Defects in Rutile. III. Optical and Electrical Properties of Impurities and Charge Carriers*

O. W. JOHNSON, W. D. OHLSEN, AND PAUL I. KINGSBURY, JR.†
Department of Physics, University of Utah, Salt Lake City, Utah 84112
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Optical absorption spectra of various OH (OD) complexes in rutile have been studied as a function of light polarization, impurity concentration, and temperature. It is shown that the H^+ (D^+) occupies sites in the basal plane, probably displaced somewhat from $\frac{1}{2}00$, and can associate with various $+3$ substitutional cations, causing a shift of the OH (OD) stretching vibration to higher frequencies. Harmonic and combination-mode absorption has also been observed. Detailed absorption spectra and their polarization dependence for conduction-band electrons and for electrons in an Fe impurity band are presented, and the strength of the absorptions is related to the carrier concentration. These spectra apparently result from intra- or interband transitions of electrons. In neither case is a simple Drude-type absorption (as in a metal) adequate to account for the spectra. Preliminary data on the Fe impurity band indicate conductivity $>0.1\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature for a carrier density of $\sim 7\times 10^{19}/\mathrm{cm}^3$. Qualitative information on diffusion and solubility of various cation impurities is given. These data and results presented in the preceding papers permit a fairly complete, though not yet quantitative, description of the electronic defect structure of rutile. In particular, it is concluded that rutile does not normally exhibit *p*-type conductivity, because of the ease of formation of Ti^{4+} interstitials; and that the donor defect in "reduced" rutile may be either Ti^{4+} or H^+, depending on reduction temperature and ambient atmosphere, or may be any of a wide variety of metal impurities if these are present.

I. INTRODUCTION

RUTILE (TiO_2) in its stoichiometric state is a pale yellow, transparent insulating crystal. The crystal structure is described in the preceding paper.[1] Departure from stoichiometry and doping with various impurities give rise to a variety of interesting optical and electronic properties that have been studied rather extensively.[2–7] These will be summarized very briefly here only as they pertain to the present work, without attempting a comprehensive review.

Electronic conductivity can be induced in rutile either by introducing any of a variety of donor interstitials or by substituting cations of higher valence for Ti. Room-temperature conductivity up to $>10\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (representing a change of at least a factor of 10^{13} relative to the stoichiometric state) can be produced, corresponding to carrier density of $\sim 10^{20}/\mathrm{cm}^3$. Ti interstitials can be produced by heating in a reducing atmosphere, and diffusion doping with various other cations (H, Li, Na, Mg, etc.) can be achieved at moderate temperatures.[1] A broad optical absorption band, with a maximum at $\sim 1.5\ \mu$, which is associated with these free carriers, imparts a blue coloration to the conductive material.[5] This absorption band has previously been interpreted as resulting from electrons trapped at oxygen vacancies[5] or as involving formation of Magneli interfaces,[3] but low-temperature doping experiments with donor impurities[8] have clearly established the relationship with conduction-band electrons. Weak *p*-type conduction has been reported, presumably associated with trivalent substitutional impurities,[3] but this effect has been erratic and difficult to reproduce. Lack of *p*-type conductivity has prevented the development of various electronic applications.

The band-gap absorption edge is at about 4100 Å in "pure" crystals. An apparent shift of the absorption edge to longer wavelengths results from doping with Fe. This has been interpreted as a narrowing of the band gap.[9] In the absence of the free-carrier band, centered at $1.5\ \mu$, the optical absorption spectrum is essentially featureless between the electronic absorption edge and the lattice absorption bands that start at $\sim 6\ \mu$, except for several sharp absorption peaks associated with hydrogen and deuterium. These absorption peaks were first reported by Soffer.[4] Soffer reported H peaks at 3277 and 3322 cm^{-1}, with a corresponding peak at 2442 cm^{-1} for D. Soffer also reported weak absorptions associated with H at 4340, 3170, and 3070 cm^{-1}. Von Hippel *et al.*[3] subsequently reported on the same spectrum, locating the H peaks at 3276 and 3317 cm^{-1}, with D peaks at 2435 and 2463 cm^{-1}. Primarily on the basis of a reported dichroism of "at least a factor of 7," von Hippel *et al.*[3] suggested that the site of the H (D) was along a line between the O^{2-} ions located at $xx0$ and $(x, 1-x, \frac{1}{2})$, where $x=0.305$ (see preceding paper[1]). The two peaks were accounted for on the basis of slightly different O-Ti distances for such sites. This conclusion, incidentally, cannot be correct, since all such sites are equivalent when account is taken of the three nearby

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† Present address: Sullivan Park, Corning Glass Works, Corning, N. Y.
[1] P. I. Kingsbury, Jr., W. D. Ohlsen, and O. W. Johnson, paper I of this series, Phys. Rev. **175**, 1091 (1968).
[2] F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).
[3] A. von Hippel, J. Kalnajs, and W. B. Westphal, J. Phys. Chem. Solids **23**, 779 (1962).
[4] B. H. Soffer, J. Chem. Phys. **35**, 940 (1961).
[5] D. C. Cronemeyer, Phys. Rev. **87**, 876 (1952); **113**, 1222 (1959).
[6] G. A. Ackett and J. Volger, Physica **32**, 1680 (1966).
[7] J. H. Becker and W. R. Hosler, Phys. Rev. **137**, A1872 (1965).
[8] O. W. Johnson, Phys. Rev. **136**, A284 (1964).
[9] J. P. Wittke, J. Electrochem. Soc. **113**, 193 (1966).

Ti ions. Data to be presented below appear to rule out this site, and establish that the smaller peaks are associated with an Al-H (D) complex.

Hill has recently used these infrared (IR) absorption peaks to monitor H concentration in H-diffusion measurements.[10]

II. EXPERIMENTAL

Sample material was purchased as single-crystal boules from Linde Company, National Lead Company, and Nakazumi Crystals Corporation.[11] These crystals typically contain a variety of impurities in concentrations in the 10-ppm range, except for the Linde crystals that had significantly higher concentrations of both Fe and Al. The latter crystals also tended to be rather imperfect; voids up to 50 μ diam were common. Small-angle boundaries were common in all of the crystals and impurities tended to be distributed quite nonuniformly. These problems were not of serious consequence in the work reported here, since most of the specimens used were subsequently doped to considerably higher concentrations, and it was possible to "override" the effects of the grown-in impurities and defects.

Crystals were oriented by x-ray diffraction or, in cases where precise location of the c axis was required, by use of the Li-diffusion technique previously described.[1,8] Accuracy of better than 0.1° is readily attainable with the latter technique.

Specimens were cut from the oriented boules using a high-speed diamond wheel, followed by lapping, and polishing with diamond abrasive.

A variety of doping techniques were employed to produce the desired impurity concentrations. Substitutional cation impurities (Fe, Al, Ga, In, Ni, etc.) were introduced by heating to ~1050°C in an evacuated Vycor brand capsule for periods ranging from 20 to 200 h, depending on sample size, followed by reoxidation as described below, since the doping produced strong reduction of the crystals. Dopants were introduced in the form of either metal or chloride salts. Equivalent results were obtained in either case. Mg diffusion was carried out in the same way, except that the diffusion temperature was ~550°C. Precise measurements of impurity concentration were not attempted, but both IR-absorption measurements (discussed below) and weight-gain measurements indicated concentrations $\sim 10^{19}/\text{cm}^3$, except for Fe, which apparently has a solubility considerably higher. Effective concentrations would in any case be somewhat lower than the actual concentration, because of precipitation on dislocations and other defects.[12] Measurement of diffusion coefficients also was not attempted, but adequate diffusion rates were not achieved for any of the substitutional impurities except Mg at temperatures much below 1000°C.

Crystals were doped with a variety of donor interstitial impurities in addition to H and D, which were required for the IR-absorption studies. These included Li, Na, and Mg, all of which diffuse readily below 550°C, as well as Ti, which diffuses at an appreciable rate only at somewhat higher temperatures. Doping techniques for these are described elsewhere.[1,8] In addition, n-type conductivity was induced by heating to temperatures above 550°C in contact with a variety of metals, including K, Rb, Cu, Hg, Cd, Pb, and others. However, it is not clear as yet which (if any) of these impurities actually penetrated the crystals, since at these temperatures it is also possible to produce donor centers by the reduction of Ti at the surface. Detailed studies of these competing reactions for the case of H reduction will be described in a subsequent paper; for present purposes it is adequate to note that no significant Ti reduction occurs below ~550°C, but that at higher temperatures both H and Ti diffusion occur simultaneously.

Several attempts were made to diffuse B into the lattice, using B_2O_3 as a dopant, in vacuum as well as oxidizing and reducing atmospheres. No changes in the optical absorption spectrum attributable unambiguously to B were detected. In particular, we were not able to reproduce the results reported by Bogomolov,[13] who reported strongly anisotropic diffusion and donor behavior for B. Because of the close similarity of his results to the previously reported Li diffusion,[8] it seems likely that his dopant was contaminated with Li or Na salts. It is also possible that the blue "spikes" (representing c-axis diffusion of a donor impurity) that he observed to result from heating in contact with B_2O_3 resulted from H diffusion. Since the distorted surface layer that results from cutting or polishing serves to strongly inhibit interstitial diffusion,[8] localized removal of such a layer as a result of etching by the B_2O_3 could cause preferential doping at that point by an available impurity (most likely Na or H).

For the H and D IR-absorption studies, doping was normally achieved by heating in an atmosphere of H_2O or D_2O vapor and O_2 to temperatures of ~850°C for a few hours, although heating in pure H_2 or D_2 below 550°C was also used in some cases. The former technique was more convenient, since it provided a simple means of achieving the necessary close control of the H concentration, which was required to avoid strong absorption due to the 1.5-μ free-carrier peak. Changing O_2 pressure in the range 10^{-2}–500 Torr with H_2O vapor pressure maintained at ~20 Torr resulted in H concentrations in the required range.

In order to minimize problems associated with variation in sample perfection and purity, it was desirable to perform a series of experiments on a single specimen,

[10] G. J. Hill, Brit. J. Appl. Phys. **1**, 244 (1968).
[11] Nakazumi Crystals Corp., 11-2, Masumi-cho, Ikedashi, Osaka-fu, Japan.
[12] O. W. Johnson, J. Appl. Phys. **35**, 3049 (1964).
[13] V. N. Bogomolov, Fiz. Tverd. Tela **5**, 2011 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1468 (1963)].

which necessitated removing the H or D from the specimen and returning it to a "standard" state following each test. This was accomplished by heating the specimen in an O_2 atmosphere at $\sim 850°C$ for 20 h in a liquid-nitrogen cold-trapped system. The system was sealed after filling with O_2 and was fabricated entirely from Vycor brand glass, except for one O-ring seal that was maintained at room temperature. This treatment reproducibly reduced the H concentration below $10^{18}/cm^3$, which was adequate for the measurements reported here. The D concentration was consistently reduced below the level detectable from the IR-absorption peaks (estimated to be $<10^{17}/cm^3$), indicating that the residual H resulted from nonequilibrium H_2 concentration in the gas (the theoretical equilibrium H_2 partial pressure under these conditions is $<10^{-20}$ Torr), presumably because of outgassing of hydrocarbons from the O ring. A somewhat more elaborate system would doubtless allow essentially complete removal of H from the specimen.

Optical absorption measurements were made using a Cary model 14R spectrophotometer for wavelengths $<2.5\,\mu$ and a Beckman model IR-12 for longer wavelengths. A Brewster-angle Ge mirror was used for IR-polarization measurements, providing a beam that was $>99\%$ polarized. Weight loss and gain was measured with a Mettler model M5 microbalance. After making appropriate corrections for atmospheric buoyancy, these measurements were reproducible to $\pm 3\,\mu g$ for a 15-g specimen.

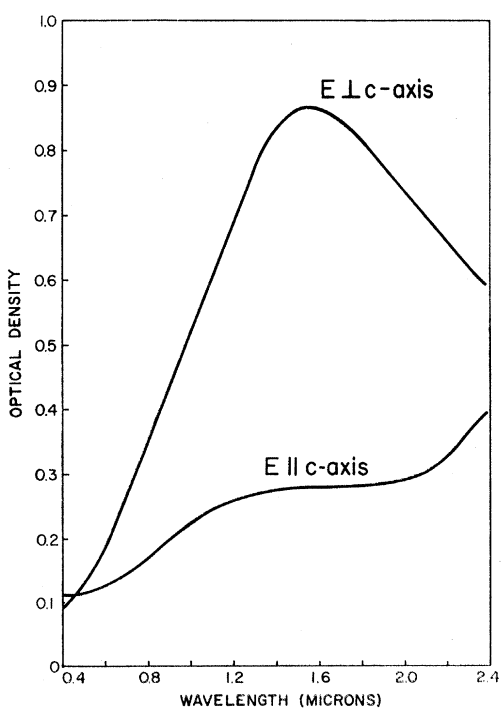

FIG. 1. Optical absorption for conduction-band electrons in a specimen with carrier density of $\sim 3.7\times 10^{17}/cm^2$, at 300°K. Evaluated from measurement of weight gain of 15-g specimen.

III. RESULTS

Free-Carrier Absorption

Because of its usefulness in evaluating the free-electron density and potential significance in analysis of band structure, the free-carrier absorption spectra for both $\mathbf{E}\|c$ and $\mathbf{E}\perp c$ are presented in Fig. 1. It is important to note that serious errors can result from failure to take proper account of the wavelength and polarization dependence of the absorption. Intrinsic sample absorption and reflection losses were eliminated by placing an undoped specimen in the reference beam of the spectrophotometer. Identical spectra were obtained for all donor impurities studied, including H, Li, Na, Mg, Ti, and W. The location of the maximum in this absorption spectrum has been reported[5] to shift at high concentrations. No detectable change was observed in the present work but the free-carrier density was well below the range where this shift was observed. The absorption spectrum for $\mathbf{E}\perp c$ at 79°K shows only minor changes from the room-temperature spectrum.

The free-carrier concentrations quoted in Fig. 1 were calculated from measurements of mass increase of the crystals resulting from heating in H_2 (or D_2). The implied relationship between carrier density and absorption coefficient agree within experimental error with previous measurements[8] based on chemical analysis of Li-doped samples. The absolute values of the absorption coefficient/electron that may be obtained from Fig. 1 are estimated to be accurate to $\pm 20\%$ (the major error being due to uncertainty as to the initial unfilled trap density), while the relative values for different wavelengths and polarizations should be correct to $\pm 5\%$.

IR Absorption Spectra

In addition to the two peaks previously reported,[3] several additional peaks associated with both the H and D spectra have been observed. Further, it has been established that at least three of these are associated with substitutional impurities: Ga, Al, and Mg (see Table I). A fourth peak (at 3279 cm^{-1} for H and 2439 cm^{-1} for D) is apparently not associated with a substitutional impurity and is hereafter referred to as the "unassociated" peak. The Al peak is observable in as-grown specimens (after H doping), although it is usually quite weak. The Ga and Mg peaks were not detectable in undoped crystals. The Ga peak was obtained only after diffusion doping (with 99.999%-pure Ga). The Mg peak occurred both in diffusion-doped crystals and in crystals with grown-in Mg (0.05-wt% MgO in starting material). Otherwise, the behavior of the Ga and Mg peaks were the same as for Al.

A weak absorption peak unambiguously observable only below room temperature (at 3314 cm^{-1} at N temperature, with a corresponding peak at 2461 cm^{-1} for D) was consistently observed in Ni-doped crystals (both diffusion-doped and grown-in). This peak was

TABLE I. OH (OD) absorption peaks in rutile.

Associated substitutional impurity	Frequency (cm^{-1}) H 300°K	H 79°K	H 10°K	D 300°K	D 79°K	D 10°K
Unassociated	3279 ±1	3287±1	3288.5±1	2439±1	2445 ±1	2446 ±1
Ni	[a]	3314±1	···	2456±2	2461 ±1	2462 ±1
Ga	3311 ±1	3317±1	3318 ±1	2459±1	2463.5±1	···
Al	3326 ±1	3331±1	3332 ±1	2469±1	2473.5±1	2475.1±1
Mg	3347.5±1	3354±1	···	2483±1	2488 ±1	···
Unidentified	···	···	···	···	2451 ±2	···
	···	···	···	···	2477 ±2	···
Minimum width (at half-maximum) observed	17	6	≈4	6	2.5	<2.5

[a] Not resolved at 300°K.

very weak, even in fairly heavily doped specimens, however, and its identifications with Ni is only tentative. This may well be a result of the known tendency of Ni to remain in interstitial sites[9] even after strong oxidation. Crystals were successfully doped with In, but no OH centers were produced. Doping with Mo and V was attempted, but results were ambiguous and no OH centers were observed.

Because of the large solubility of Fe in rutile, the 3279-cm^{-1} unassociated peak appeared initially to be associated with Fe^{3+} substitutionals, and was tentatively identified as such in a previous publication.[14] This has subsequently been shown to be incorrect.

Exploratory studies of the kinetics of formation of OH-impurity complexes were undertaken, although quantitative measurements were not attempted. Annealing of an Al-doped crystal in an atmosphere that maintained an essentially constant total H concentration at temperatures in the range 300–400°C for several hours resulted in a decrease of OH-Al peak height relative to the unassociated (3279-cm^{-1}) peak, measured at room temperature. Subsequent heating to >650°C for periods of 1 h or more followed by rapid cooling to room temperature restored the original peak-height ratio. Heating to higher temperatures and quenching produced no further change. This behavior presumably reflects the precipitation of Al on dislocations and subsequent redissolution at higher temperatures. "Annealing" of crystals containing Ga, Al, or Mg (regardless of thermal history) at temperatures between −50°C and room temperature resulted in enhancement of the OH-impurity peaks relative to the unassociated peak, measured at nitrogen temperature (typically by a factor of ~2), although rapid cooling (<2 min) from room to nitrogen temperature essentially preserved the relative heights.

All of the absorption peaks shifted to shorter wavelength as the specimen temperature was reduced, although there were systematic differences in the amount of the shift, as indicated in Table I. The peaks narrowed considerably on cooling to 79°K, and some further narrowing was noted at He temperature. Peak widths varied somewhat from crystal to crystal, particularly at low temperatures, suggesting that lattice strain or perhaps longer-range impurity interactions cause some broadening. The peak widths listed in Table I are the minimum values observed. The unassociated peak was frequently observed to be broadened by several cm^{-1} and appeared in some cases to have unresolved structure. Peak height for the unassociated peaks typically increased by a factor of 2.8 on cooling from 300 to 79°K, with a further increase of $\sim 2x$ on cooling to 10°K.

In all cases, it was found that the optical absorption associated with the H (or D) impurity was >99% dichroic, absorbing only that component of the light with $\mathbf{E} \perp c$.

Absorption peaks uniquely associated with H were also observed at ~3650 and 4350 cm^{-1} at room temperature (Fig. 2) in heavily doped specimens. The heights of these peaks relative to the 3279-cm^{-1} peak were 0.002 and 0.007, respectively. The width of the 3650-cm^{-1} peak was considerably greater than that of the 3279-cm^{-1} peak, so that the integrated absorption ratio would be roughly 0.01. The 4350-cm^{-1} peak is presumably the harmonic absorption of the unassociated

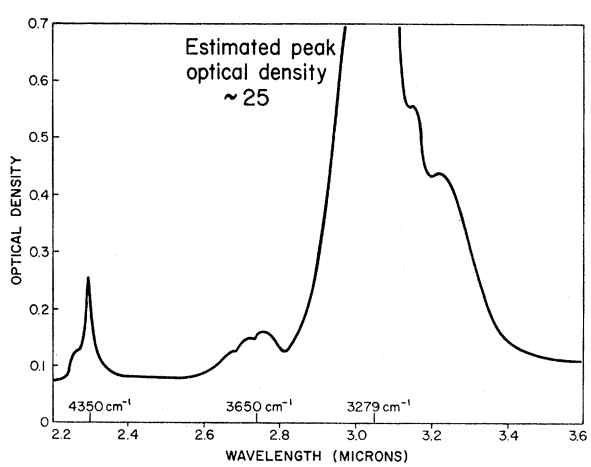

FIG. 2. Optical absorption due to H^+ in specimen with H^+ density of $6.3\times10^{19}/cm^2$, at 300°K ($\mathbf{E}\perp c$ axis). An optical density of 1.0 at 3279 cm^{-1} corresponds to an H^+ density of $\sim 2.5\times10^{18}/cm^2$, evaluated by comparison of free-carrier absorption at 1.5 μ (see Fig. 1) in the same specimen, after allowing for electron-trapping states.

[14] O. W. Johnson, Bull. Am. Phys. Soc. 12, 923 (1967).

OH, while the 3650-cm^{-1} absorption may result from a combination mode. The position of the harmonic absorption peak, if indeed this interpretation is correct, is considerably shifted from the position expected for a rigid harmonic-oscillator potential (6558 cm^{-1}). A careful search was made in the range from the fundamental absorption to 10 000 cm^{-1}; no other absorption peaks with relative amplitude as large as 0.0005 were found. The "combination-mode" absorption can be viewed as resulting from simultaneous excitation of the OH stretching vibration mode and an oscillation mode of the proton perpendicular to the OH dipole moment. A corresponding absorption occurs at $\sim$2800 cm^{-1} for D-doped crystals. No study of the polarization, orientation, or temperature dependence of these absorptions was attempted. As can be seen in Fig. 2, the shape of the 4350-cm^{-1} peak is complex. At these very high doping levels, some structure is also apparent on the long-wavelength side of the 3279-cm^{-1} peak, as was previously reported by Soffer.[4]

Effect of Fe Doping

It is well known that Fe-doped rutile crystals exhibit an enhanced optical absorption near the electronic absorption edge.[9] This has usually been interpreted as resulting from a narrowing of the band gap. In the course of the present work, absorption spectra of Fe-doped crystals in the range 0.4–2 μ with various concentrations of H were studied, in addition to the IR studies discussed above. It was found that the enhanced absorption near the electronic absorption edge occurs only when *both* Fe and a donor impurity such as H are present. The absorption spectra for a 1.3-mm thick specimen with H concentration of $5\times10^{18}/cm^3$ and Fe concentration $>7\times10^{19}/cm^3$ are shown in Fig. 3. These spectra were observed as a function of H concentration up to $7\times10^{19}/cm^3$ (Fe concentration unchanged); the strength of the absorption was proportional to H concentration within experimental limits and no significant changes in the shape of the spectra were observed. Figure 3 represents only the absorption due to H doping, since an identical specimen with negligible H concentration was placed in the spectrometer reference beam. Even when the specimen was doped with 6.7×10^{19} H/cm^3, the usual 1.5-μ free-carrier band appears to be completely absent, thus apparently ruling out the possibility of the darkening being due to normal conduction-band electrons. Furthermore, such a specimen also exhibits moderately high electrical conductivity. Although no detailed studies were undertaken, the resistivity of this specimen when doped with 6.7×10^{19} H/cm^3 was determined, using four-terminal dc measurements, to be $\sim$7.5 Ω cm at 300°K, decreasing monotonically to $\sim$3 Ω cm at 79°K. Both the absorption indicated in Fig. 3 and the normal 1.5-μ free-carrier absorption have been simultaneously observed in crystals with lower Fe concentration and H concentration somewhat greater than the Fe concentration. Thus it seems more plausible to interpret the absorption associated with Fe as resulting from excitation of electrons from acceptor states (or an acceptor band), near the bottom of the gap, to the conduction band. The enhanced conductivity, which occurs only when donor impurities cause these acceptor levels to be populated, would be accounted for on the basis of impurity-band conduction. Existence of significant conductivity in such a band is reasonable in view of the high concentration of Fe, resulting in significant overlap of the electron wave functions. The small enhancement of optical absorption in Fe-doped crystals in the absence of donor impurities could be accounted for by thermal excitation of carriers from the valence band to the impurity states. Interpretation of these phenomena is complicated by the fact that Fe is known to form precipitates[12] when present in these concentrations, and part of the optical absorption is due to these. In fact, the brown coloration that has usually been assumed to be characteristic of Fe-doped specimens can readily be seen with an optical microscope to result from precipitates of a second phase. The specimen described above, with Fe concentration $>7\times10^{19}/cm^3$, was a light yellow when all hydrogen was removed and the crystal was rapidly cooled from $>$800°C. Annealing of the crystal at lower temperatures resulted in formation of the brown precipitates. These could subsequently be redissolved by heating above 800°C and quenching.

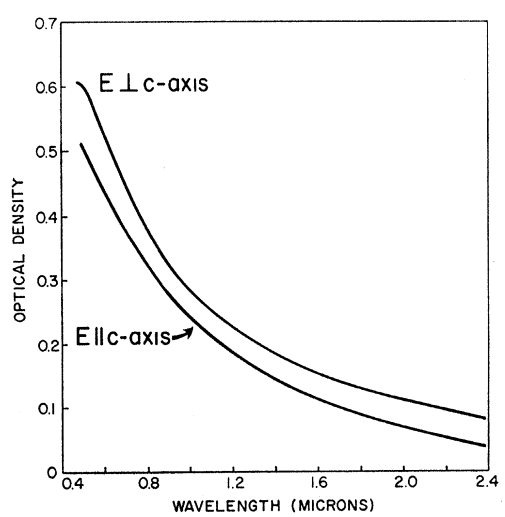

FIG. 3. Optical absorption due to impurity-band carriers in specimen with carrier density of $6.5\times10^{17}/cm^3$, at 300°K.

IV. DISCUSSION AND CONCLUSIONS

Conduction-Band Carrier Absorption

The 1.5-μ absorption band cannot be accounted for on the basis of the simple free-electron absorption predicted by Drude theory. Calculations based only on measured dc conductivity predict absorption much

greater than that observed, and no significant dependence on frequency in the visible and near IR. Furthermore, cooling to 79°K produces an increase of a factor of 8 in the dc conductivity, with no significant change in the 1.5-μ band, in sharp contradiction to predictions of the simple theory. Failure of the Drude theory is, of course, not particularly surprising in view of the polaron nature of the carriers. No attempt has been made to analyze this spectrum in detail; however, it seems most likely that the absorption results from intraband transitions of the conduction electrons and that the structure of the absorption spectrum is a reflection of the density of accessible states, possibly somewhat modified by phonon absorption and emission. The absorption spectra of the Fe-H-doped crystals seem to be consistent with absorption by electrons in an impurity band located a few tenths of an eV above the valence band. The Drude picture again is quite inadequate to account for the absorption.

H^+ (D^+) IR Absorption

Even though the diffusing specie in this case is clearly established as an H^+ (D^+), the IR absorption spectrum is essentially that of the fundamental stretching vibration of an OH (OD) molecule, as was pointed out by Soffer.[4] The apparently complete dichroism of the absorption would seem to rule out the site suggested by von Hippel,[3] and appears to require that the axis of the OH dipole lie in the basal plane of the crystal. Potential calculations, described in detail in the preceding paper,[15] indicate two possible sites for the H^+: $\frac{1}{2}\frac{1}{2}0$ or $\frac{1}{2}00$, both of which lie between neighboring O^{2-} ions. The OH separation distance in various crystals and compounds typically lies in the range of 1.0–1.15 Å, depending only weakly on the crystalline field, so that the H^+ site is doubtless displaced somewhat in either case toward one of the two adjacent O^{2-} ions, since the separation in the two cases is 2.52 and 3.33 Å, respectively. These potential calculations indicate the displaced $\frac{1}{2}\frac{1}{2}0$ site to be more favorable by 1–2 eV, but are probably inadequate to decide between the sites, however, since the results are quite sensitive to OH distance that would doubtless be different. Also, there are several important contributions to the potential that are not taken into account, including the OH repulsive interaction and the alteration of the O^{2-}-dipole energy. Furthermore, the calculations are based on an assumption of point dipoles and thus do not take account in detail of the charge distribution near the O^{2-} ions, which would be quite different for the two sites.

Since the potential calculations did not appear to be conclusive, an attempt was made to extract some information regarding the proton site from computer calculations of the vibrational energy levels of a proton in a double-well potential. These calculations were based on an assumed potential that varied sinusoidally between the two minima and increased harmonically outside the minima. Barrier height was obtained by matching the curvature at the bottom of the potential well to that of a pure harmonic potential that would yield the observed transition energy (3300 cm^{-1}) between the ground and first excited states. As expected, the major effect of the second potential on the single-well harmonic-oscillator wave functions is to split the energy levels. This splitting is usually referred to as the tunneling splitting, because of its intimate relationship to frequency of tunneling of the particle between the two potential wells. The results of the calculations indicate that the absorption line representing transitions from ground to first excited state should be split into two components, since there will be two allowed transitions between the split levels. The predicted splitting of the absorption line was >100 and <0.1 cm^{-1} for the $\frac{1}{2}\frac{1}{2}0$ and the $\frac{1}{2}00$ sites, respectively. The minimum peak widths observed were ~ 3 cm^{-1}; thus it is unlikely that a splitting of 0.1 cm^{-1} could have been detected. Since no structure that could be associated with such a splitting was observed, the $\frac{1}{2}00$ site seems to be the more likely. This conclusion must be taken as tentative, however, until more compelling evidence is available.

The ratio ν_H/ν_D, which is seen from Table I to be ~ 1.345 for rutile, contains (at least in principle) information regarding the anharmonicity of the potential seen by the H^+ (D^+), since the D^+ energy levels are all lower than those of the H^+ and hence departures from a pure harmonic potential would be reflected in the transition energies. The situation is complicated, however, by uncertainty as to the effective mass of the ions. A rough approximation would be to use the reduced mass appropriate to the proton (or deuteron) in an isolated OH (OD) molecule. This assumption would predict $\nu_H/\nu_D = 1.376$, as opposed to $\sqrt{2} = 1.414$ for the same particles in a rigid well, assuming perfect harmonicity. This value is fairly close to the maximum value of ν_H/ν_D that has been observed in a large number of systems for which OH stretching vibrations have been studied.[16] It also seems reasonable to assume that the average potential in the systems being considered increases somewhat more slowly with displacement from the equilibrium site than for a harmonic well, because of the presence of the perturbing well nearby, so that anharmonicity would tend to reduce the ν_H/ν_D value still further. Thus the observed value of $\nu_H/\nu_D = 1.345$ seems to suggest a relatively large anharmonicity for rutile. The ratio of the integrated absorption for the harmonic and the fundamental peaks (~ 0.007 for H^+) also yields information about shape of the potential, since this transition would be forbidden

[15] P. I. Kingsbury, Jr., W. D. Ohlsen, and O. W. Johnson preceding paper, Phys. Rev. **175**, 1099 (1968).

[16] G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Co., San Francisco, Calif., 1960).

for a symmetric potential. Thus these two parameters (the frequency and the relative intensity of the harmonic absorption) give slightly different and in a sense complementary information, since the frequency ratio reflects primarily the width and shape of the well and the ratio of absorption intensities relates mainly to the degree of asymmetry. Elasto-optical studies are planned to obtain additional information regarding the shape of the potential well and also to verify the equilibrium site for the H^+.

No detailed information regarding the position of the substitutional impurity in the Mg-, Al-, and Ga-associated peaks is available. However, the apparently complete dichroism of the absorption suggests that the OH dipole and the trivalent substitutional all line in the basal plane. Also, the 000 cation lattice site is the closest one to the displaced $\frac{1}{2}00$ proton site, making this a likely choice.

Some qualitative conclusions can be drawn regarding the source of the frequency shift for these impurity complexes. It is useful at this point to summarize the relevant data:

(1) Reduction of the lattice constant (with resulting decrease in O-O distance) by cooling results in a shift to higher frequency. This result is the opposite of what one would expect from hydrogen-bonding lore, since negative shifts are normally observed for shorter O-O distances.[16] Presumably, this result reflects the overriding importance of the other nearby ions in determining the frequency. It is interesting to note that the frequency shift can be either positive or negative in crystals, since the analogous spectrum in crystalline quartz was observed to shift by -3 cm^{-1} on cooling from 79 to 10°K.

(2) The smaller the substitutional impurity ion, the larger the shift to higher frequencies (Table I). Al^{3+} has a radius of $\sim$0.50 Å, causing a shift of 48 cm^{-1}, and Ga^{3+} and Ni^{3+} have radii of $\sim$0.62 Å and cause shifts of 31 and 28 cm^{-1}, respectively. Mg^{2+}, with a radius of 0.65 Å, causes a shift of 68 cm^{-1}, but this shift is due in part to the larger effective charge in the lattice. Fe^{3+}, In^{3+}, V^{3+}, and Cr^{3+} either do not form stable complexes or have shift too small to detect; all have radii larger than Ga^{3+} and Ni^{3+}.

(3) The larger the effective charge, the larger the frequency shift.

(4) The binding energy of the H^+ to these impurity complexes must be of the order of kT at room temperature, since the relative concentration is a strong function of temperature in this range.

Presumably, the nearest-neighbor O^{2-} ions relax outward when a Ti^{4+} is replaced with an impurity with charge less than 4, with the outward relaxation being greater for impurities with larger radii. Unfortunately, the conflicting results of hydrogen-bonding data and the low-temperature data discussed in (1) above, plus the complex state of stress near such a defect, do not permit a simple argument indicating the effect of this relaxation on the OH absorption frequency. However, the data discussed in (2) above strongly suggest that the outward relaxation produces a negative shift in frequency. For reasons already discussed, this conclusion is not necessarily inconsistent with other results, such as the low-temperature shifts. To complete the picture, we need only note that the difference in the repulsive force on the H^+ due to the Ti^{4+} or the impurity ($+3$ or $+2$) would result in a decrease in the OH distance for the assumed defect-complex geometry, which would certainly result in a positive frequency shift.

An estimate of the binding energy of the H^+ to the defect complex relative to the perfect lattice can be made by calculating the Coulomb interaction, assuming a bulk dielectric constant of $\sim$80. This calculation yields an energy of 0.04 eV for $+3$ impurities and 0.08 eV for $+2$. This agrees well with the limited experimental data.

Thus, in summary, it appears that the Coulomb interaction of the H^+ and the substitutional impurity results in a positive shift in OH absorption frequency, proportional to the effective charge of the substitutional, which is partially offset by a negative shift due to lattice relaxation, which increases with the ionic radius of the impurity. More detailed data are required to verify these conclusions. Studies of the kinetics of formation of these defect complexes are planned.

Miscellaneous

A rough estimate of the binding energy of H^+ to the rutile lattice can be obtained from the observed pressure dependence of the equilibrium H^+ concentration. Note that this binding energy will be a strong function of H^+ concentration in the lattice (among other things), since any change in the electron Fermi level of the crystal will be reflected directly in the H^+ binding energy. Thus accurate evaluation of this parameter will require detailed knowledge of the energy bands and impurity levels of the crystal. Alternatively, very precise measurements of equilibrium H^+ concentration as a function of temperature and ambient H_2 partial pressure could be used to infer both the trap density and energy levels in a particular crystal, as well as the density of states near the bottom of the conduction band. The effect of the Fermi level on the H solubility (and other donor impurities as well) will be unusually large in rutile, since the Fermi level may be expected to shift from near the valence band (as determined by traps associated with impurities such as Fe^{3+}) to within a few meV of the conduction band as the electron trapping levels are filled, which may constitute a change of as much as 3 eV per atom. Referred to gaseous H_2 as the "standard" state, the binding energy per atom appears to be of the

order of 1.3 eV when E_F is near the bottom of the conduction band.

The unusually high affinity of rutile for H suggests the possible usefulness of thin films or filaments of this material as a simple, sensitive H_2 detector. Such a device has recently been made using WO_3.[17] The usable range and sensitivity of such a device fabricated from rutile could be extended by doping with Fe and utilizing conduction in the impurity band as a means of H detection. Detection of H_2 partial pressures as low as 10^{-13} Torr or lower should be possible.

Little information regarding diffusion mechanisms for the substitutional impurities utilized in this investigation is currently available. However, the observed diffusion rates are consistent with diffusion activation energies estimated from the calculations outlined in the preceding paper,[15] assuming that the impurities diffuse as positively charged interstitials. The diffusing impurity then apparently displaces a lattice Ti, forming a Ti^{4+} interstitial, thus accounting for the observed reduction of the crystal upon doping with Fe, Al, etc. Subsequent reoxidation of the crystal would result from migration of $\frac{3}{4}$ of the Ti interstitials to the surface for recombination with O_2, leaving behind one Ti^{4+} interstitial for every four Fe^{3+} substitutionals, resulting in complete compensation of the crystal (i.e., no extrinsic free carriers of either sign). Thus the chain of reactions that occurs when a crystal is doped with Fe and then reoxidized is

$$4\text{Fe (metal)} \rightarrow 4\langle\text{Fe}\rangle^{3+}+12e^-,$$
$$4\langle\text{Fe}\rangle^{3+}+4[\text{Ti}]^{4+} \rightarrow 4[\text{Fe}]^{3+}+4\langle\text{Ti}\rangle^{4+},$$
$$3\langle\text{Ti}\rangle^{4+}+12e^-+3\text{O}_2\text{ (gas)} \rightarrow 3\text{TiO}_2,$$

where $\langle\ \rangle$ represents an interstitial defect and $[\ ]$ represents an ion in a substitutional site. It is not yet clear at what stage the second reaction occurs. The net reaction for the whole process is then

$$4\text{Fe (metal)}+4[\text{Ti}]^{4+}+3\text{O}_2\text{ (gas)} \rightarrow 4[\text{Fe}]^{3+}+\langle\text{Ti}\rangle^{4+}+3\text{ TiO}_2.$$

Presumably, the other substitutional impurities studied (Al^{3+}, Ga^{3+}, Ni^{3+}, and Mg^{2+}) behave in an analogous way, except for their smaller solubilities. This interpretation is consistent with EPR results,[1] which indicate a substantial concentration of Ti^{4+} interstitials in Fe-doped crystals, even after strong oxidation. The ease of formation of Ti interstitials is thus seen to account for the lack of *p*-type conductivity in rutile. It may, of course, be possible to induce some *p*-type conductivity by treatment with some combination of temperature, ambient atmosphere, etc., as suggested by the work of von Hippel[3]; it is also possible that his observation of weak *p*-type behavior resulted from conduction in the Fe impurity band discussed above.

Failure to observe B^{3+} diffusion would seem to require that its diffusion activation energy be larger than that for Ti^{4+}. This observation cannot be accounted for simply on the basis of the contributions to the potential energy calculated in the preceding paper[15] (point ion, O^{2-} dipole, repulsive and lattice polarization), since these calculations would predict a smaller activation energy for B^{3+} than for Ti^{4+}. However, these calculations do not allow for the effect of relaxation in the immediate neighborhood of the interstitial. Any such relaxation will tend to raise the diffusion energy, of course. The O^{2-} nearest neighbors apparently relax inward for any of the cations that have been studied, since the attractive force between the interstitial and the O^{2-} ion would be greater than the repulsive force in the absence of relaxation. For example, the (rigid-lattice) forces on an Li^+ ($R\sim0.60$ Å) in a $\frac{1}{2}00$ site are 4.65 repulsive and 10.3 eV/Å attractive (using the parameters described in Ref. 15). Thus such relaxation can be expected to contribute somewhat to the activation energy, with larger contributions for smaller ions and ions with larger charge. B^{3+}, with a radius ≈0.21 Å, would experience attractive and repulsive forces of ~30.9 and 1.55 eV/Å, respectively, so that considerable relaxation is to be expected. If the relaxation energy is assumed to be approximately proportional to the square of the unbalanced force on the neighboring O^{2-} ions (i.e., linear elasticity), the relaxation energy for B^{3+} would be greater than that for Li^+ by a factor of 25. This conclusion is clearly not realistic, but does indicate that a relatively large diffusion energy for B^{3+} should not be surprising. [Diffusion measurements for Be^{2+} ($R=0.31$ Å) would provide a critical test of this interpretation.] In fact, the imbalance in the forces on the B^{3+} is so great as to make an "off-center" site appear quite likely. Similar displacement of the Ti^{4+} is also possible.

Note added in proof. V. N. Bogomolov *et al.* [Fiz. Tverd. Tela **9**, 2077 (1967) [English transl.: Soviet Phys.—Solid State **9**, 1630 (1967)]] recently published data on optical absorption due to conduction electrons in reduced rutile which are in approximate agreement with our results. An analysis of the absorption spectrum in terms of polaron theory was attempted. Subsequent study of analogous absorption spectra in CoO and NiO by I. G. Austin *et al.* [Solid State Commun. **6**, 53 (1968)] shows good agreement with the Bogomolov theory.

[17] P. J. Shaver, Appl. Phys. Letters **11**, 255 (1967).