from zero, i.e.,

$$\frac{\partial}{\partial\beta_j}\left\langle x_n\frac{\partial a_i}{\partial x_n}\right\rangle_{\text{Av}}-\frac{\partial}{\partial\beta_i}\left\langle x_n\frac{\partial a_j}{\partial x_n}\right\rangle_{\text{Av}} =\left\langle x_n\left[\frac{\partial a_i}{\partial x_n}(a_j+\langle a_j\rangle_{\text{Av}})-\frac{\partial a_j}{\partial x_n}(a_i+\langle a_i\rangle_{\text{Av}})\right]\right\rangle_{\text{Av}}\neq 0,$$

$$\text{with}\quad i,j=1,2,\cdots t. \tag{11}$$

To conclude, we have derived an equipartition principle of generalized canonical ensembles and shown it to be useful in the calculation of certain interesting averages of functions of the parameters of a system. Needless to say, the averages thus found often can be obtained by other methods perhaps more directly. This is, of course, true also of the equipartition of energy in equilibrium statistical mechanics.

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Electrical Properties of Titanium Dioxide Semiconductors

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Measurements have been made of the electrical resistivity and Hall coefficient of semiconducting rutile both in the form of ceramics and single crystals from −190°C to +500°C. The samples were reduced in pure hydrogen for various times and temperatures to provide a range of resistivities, all corresponding to rather large numbers of charge carriers. The single crystal samples were measured in different orientations to study the directional dependence of resistivity and mobility. From these measurements the variations of mobility and charge carrier concentration with temperature have been determined. The mobility data can be satisfactorily described in terms of an electron scattering by the optical modes of lattice vibration predominant at high temperatures combined with a scattering by ionized impurities predominant at low temperatures. The low values of the mobility in all samples indicate an anomalously large effective electron mass. In the crystalline samples the mobility in the *c* direction is approximately twice as great as in the *a* direction. The data on the temperature dependence of the electron concentration may be represented by a sum of two Boltzmann terms, indicating two types of donor centers. It is suggested that these centers may be oxygen ion vacancies at which one or two electrons are trapped as Ti^{+3} ions. An energy level diagram is proposed which explains many of the electrical and optical observations on rutile semiconductors.

I. INTRODUCTION

It has been known for some time that titanium dioxide of nonstoichiometric composition containing an excess of titanium is an *n* type semiconductor with properties showing promise of practical utility.[1–6] These previous studies on titania semiconductors, however, had not obtained information about the electron mobility and the number of charge carriers in this material although this information is needed for a detailed analysis of the conduction process. Recently synthetic single crystals of titanium dioxide in the form of rutile have become available,[7] and it seemed desirable to investigate the electrical properties of semiconducting crystals and compare them with the properties of highly purified titanium dioxide ceramic semiconductors. Similarly, since rutile is tetragonal, an investigation of the electron mobilities in the two crystal directions would be expected to be instructive.

For such a study of the electron mobility and number of charge carriers in a semiconductor, two measurements are needed. The measurements chosen here are the electrical resistivity and Hall coefficient over a wide temperature range. Such measurements have been made on both ceramic and single crystal samples. Both for convenience in making the Hall effect measurements and because of the practical interest in the properties of relatively good conducting titania semiconductors, our measurements have been concerned with samples that have been reduced in hydrogen at elevated temperatures so that their resistivities are in the range 0.1 to 100Ω cm. The study of these reduced materials is also useful in that it is possible to observe the variation of the properties with temperature independent of changes in the oxide composition which is the predominant factor in studies on the pure oxide. As a result of this simplification it is possible to observe a number of details in properties that are normally masked by larger effects or unmeasurably small. It will be shown that the observations on these highly conducting materials can tentatively be correlated with other studies on rutile to produce a reasonably consistent picture of the energy levels in rutile.

II. PROPERTIES OF TITANIUM DIOXIDE

Titanium dioxide crystallizes in three modifications: rutile, anatase, and brookite. Of these, rutile is the form

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[1] W. Meyer, Physik. Z. **36**, 749 (1935).
[2] W. Meyer and H. Neldel, Physik. Z. **38**, 1014 (1937).
[3] M. Earle, Phys. Rev. **61**, 56 (1942).
[4] Von Hippel, Breckenridge, de Bretteville, and Brownlow, Massachusetts Institute of Technology Laboratory for Insulation Research Report N.D.R.C. 540, October, 1945 (unpublished).
[5] H. K. Henisch, Elec. Commun. **25**, 163 (1948).
[6] R. G. Breckenridge and W. R. Hosler, J. Research Natl. Bur. Standards **49**, 65 (1952).
[7] National Lead Company, South Amboy, New Jersey; Linde Air Products Company, North Tonowanda, New York.

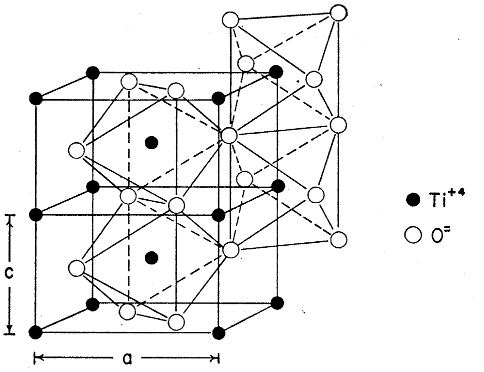

FIG. 1. Crystal structure of rutile (TiO$_2$).

stable at temperatures greater than 820°C and is the one obtained on firing ceramic samples of TiO$_2$. The crystal structure of rutile is tetragonal with $a=4.4923$A and $c=2.8930$A,[8] as shown in Fig. 1. The structure may be considered as built up from somewhat distorted TiO$_6$ octahedra, the octahedra forming chains in the c direction, each octahedron sharing an edge with the adjacent members of the chains. The crystal density is 4.26 g/cm^3 from x-ray measurements.

The dielectric properties of rutile are rather unusual and have been studied on both single crystals and ceramics. It was found by Schmidt[9] that in single crystals of rutile the dielectric constant in the c direction was 173 and in the a direction 89. An average value of 114 for a randomly oriented ceramic is computed from these results in rough agreement with the value *ca* 100 found experimentally for densely fired ceramic samples.[10] When care is taken to prevent the loss of oxygen during firing of the ceramics, the dielectric loss of rutile is very low, values of $\tan\delta \cong 0.0003$ at 10^3 cps[10] being typical. This corresponds to a room temperature resistivity *ca* $10^{13}\Omega$ cm.

The optical properties of rutile are also of interest, particularly as they shed some light on the electrical properties to be considered later. The refractive index at 5896A of rutile is 2.903 in the c direction and 2.616 in the a direction.[11] The optical transmission in rutile has been measured for single crystals by the Radiometry Section of the National Bureau of Standards (Fig. 2) and will be described in detail elsewhere. It was found that there is a strong absorption band at about 4100A at room temperature with no other marked absorption in the visible region of the spectrum. Measurements at infrared wavelengths show a strong absorption at about 7 microns. This is in agreement with the observations of Cronemeyer and Gilleo[12,13] and also agrees with observations of the reflection from natural rutile single crystals made by Liebisch and Rubens[14] who extended their measurements to 300μ. It has been shown[10] that the measurements of Liebisch and Rubens can be satisfactorily explained by assuming two fundamental vibrations at 180 cm^{-1} and 500 cm^{-1}, the one at 180 cm^{-1} corresponding to a deformation of the TiO$_2$ groupings, and that at 500 cm^{-1} to a valence vibration of the titanium relative to the oxygen.

III. TITANIUM DIOXIDE SEMICONDUCTORS

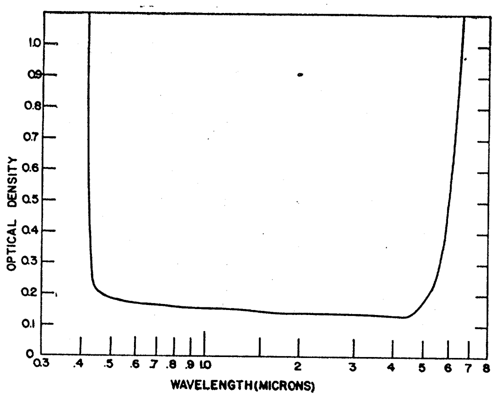

FIG. 2. Optical density of clear rutile.

When the titanium dioxide is treated so as to cause a loss of oxygen in the lattice either by heating in a low oxygen pressure or in hydrogen, the material becomes an n type semiconductor whose properties depend on the extent of oxygen loss.[1-6] Several previous observations on the conductivity of unreduced rutile show a dependence on the equilibrium conditions of temperature and oxygen pressure. Earle[3] has found that

$$\sigma \sim P\mathrm{O}_2^{-1/\alpha}, \tag{1}$$

with $\alpha=4.3$ for oxygen pressures greater than 30 mm Hg. At lower pressures the α was variable ranging from 2 at low temperatures to 3 at higher temperatures. Earle's measurements of conductivity as a function of temperature showed an exponential relation

$$\sigma=\sigma_0 e^{-\Delta E/kT}, \tag{2}$$

with $\Delta E=1.7$ ev for fired ceramics. A similar temperature dependence with values of $\Delta E=1.834$ ev for $T>900$°C and $\Delta E=1.526$ ev for $T<900$°C has been reported by Cronemeyer[13] for single crystals of unre-

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[8] R. W. G. Wyckoff, *Crystal Structures Handbook* (Interscience Publishers, New York, 1948).

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[10] E.g., von Hippel, Breckenridge, Chesley, and Tisza, Ind. Eng. Chem. **38**, 1097 (1946).

[11] A. Schröder, Z. Krist. **67**, 485 (1928).

[12] D. C. Cronemeyer and M. A. Gilleo, Phys. Rev. **82**, 975 (1951).

[13] D. C. Cronemeyer, Massachusetts Institute of Technology, Laboratory for Insulation Research Technical Report 46, August, 1951 (unpublished); Phys. Rev. **87**, 876 (1952).

[14] T. Liebisch and H. Rubens, Sitzber. preuss. Akad. Wiss., Physik-math. Kl. **211** (1921).

duced rutile, the same values of ΔE being found for both crystal directions.

When the material is reduced an increased optical absorption at longer wavelengths is noted, the crystals become blue in color and on continued reduction opaque. This is shown in Fig. 3 for a slightly reduced crystal (2.5 min in H_2 at 600°C) measured at the National Bureau of Standards. It will be noted that the absorption of 0.41μ and 7μ are apparently unchanged by the treatment, but a broad absorption band centered at about 1.2μ is introduced. Prior to the present work no detailed studies have been reported on the conductivity and Hall coefficient of such reduced materials. However, the measurements available have indicated a typical exponential variation of the conductivity with temperature [Eq. (2)] with an activation energy $\Delta E \cong 0.2 - 0.3$ ev[4,5,13] between room temperature and about 200°C. A similar activation energy was found from studies of the thermoelectric power.[5] These preliminary studies have now been extended sufficiently to allow a rather detailed picture to be drawn of the electrical properties of titania semiconductors.

IV. EXPERIMENTAL PROCEDURE

The ceramic samples studied in this investigation were fired from very high purity rutile by the Porcelain and Pottery Section of the National Bureau of Standards. A spectroscopic analysis of the samples showed that the chief impurity was aluminum present in amounts $\leqslant 0.001$ percent, all others being $\leqslant 0.0005$ percent. The firing temperature was 1450°C, and the samples were held at this temperature two hours. The density was measured[15] to be 4.10 g/cm^3. The color of the fired ceramic was rather gray, indicating some loss of oxygen in the firing. Using a small diamond saw, the fired ceramics were cut into rectangular parallelepipeds *ca* 1 mm×3 mm×10 mm. After cutting, they were lightly ground with No. 600 Alundum and washed.

The rutile crystals studied included a crystal obtained from the National Lead Company and one from the Linde Air Products Company. Spectroscopic analyses of the crystal showed the presence of Ba as a chief impurity *ca* 0.01 percent, minor impurities of Al and Mg present in amounts of 0.001 to 0.01 percent, with traces of Ag, Cu, Ca, and Fe in both cases. The Linde crystal also contained a minor amount of Pb. The alkalies, if present, are in amounts less than 0.05 percent.

The crystallographic axes of these boules were determined by an x-ray study in the Mineral Products Section of the Bureau, and samples of approximately the same size as the ceramics were cut from the boule using the diamond saw. Cuts were made with the c axis in the thickness direction and with the c axis parallel with the length of the sample. These crystals were also lightly ground with Alundum and washed.

Although no detailed investigation of the reduction process was attempted, an effort was made to treat the samples under controlled conditions. For reduction, the samples of both ceramic and single crystal were placed on a small platinum cradle in a combustion boat to allow free access of the hydrogen to the entire sample and placed in a 1-inch diameter quartz tube, heated by a tube furnace, the temperature of which was controlled to ±5°C. A preliminary calibration showed that the indicated and actual temperature agreed within ±5°C at the center of the furnace. In order to control the time of reduction the furnace was heated to the desired temperature with purified helium gas flowing slowly through the tube, then pure hydrogen obtained by passing tank hydrogen through a dry-ice trap and a charcoal trap at liquid nitrogen temperature was admitted to the system. After the desired reduction, the hydrogen was again swept out with helium, and after a further heating at the peak temperature for about twenty minutes to insure sample homogeneity, they were cooled to room temperature under helium. The ceramic samples were reduced for ten minutes at temperatures ranging from 600°C to 900°C and for three different times at 800°C. Appropriate conductivities were usually obtained in the single crystals by reduction for five minutes for the same range of temperatures although in a few cases a longer time was required. The precautions described were, in general, sufficient to produce a reasonably regular dependence of the number of charge carriers, etc. on the times and temperatures of reduction although in a few cases anomalous values were found for some unknown reason.

The electrical conductivity and Hall effect measurements were made on a dc instrument of conventional design shown schematically in Fig. 4. The magnet produced a homogeneous field over a volume much larger than the sample, the field strength being *ca* 4000 gauss at the sample with a gap of $1\frac{3}{8}$ in. The field was measured with a Leeds and Northrup fluxmeter. The temperature was measured by a calibrated Chromel Alumel thermocouple in close proximity to the sample. The measurement of resistivity was made by the

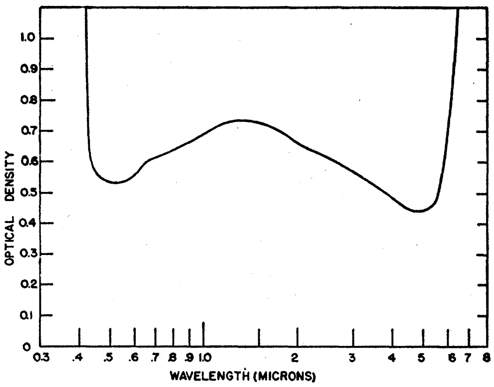

FIG. 3. Optical density of slightly reduced rutile.

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[15] Determined by the Capacity, Density and Fluid Meters Section of the Mechanics Division of the National Bureau of Standards.

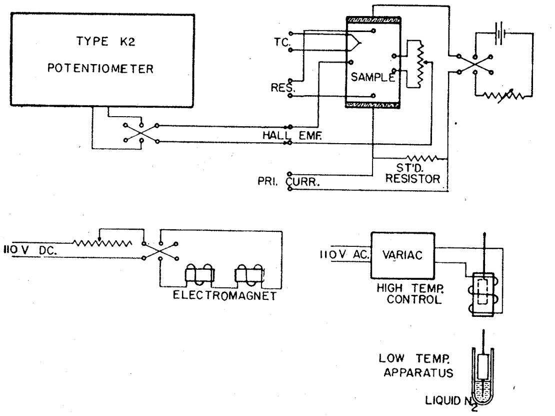

FIG. 4. Schematic diagram of equipment for Hall effect and resistivity measurements.

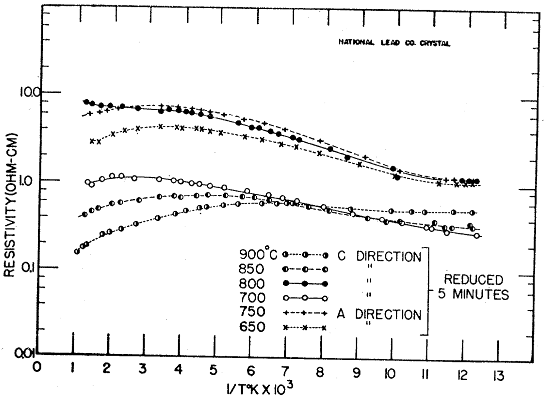

FIG. 5. Resistivities of reduced National Lead Company rutile single crystals.

potential probe method. A three-electrode system was used for the Hall effect measurements; in this way difficulties with electrode asymmetries are eliminated. The primary current through the sample was controlled by a resistance box and was measured from the voltage drop across a precision 8-ohm resistor. All emf's were measured with a Leeds and Northrup Type K-2 potentiometer.

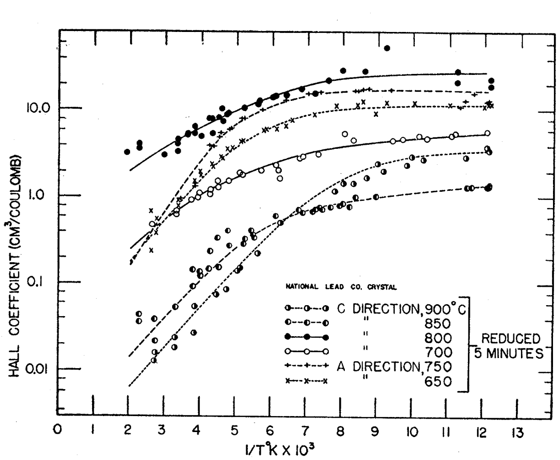

FIG. 6. Hall coefficients of reduced National Lead Company rutile single crystals.

The sample holder consisted of a thin quartz plate carrying small binding posts for the electrical leads. These leads were 20-mil platinum-rhodium wire sharpened and sprung into contact with the sample. They were then soldered to the sample with indium metal. Even though measurements were made at temperatures above the melting point of the indium, no difficulties were experienced since the indium wets the TiO_2 and is held in place by its surface tension. The quartz plate was bolted to a half-round brass backing plate to aid in maintaining a uniform sample temperature. The brass backing plate was supported on a rod and the electrical leads were brought out from the sample holder through Teflon spacers mounted on the rod. For high temperatures the rod was brass, but for low temperatures it was of Bakelite in order to provide thermal insulation.

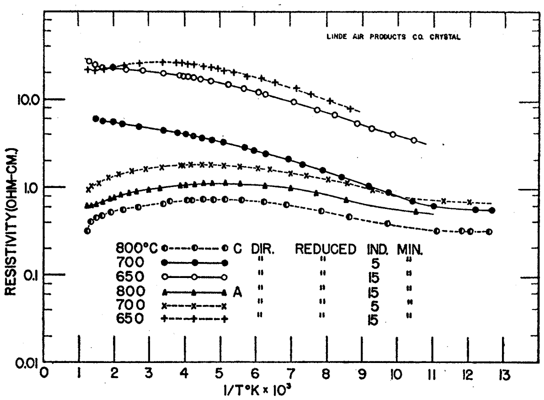

FIG. 7. Resistivities of reduced Linde Air Products Company rutile single crystals.

The low temperatures were obtained by cooling the sample holder in a small covered Dewar flask containing liquid nitrogen. This flask in turn was surrounded by a larger Dewar flask also containing liquid nitrogen. High temperatures were obtained with a small tube furnace. In both cases temperature fluctuations were avoided by enclosing the sample.

In the measurement of conductivity, some potential probe studies were made to investigate the possibility of field distortion in the samples. No such effects were noted with fields of the magnitude used for measurement (<0.5 volt/cm). The variation of Hall effect with primary current was also investigated and found to be linear for currents used in these measurements.

V. RESULTS

The results of measurements of the resistivities of National Lead Company crystal samples plotted as logρ in Ω cm as a function of the reciprocal of the absolute temperature are shown in Fig. 5. A linear dependence of logρ as a function of $1/T$ is not observed; instead, the resistivity varies only slightly over the entire temperature range in a manner resembling that found for degenerate or partially degenerate semiconductors in other cases.[16,17] With the apparatus available it was not possible to observe the intrinsic conductivity at high temperatures since the material begins to reoxidize at temperatures much above 500°C in air.

The Hall voltages for these samples were measured as a function of temperature and the Hall coefficient R in cm^3/coulomb calculated from the relation

$$R=10^{-8}V_H t/HI, \tag{3}$$

where V_H is the Hall voltage in volts, t the sample thickness in cm, H the magnetic field in gauss, and I the current in amperes. For the sample sizes used the shorting effect of the current electrodes is small. For all samples the sign of R was always negative, indicating conduction by electrons. The measurements of Hall voltage were made in two of the three orientations possible for rutile. Those designated as c direction are with the primary current parallel to the c axis, those designated as a direction are with I perpendicular to c and H parallel to c. Appropriate size samples with the third possible orientation could not be cut from the crystals on hand. The values of log$R$ plotted as a function of the reciprocal temperature are given in Fig. 6. For all samples log$R$ changes very slowly with temperature at low temperatures but shows a more pronounced linear dependence on the reciprocal temperature at somewhat higher temperatures.

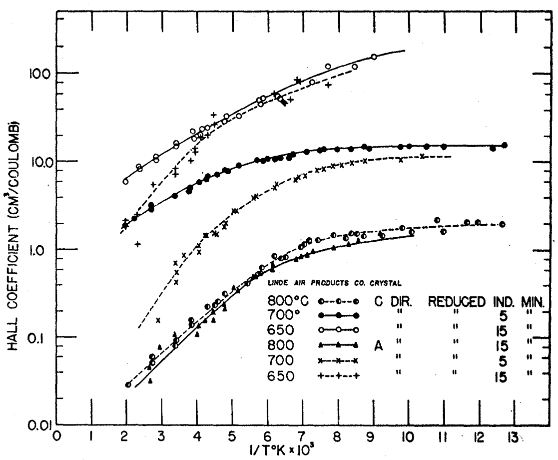

FIG. 8. Hall coefficients of reduced Linde Air Products Company rutile single crystals.

Similar measurements on the Linde crystal are shown in Figs. 7 and 8 and on the pure ceramics samples in Figs. 9 and 10. In all cases the same characteristic features are found.

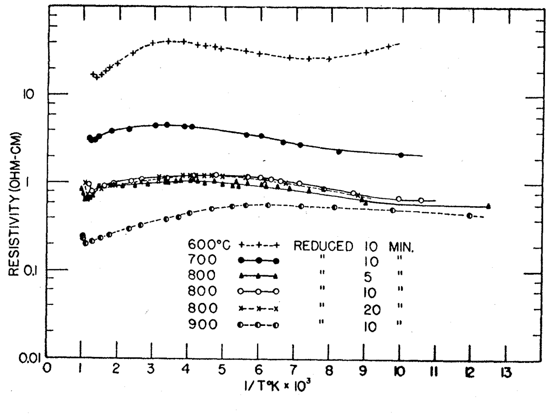

FIG. 9. Resistivities of reduced rutile ceramics.

From the measured values of the Hall coefficient R, the number of charge carriers n_ϵ present in the sample may be calculated using the relation

$$R=-(3\pi/8e)[G(\zeta)/n_\epsilon], \tag{4}$$

where $G(\zeta)$ is a function of the Fermi level varying between 1 for nondegenerate samples to $8/3\pi$ for completely degenerate samples.[18] From evidence to be described later in this paper, it may be shown that, even though the numbers of charge carriers are large, the samples are not degenerate; hence, $G(\zeta)$ was assumed to be 1. Then the number of charge carriers per cm^3 is given by

$$n_\epsilon=-7.40\times10^{18}/R, \tag{5}$$

where R is in cm^3/coulomb.

Similarly, the Hall mobility, μ_H, in cm^2/volt sec is given by the relation

$$\mu_H=1/ne\rho=-(8/3\pi)(R/\rho), \tag{6}$$

for ρ in ohm^{-1} cm^{-1}.

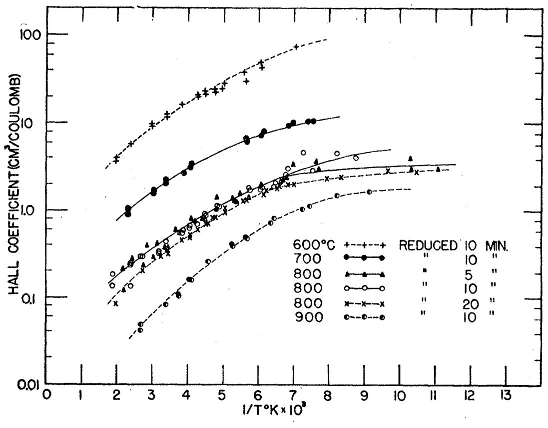

FIG. 10. Hall coefficients of reduced rutile ceramics.

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[17] G. Busch and H. Labhart, Helv. Phys. Acta **19**, 463 (1946).

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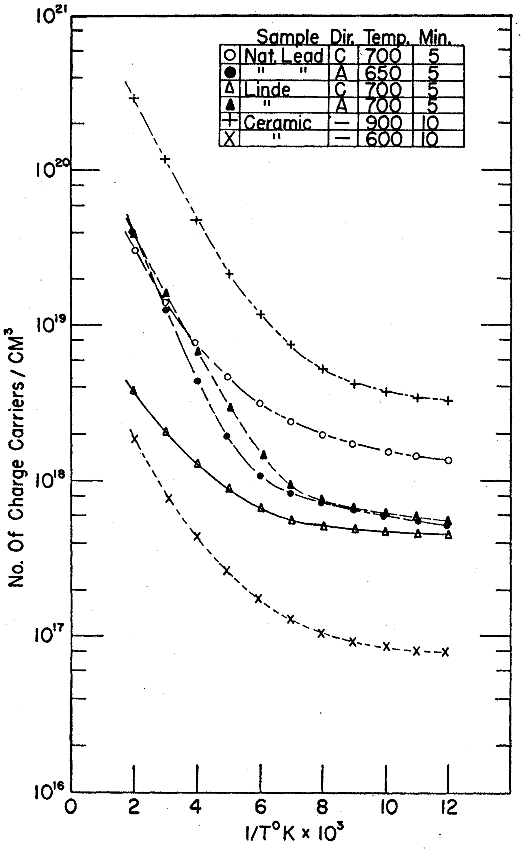

FIG. 11. Electron concentrations in reduced TiO_2 samples.

VI. ELECTRON CONCENTRATIONS IN RUTILE

The number of charge carriers n_ϵ at various temperatures was calculated from Eq. (5). Representative results are shown in Fig. 11 for the various samples. A reasonably satisfactory description of the change of n_ϵ with temperature can be given for all samples with a simple expression of the form

$$n_\epsilon = n_1^0 e^{-\Delta E_1/2kT} + n_2^0 e^{-\Delta E_2/2kT}, \tag{7}$$

with $\Delta E_1 \ll \Delta E_2$ and $n_1^0 \ll n_2^0$. This suggests two sources of conduction electrons, one of which has a very small activation energy so that it was considerably ionized even at liquid air temperature. For most of the samples satisfying this relation, the values of n_ϵ were large enough to indicate a degenerate behavior as calculated from the well-known relation between n_ϵ and the degeneracy temperature,

$$T_0 = \frac{h^2}{8km^*}\left(\frac{3}{\pi}\right)^{\frac{2}{3}} n_\epsilon^{\frac{2}{3}} = 4.2\times 10^{-11} n_\epsilon^{\frac{2}{3}}, \tag{8}$$

if the effective electron mass m^* is taken to be the free electron mass; hence the validity of the Boltzmann expression was surprising. However, observations on the electron mobility in rutile to be described later in this paper indicate that the effective electron mass is much larger than the free electron mass, and, if the effective masses found from the mobility data are used in Eq. (8), it is found that our samples are not degenerate in the temperature range covered. The values of n_1^0, n_2^0, ΔE_1, and ΔE_2, obtained by fitting the two terms to the observed values of n_ϵ at high and low temperatures, are given in Table I. The activation energies show a dependence on n_ϵ, but the dependence is not as clearly indicated as in the silicon case,[16] and actually is in the opposite direction, i.e., ΔE increases for increasing n_ϵ.

VII. ELECTRON MOBILITIES IN RUTILE

The values of the Hall mobility μ_H found using Eq. (6) are of the order of 0.1 to 1.0 cm^2/volt sec at room temperatures for both the single crystal samples and the ceramics, although the ceramics have the smaller values. An interpretation of the observations on electron mobilities in rutile may be given using the theoretical treatment of the scattering of slow electrons by the optical lattice vibrations developed by Fröhlich and co-workers.[19,20] This work showed that the microscopic mobility μ_m is given as

$$\mu_m = A_i(e^{\theta/T} - 1), \tag{9}$$

where A_i is a constant and θ is the Debye temperature. In reference 20 it was shown that

$$A_i = \frac{1}{(m^*)^{\frac{3}{2}}}\,\frac{h^2}{e}\,\frac{\sqrt{3}}{2\pi^{5/2}}\,\frac{K_s'K_\infty'}{K_s' - K_\infty'}\,\frac{1}{(k\theta)^{\frac{1}{2}}}, \tag{10}$$

where K_s' and K_∞' are the static and optical dielectric constants. In the absence of any detailed information as to the relation between μ_H and μ_m in this material,

TABLE I. Properties of rutile semiconductors.

Sample	ΔE_1 ev	ΔE_2 ev	n_1^0 No./cm^3	n_2^0 No./cm^3	A cm^2/volt sec	$\beta = \frac{m^*}{m}$	N_I No./cm^3
National Lead Company crystal							
700 *c*	0.011	0.14	2.73×10^{18}	1.29×10^{20}	0.063	37	7.60×10^{19}
800 *c*	0.0	0.12	2.90×10^{17}	1.44×10^{19}	0.055	43	5.16×10^{19}
850 *c*	0.018	0.20	1.82×10^{19}	5.91×10^{21}	0.011	125	2.60×10^{20}
900 *c*	0.018	0.19	7.95×10^{18}	1.01×10^{22}	0.010	133	1.18×10^{20}
650 *a*	0.0094	0.21	1.06×10^{18}	4.18×10^{20}	0.033	60	1.20×10^{20}
750 *a*	0.0043	0.25	5.41×10^{17}	8.41×10^{21}	0.033	60	9.85×10^{19}
Linde Air Products Company crystal							
650 *c*	0.0091	0.11	6.39×10^{16}	3.43×10^{18}	0.077	34	8.42×10^{18}
700 *c*	0.0	0.12	4.50×10^{17}	1.30×10^{19}	0.094	29	5.00×10^{19}
800 *c*	0.0044	0.16	4.42×10^{18}	1.47×10^{21}	0.016	46	1.39×10^{20}
650 *a*	0.0065	0.18	8.62×10^{16}	2.83×10^{19}	0.050	46	2.02×10^{19}
700 *a*	0.0062	0.17	8.38×10^{17}	2.59×10^{20}	0.044	49	5.80×10^{19}
800 *a*	0.010	0.15	6.87×10^{18}	1.29×10^{21}	0.0084	114	2.33×10^{20}
National Bureau of Standards ceramic							
600–10	0.0056	0.14	1.13×10^{17}	8.37×10^{18}	0.023	77	4.21×10^{20}
700–10	0.0078	0.14	7.66×10^{17}	4.04×10^{19}	0.046	48	2.35×10^{20}
800–10	0.0084	0.12	2.12×10^{18}	1.58×10^{20}	0.033	60	1.32×10^{20}
900–10	0.0069	0.16	5.07×10^{18}	1.83×10^{21}	0.021	81	2.94×10^{20}
800–5	0.0037	0.14	2.19×10^{18}	2.86×10^{20}	0.038	55	2.15×10^{20}
800–20	0.0053	0.16	2.94×10^{18}	4.64×10^{20}	0.030	64	3.13×10^{20}

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[19] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 496 (1939).

[20] Fröhlich, Pelzer, and Zineau, Phil. Mag. **41**, 221 (1950).

they may be assumed equal without serious error. We thus may use the experimentally determined values of A_i to find the effective electron mass if a value of θ is available.

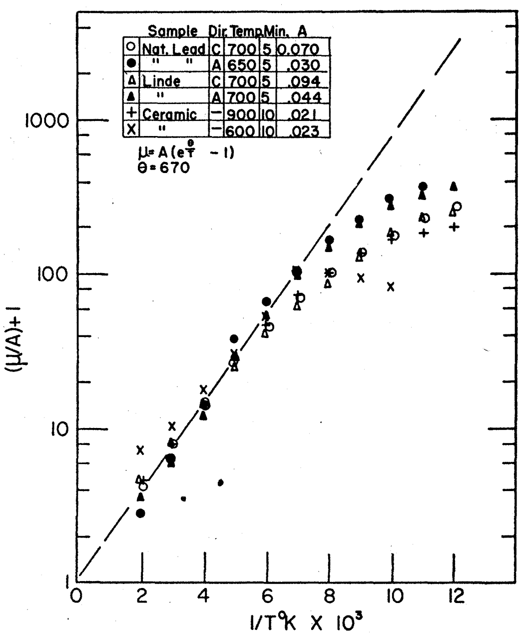
The choice of θ may be made in several ways. Studies of the specific heat of rutile[21] have indicated that an Einstein function with a characteristic θ of 670°K will describe the heat capacity measurements in the temperature range of interest here.

An independent estimate of θ may be obtained from the infrared studies previously mentioned.[10,14] In reference 19 it was shown that

$$\theta = (he/k\lambda_t)(K_s'/K_\infty')^{\frac{1}{2}}, \tag{11}$$

where λ_t is the longest wavelength of the optical absorption in the infrared. Using the band at 180 cm^{-1}, θ_a is found to be 936°K and θ_c is 1161°K. It was found that somewhat better agreement at higher temperatures could be obtained for almost all samples using $\theta = 670$°K instead of the larger θ's calculated from Eq. (11), so this value was adopted.

A plot of $\log[(\mu/A_i)+1]$ as a function of $1/T$ for a number of samples is shown in Fig. 12. The values of A for the various samples were chosen to give the best agreement at temperatures slightly above room temperature. As will be shown, the deviations observed at low temperatures can be explained as an impurity scattering contribution. The most pronounced deviations at high temperatures are observed for the crystal samples. This is probably an effect of the crystal anisotropy. Different values of θ, although possibly differing from those calculated from Eq. (11), should be used in the two directions for the single crystal results, while in the ceramic an average value would be anticipated. Such an average presumably is obtained from the heat capacity measurements.



	Sample	Dir.	Temp.	Min.	A
○	Nat. Lead	C	700	5	0.070
●	" "	A	650	5	.030
△	Linde	C	700	5	.094
▲	"	A	700	5	.044
+	Ceramic	—	900	10	.021
X	"	—	600	10	.023

FIG. 12. Electron mobilities in reduced TiO₂ samples.

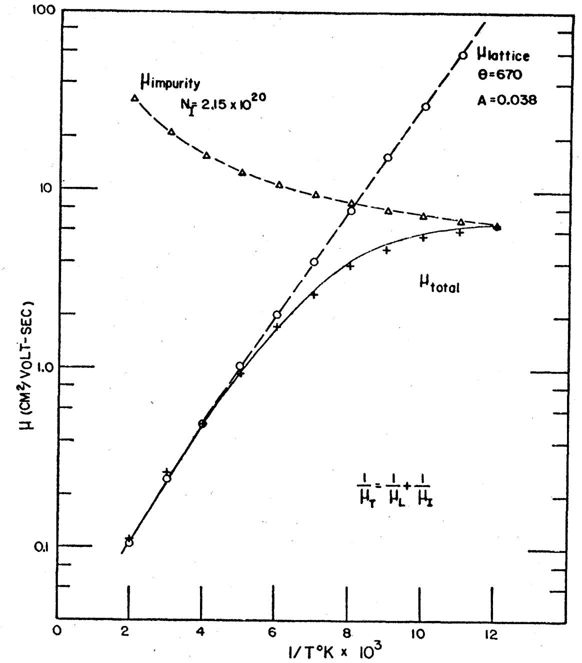


FIG. 13. Impurity and lattice scattering of electrons in reduced rutile ceramics.

Of particular interest are the effective electron masses calculated from the empirical values of A in Eq. (10). Using $\theta = 670$°K and averaged values for K_s' and K_∞', one finds values of m^* to be 30 to about 100 times the free electron mass. These results are given in Table I.

Scattering of the electrons by acoustic vibrations is apparently negligible in these materials, since the data cannot be satisfactorily described by a $T^{-\frac{3}{2}}$ term which is predicted for this effect.[22]

At low temperatures the effects of scattering by ionized impurities becomes important. Conwell and Weisskopf[23] give for this scattering

$$\frac{1}{\mu_I} = \frac{\pi^{\frac{3}{2}}}{2^{\frac{7}{2}}} \frac{e^3 N_I m^{*\frac{1}{2}}}{K_s'^2 (kT)^{\frac{3}{2}}} \ln\left[1 + \left(\frac{3K_s'kT}{e^2 N_I^{\frac{1}{3}}}\right)^2\right]. \tag{12}$$

Using the appropriate value of m^* from the lattice scattering term and a value of 83 for K_s', it is possible to fit observed mobility values at the lowest temperature, where the contribution of the lattice scattering is negligible, with reasonable values of N_I, the number of scattering centers/cm³ (Table I). It is usually assumed[22] that the total mobility may be given as

$$1/\mu = 1/\mu_L + 1/\mu_I. \tag{13}$$

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[21] H. J. McDonald and H. Seltz, J. Am. Chem. Soc. **61**, 2405 (1939).

[22] E.g., W. Shockley, *Holes and Electrons in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

[23] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).

A typical result of such a calculation is shown in Fig. 13 for the 800° five-minute ceramic sample, with quite satisfactory agreement with observations over the entire range of temperatures studied. The values of N_I given in Table I vary roughly according to the degree of reduction, which suggests that ionized donor centers are the chief source of the low-temperature scattering although there may be a considerable contribution from the foreign ions known to be present.

An interesting feature of the mobility observations is the similarity in the mobility values found between the ceramic samples and the single crystals. In previous work on oxide semiconductors in the sintered form, it has usually been assumed that the low values of μ resulted from trapping of the charge carriers at grain boundaries.[24] From these measurements it would appear, at least in a very densely fired rutile sample, that the grain boundaries are not the predominant effect, although this need not be true if the grains are in poor contact as in a pressed powder sample, or even in a lightly sintered ceramic. Similarly, frequency effects such as noted in reference 24 can still be attributed to the presence of grain boundaries and inhomogeneous grains.

These results show that there is a difference in electron mobilities in the two directions studied as would be predicted by Eq. (9) assuming equal effective masses for the two directions and previously given values of K' and θ; the calculated value of the ratio μ_c/μ_a being 1.8 at 500°K. This is illustrated for pairs of samples having about the same numbers of charge carriers and presumably nearly equal numbers of scattering centers, for example, the 800° Linde samples, where the mobility ratio μ_c/μ_a has an average value of 1.8 and varies only slowly with temperature. Similar values are found for the National Lead Company crystals; the 700 *c* and 650 *a* samples give an average ratio of 2.0 but with a greater temperature variation. The slightly greater values of the ratio found experimentally presumably arise from the larger effective mass found in the *a* direction.

VIII. DISCUSSION

While it is possible to give a rather detailed picture of the electrical properties of the elementary semiconductors in terms of a simple band picture involving filled and conduction bands with one donor or acceptor impurity level, or possibly both,[16] such a simple model cannot explain the variety of observations on rutile.

The conductivity at high temperature of *n* type oxide semiconductors is believed to arise from the thermal decomposition of the oxide resulting in the introduction of donor "impurities" in the form of an excess of the metallic constituents of the oxide. This excess may be present as interstitial metal atoms or as metal ions of a different valence in the normal lattice accompanied by oxygen vacancies. There may in addition be present in the oxide true foreign impurities that will behave similarly.[25]

There are a number of reasons for believing that in TiO_2 the donor centers are not interstitial titanium atoms. Ehrlich[26] has shown that the rutile lattice is preserved quite precisely for about 1 percent reduction, and no marked changes were noted until the material was about 10 percent reduced. This would seem unlikely for an excess of an interstitial atom of radius *ca* 1.4A but is quite reasonable for ions as similar in size as Ti^{+3} and Ti^{+4} located on a normal site. The radii quoted by Pauling[27] are 0.69A and 0.68A, respectively.

There is also a considerable amount of thermodynamic evidence that the product of the oxide decomposition is not the free metal. It has been shown by Richardson and Jeffes[28] that the free energy of dissociation of most simple oxide systems can be represented with an accuracy of a few percent over wide temperature ranges by simple expressions of the form

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \tag{14}$$

with ΔH^0 and ΔS^0 independent of temperature. The actual values of ΔH^0 and ΔS^0 are, however, less accurate than those obtained from more detailed formulas. These authors give a value of ΔG^0 for the chemical reaction

$$TiO_2 \rightleftharpoons Ti + O_2, \tag{15}$$

$$-\Delta G^0 = RT \ln K_p = -217\,500 + 41.4T, \tag{16}$$

valid from 298°K to 2080°K with an accuracy of ±10 percent. Since for this system $K_p = Po_2$, this relation gives a calculated oxygen pressure even at 2000°K of only 1.9×10^{-15} atmos, indicating a very small degree of dissociation. We can obtain a similar expression for the free energy of the reaction

$$2\,TiO_2 \rightleftharpoons Ti_2O_3 + \tfrac{1}{2}O_2, \tag{17}$$

using the data of Nasu[29] for the equilibrium constant of the reaction

$$2\,TiO_2 + H_2 \rightleftharpoons Ti_2O_3 + H_2O. \tag{18}$$

He found for this reaction

$$\log_{10} K_p = 1.9305 - 2754/T, \tag{19}$$

valid for temperatures of 1022°K to 1282°K. Expressing this equation in terms of free energy, we have

$$-\Delta G^0 = 12\,600 - 8.83T. \tag{20}$$

Combining Eq. (20) with an expression for the free

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[24] E.g., P. H. Miller, in *Semiconducting Materials* (Butterworths Scientific Publications, London, 1951).

[25] E.g., E. J. W. Verwey, in *Semiconducting Materials* (Butterworths Scientific Publications, London, 1951).

[26] P. Ehrlich, Z. Elektrochem. **45**, 362 (1939).

[27] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).

[28] F. D. Richardson and J. H. E. Jeffes, J. Iron and Steel Inst. (London) **160**, 261 (1948).

[29] N. Nasu, Sci. Repts. Tohoku Imp. Univ. **25**, 510 (1936).

energy of the dissociation of water,[28]

$$\Delta G^0 = -118\,000 + 26.75T, \tag{21}$$

we obtain for the free energy of the reaction (17)

$$-\Delta G^0 = -71\,600 + 22.20T. \tag{22}$$

Since for the reaction (17) $K_p = P_{O_2}^{\frac{1}{2}}$, this indicates a partial pressure of oxygen at 2000°K of 6.9×10^{-6} atmos, hence a degree of dissociation sufficient to account for the observed conductivity of rutile at elevated temperatures. Thus it seems reasonable to assume that the source of electrons in semiconducting rutile is Ti^{+3} ions in the lattice

To preserve electrical neutrality in this situation there must be present oxygen defects; and, since these defects can act as electron traps, it would be anticipated that the Ti^{+3} ions would be on sites adjacent to the oxygen vacancy. The oxygen vacancy has an effective charge of +2, thus it is possible to have present in the crystal neutral centers $(O_v \cdot 2\,Ti^{+3})^0$, singly ionized centers $(O_v \cdot Ti^{+3})^+$, or free vacancies $(O_v)^{++}$. Since two types of donor centers were found in the conductivity studies, it seems reasonable to assume that the centers are those suggested by the structural possibilities, the neutral centers being those with the small activation energy for ionization $\Delta E_G \cong 0.01$ ev and the singly ionized centers those with the larger energy $\Delta E_G \cong 0.2$ ev. In addition to the large number of centers produced by the reduction, there may be present a considerable number of free oxygen vacancies, probably of the order of $10^{17}/\text{cm}^3$, produced along with a corresponding number of vacant Ti^{+4} sites as normal Schottky lattice defects either in the firing of the ceramic or in the growth of the single crystal by the Verneuil furnace method.

There is an interesting consequence of this high density of impurity centers in a medium of remarkably high dielectric constant, $K_{\text{Av}}' = 114$. Because of this high dielectric constant an electron is very loosely bound to the center and has a considerable probability of jump to a neighboring vacancy. A rough estimate of the exchange frequency can be made based on a simple calculation analogous to that given by Pauling and Wilson[30] for the hydrogen molecule ion H_2^+. Our model consists effectively of two helium nuclei embedded in a continuous, homogeneous dielectric with constant $K' = 114$, and a single electron shared between the two nuclei. If we assume a density of O_v^{++} of the order of $10^{17}/\text{cm}^3$, the mean separation r_{AB} between the vacant sites will be 215A. The radius of the first Bohr orbit for the electron on one of the nuclei is given as

$$a_0^* = K' a_0 / Z, \tag{23}$$

where Z is the nuclear charge, (=2) and a_0 is the normal Bohr orbit. For our situation a_0^* is found to be 30.2A. Following the variation treatment outlined by Pauling using the 1s hydrogen-like wave functions including Z and K', the exchange integral K is found to be

$$K = -(Z^2 e^2 / a_0^*) e^{-p} (p+1), \tag{24}$$

where $p = Z r_{AB} / a_0^*$. For the value of r_{AB} indicated, K is computed to be -1.6×10^{-17} erg, corresponding to a resonant frequency of jump between nuclei of 4.8×10^9 sec^{-1}. A similar calculation for the exchange of an electron between two singly ionized centers with the same separation leads to an even greater frequency of jump and larger exchange energy.

It seems, then, that the wave functions overlap sufficiently to produce a narrow impurity conduction band, and under these conditions a large effective mass should be observed.[31] An estimate of the effective mass may be made from the value of K since it was shown in the reference cited for a cubic lattice

$$\beta = m^*/m = -\hbar^2 / 2mKa^2, \tag{25}$$

where a is the edge length of the crystal unit, here presumably the impurity center separation, since we have already assumed an average cubic distribution of the vacancies. This estimate, based on obviously approximate values of a and K, gives a value of β of 8.2 which is at least reasonable since the values of β found range from 27 to 122. It is qualitatively evident that higher mobilities and smaller effective masses should be observed in the c compared to the a direction since the dielectric constant, and hence the extent of exchange interaction, is larger in the c direction.

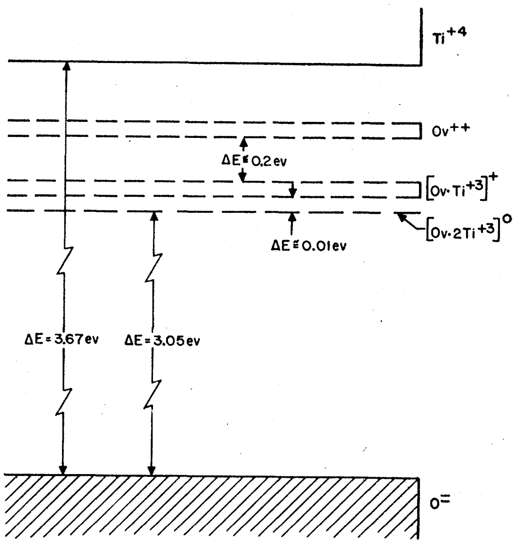

FIG. 14. Thermal equilibrium energy-level diagram of semiconducting rutile.

A proposed energy-level diagram which describes many observations on rutile is shown schematically in Fig. 14. The electronic states indicated correspond to a

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[30] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

[31] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 303.

state of thermochemical equilibrium of the system. The diagram provides a ready explanation for the change in the activation energy for conduction observed by Cronemeyer.[13] The very high-temperature branch may now be assigned to a true intrinsic conduction process that can take place without decomposition of the oxide; the lower branch is that due to the oxide decomposition producing oxygen vacancies and Ti^{+3} ions. There is some thermodynamic evidence that justifies this assignment. For our purpose Eq. (17) may be written, including the ionization of the Ti^{+3}'s, as

$$O^{=} \rightleftharpoons \tfrac{1}{2}O_2 + O_v^{++} + 2\epsilon. \tag{26}$$

Then

$$K_p = P_{O_2}^{\frac{1}{2}} X_{O_v^{++}} X_\epsilon^2. \tag{27}$$

At moderate temperatures ($\leqslant 900$°C) the number of O_v^{++} formed by the reaction is small compared to the constant number presumed present, i.e., $X_{O_v^{++}} \cong 10^{-6}$; hence,

$$X_\epsilon = (K_p / X_{O_v^{++}})^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}. \tag{28}$$

We may use the free energy expression (22) to obtain the value of K_p and find on converting to n_ϵ, the number per cubic centimeter,

$$n_\epsilon/\mathrm{cm}^3 = 8.68 \times 10^{24} (X_{O_v^{++}})^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} e^{-3.11/2kT}, \tag{29}$$

predicting a thermal activation energy in excellent agreement with that observed by Cronemeyer[13] as well as a pressure dependence in good agreement with that found by Earle.[3]

The correlation of the various optical observations with the thermal effects is difficult in rutile because of the great difference between the optical and static dielectric constants. Mott and Gurney[32] have indicated that the optical activation energies are proportional to $1/K_\infty'$, while the thermal activation energies should be proportional to $1/K_s'$. This would predict for rutile that $\Delta E_{\mathrm{optical}}/\Delta E_{\mathrm{thermal}} = 5.1$ as an average value. While Cronemeyer observed photoconductivity related to the absorption at 0.41μ (3.02 ev), it seems unlikely that it can be due to the excitation of an electron from the filled to the normal conduction band since this would require that $\Delta E_{\mathrm{optical}} \leqq \Delta E_{\mathrm{thermal}}$ and would leave no process assignable to the 3.67-ev thermal activation energy.

Observations by Dr. R. F. Blunt of this laboratory on the bleaching of the colored rutile on cooling to liquid air temperatures suggest that the band at 1.2μ (1.0 ev) arises from the process

$$(O_v \cdot Ti^{+3})^+ \xrightarrow{h\nu} O_v^{++} + \epsilon. \tag{30}$$

This work will be described in detail elsewhere. We have observed the thermal activation energy assigned to this process to be $\cong 0.2$ ev, i.e., almost exactly in the predicted ratio. This would suggest that the 0.41μ (3.02-ev) absorption corresponds to an excitation of an electron from $(O_v \cdot 2\,Ti^{+3})^0$ or $(O_v \cdot Ti^{+3})^+$ centers to the conduction band since these are presumably about 0.62 ev apart. This assignment provides an explanation for observations of Cronemeyer on the temperature dependence of the photo response. It was found that the photoconductivity showed a shift of the maximum response to higher energies as the temperature was lowered; and, at 103°K, a splitting into two maxima. The suggested model would predict a similar effect since at room temperatures the majority of the centers present would be singly ionized, and thus the photoconductivity maximum would be centered at the energy corresponding to the separation between the singly ionized centers and the conduction band. As the temperature is lowered, the number of neutral centers would be increased at the expense of the singly ionized centers, shifting the maximum photoresponse to greater energies corresponding to the energy difference between the neutral centers and the conduction band.

If the energy for the optical transition corresponding to the 3.67-ev thermal process is computed using the same ratio of 5:1, the absorption for the intrinsic process should occur at about 0.067μ (18.7 ev), in the normal region for absorption in the transparent oxides.[32] However, no crystals have shown transmission at wavelengths shorter than 0.41μ, indicating that the "impurity" absorption may overlap the fundamental absorption. This is very likely in the present situation since the absorption band presumably arises from transitions directly to the conduction band. It would seem that further exploration of the absorption in the ultraviolet, particularly at very low temperatures, might be of considerable interest.

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[32] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940).