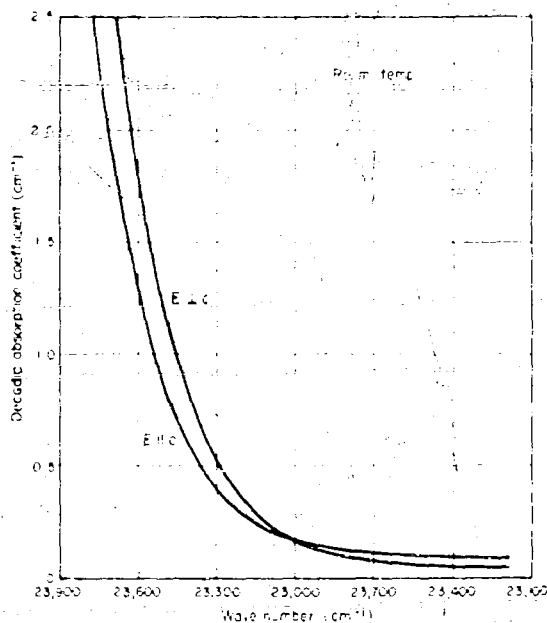


Fig. 13. Dichroism of absorption coefficient of alumina-free rutile sample (path length 8.52 mm).

these effects are in progress.

### Discussion

The most striking feature of the high-temperature spectra of rutile is the large shift in the optical absorption edge. Fan<sup>17)</sup> reviewed the theories explaining this phenomenon - all of which invoke the effect of lattice vibrations either in shifting or broadening the energy-gap levels. Macroscopically, the temperature variation of the gap, exclusive of the dilation effect of the lattice, should be given by an expression containing the change of the energy gap with temperature at constant pressure, which has been measured here, and by terms describing the effect of lattice dilation, which are of the form  $(\partial E_g / \partial p)_T$ . In order, therefore, to correlate the experimental results of this study with any theory of high-temperature behavior, measurements of the isothermal variation of gap with pressure should be made as well.

The frequency-independent high-temperature absorption (cf. Fig. 12) can be attributed to free carrier absorption according to the theories of Drude-Kronig-Zener.<sup>23)</sup> The absorption coefficient and conductivity due to free carriers in nonmagnetic media is

$$\alpha = \frac{1}{nc} \frac{\frac{\sigma_0}{\epsilon_0}}{1 + \left(\frac{\omega_{aim}}{e}\right)^2} \quad [\text{m}^{-1}], \quad (5)$$

$$\sigma = 2n\hbar\omega_0 = Ne\mu \quad [\text{ohm}^{-1} \text{ m}^{-1}],$$

where  $g_0$  is the low-frequency conductivity and the other symbols have their conventional meanings.

If  $(\omega_{aim})/e < 1$ , no significant wavelength dependence can be expected. The

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23) Cf. F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, 1940, p. 638.

inequality may be written

$$10^4 \mu \frac{\left[ \frac{m^2}{\text{volt-sec}} \right]}{\lambda [\text{microns}]} \left( \frac{m^*}{m} \right) < 1. \quad (6)$$

The Hall mobility  $\mu$  of electrons in slightly reduced rutile crystals and ceramics is  $< 10^{-4} [\text{m}^2/\text{volt-sec}]$  and decreases with increasing temperature.<sup>24)</sup>

Using the relation for the variation of mobility with temperature<sup>25)</sup> due to lattice scattering

$$\mu \propto T^{-3/2} \quad (7)$$

(which should predominate at high temperatures), we estimate that the mobility at  $1000^\circ\text{C}$  should be  $< 10^{-5} [\text{m}^2/\text{volt-sec}]$ . Assuming an effective mass between 1 and 10, we see that the inequality is obeyed. For this limit the absorption coefficient is approximately constant and equals

$$\alpha' [\text{cm}^{-1}] = \frac{\sigma \cdot 10^{-2} (\log_{10} e)}{n e_0 c} = \sigma [\text{ohm}^{-1} \text{m}^{-1}] \times 0.63 \quad (8)$$

for  $n_H = 2.6$ .

Observed is an absorption coefficient  $\alpha' = 0.42 \text{ cm}^{-1}$  at  $1000^\circ\text{C}$ , leading to a conductivity (cf. Eq. 8) of  $0.67 \text{ ohm}^{-1} \text{m}^{-1}$ . Cronmeyer reports a value of  $\sigma_{OH} = 0.77 \text{ ohm}^{-1} \text{m}^{-1}$  at  $1000^\circ\text{C}$ . At  $800^\circ\text{C}$  the optically measured  $\alpha' = 0.03 \pm 0.2 \text{ cm}^{-1}$  gives an order-of-magnitude agreement with Cronmeyer's value  $\sigma_0 = 0.04 \text{ ohm}^{-1} \text{m}^{-1}$ . The correlation is surprisingly good; there was no a priori reason to expect that lattice and impurity scattering would produce a mobility in the infrared equal to the d-c mobility.

We have demonstrated that the bands at  $3300 \text{ cm}^{-1}$  arise from the presence of hydrogen in the lattice and correspond to O-H stretching vibrations. There is

24) R. G. Breckenridge and W. R. Hosler, Phys. Rev. 91, 793 (1953).

25) H. Y. Fan, Phys. Rev. 82, 900 (1951).

probably an organized system of hydrogen bonded to the oxygen of the rutile lattice; a weak hydrogen bonding may be indicated by the splitting of the band into two absorptions at 3277 and 3322  $\text{cm}^{-1}$ . The O-H valence frequency (e.g., methyl alcohol 3682  $\text{cm}^{-1}$  and solid LiOH 3678  $\text{cm}^{-1}$ ) has been generally observed in condensed phases shifted toward longer wavelengths.<sup>26)</sup> The shifts found here, however, are unusually large and may be partly caused by the large dielectric constant of rutile. It may be noted that these bands are unusually sharp for O-H absorptions in the solid state.

Interpolating from the theory and from results obtained on other hydrogen-bonded systems,<sup>27)</sup> we can estimate from the shift in O-H frequency that the H-bond energy is about 3 kcal/mole. There is a relationship<sup>28)</sup> between the change of dipole moment with the normal co-ordinate  $\partial\mu/\partial r$ , the number of oscillators per  $\text{cm}^3$   $N$ , and the integrated absorption coefficient  $A$  ( $\text{cm}^{-2}$ ):

$$N = \frac{m^*}{\left(\frac{\partial\mu}{\partial r}\right)^2} A (1.975) \times 10^{21}, \quad (9)$$

where  $m^*$  is the reduced mass. Estimating  $\partial\mu/\partial r$  from its value in hydrogen-bonded phenols,<sup>29)</sup> we calculate that there are  $1.5 \times 10^{17}$  O-H groups per  $\text{cm}^3$  in the sample of Fig. 7. Other samples showed the same order of magnitude.

The substitution of deuterium for hydrogen should shift the frequency of vibration in the ratio  $\omega_H/\omega_D = 1.37$ . The numerical value was obtained by assuming that the vibration was normal and that the reduced mass was to be computed with the mass of oxygen. A further assumption was that the same force

26) L. Kellner, Repts. Progr. in Phys., 15, 1 (1952).

27) E. R. Lippincott and R. Schroeder, J. Chem. Phys., 23, 1099 (1955).

28) R. D. Waldron, Phys. Rev., 99, 1727 (1955).

29) H. Tsubomura, J. Chem. Phys., 24, 927 (1956).

constant could be used for both vibrations, since X-ray evidence<sup>30)</sup> showed that for weak hydrogen bonds, such as in ice, the intermolecular distance is the same for O-D and O-H. We may therefore assume that the potential energies are practically equivalent. The experimentally determined ratio is  $\omega_H/\omega_D = 1.35$ , confirming the existence of hydrogen in the lattice.

The activation energy of the dielectric dispersion discovered in rutile<sup>4)</sup> might lead one to expect an optical absorption near  $3000\text{ cm}^{-1}$ . This would correspond to the absorption of hydrogen-bonded character here found, which might allow dipole orientation by inversion.

The dielectric dispersions have the property of being strongly polarized with respect to the direction of the electric vector. The infrared absorption of the O-H group is polarized by  $90^\circ$  to the dielectric dispersion. This correlation should be studied further; since we have shown that the hydrogen can be driven out of the crystal, the relation between both effects can be investigated in detail.

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30) J. M. Robertson and A. R. Ubbelohde, Proc. Roy. Soc. (London) A170, 222 (1939); A. R. Ubbelohde, *ibid.* A173, 417 (1939).

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