

rule of thumb, with one core function in an OPW, one must penetrate to about  $\frac{1}{3}\sigma_{\max}$ . With more than one core function in an OPW, one must penetrate to about  $\frac{1}{5}\sigma_{\max}$ . The  $\Gamma_{1v}$  convergence can be judged from the free-atom anion bottom valence state maximum in  $\sigma$ . The  $\Gamma_{15v}$  convergence depends more strongly on the anion core size, with some dependence on the cation size. The  $\Gamma_{1c}$  convergence depends very strongly on the cation size. Convergence is similar throughout the zone. The fact that the OPW's must penetrate the smaller core is

a major weakness in the OPW formalism. However, beyond the first row of the Periodic Table, the OPW formalism seems adequate to handle any compound if pseudocore states are introduced to handle such things as high-lying  $d$  states.<sup>3,13,16,17</sup>

#### ACKNOWLEDGMENTS

We would like to thank R. Schultz who programmed a large diagonalization procedure for us. We are also grateful to G. Johnson and G. Schantz for their expert drafting of the many figures.

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## New Ordered Phases of Slightly Reduced Rutile and Their Sharp Dielectric Absorptions at Low Temperature

C. W. Chu

*Bell Telephone Laboratories, Murray Hill, New Jersey 07974*

(Received 2 December 1969)

The temperature dependence of the complex dielectric constant of single-crystal rutile has been studied at different frequencies and as a function of reduction. The results suggest the existence of two new ordered phases in slightly reduced rutile. Sharp dielectric absorptions have been observed in these phases. This is attributed to the hopping of low-mobility charge carriers between two ion sites. The nature of the charge carriers introduced by reduction is discussed. It is proposed that the room-temperature conductivity alone may not characterize the state of a slightly reduced rutile sample.

### INTRODUCTION

Metal-nonmetal transitions in transition-metal<sup>1</sup> oxides have long received intense interest. The recent identification<sup>2</sup> of a Mott transition in Cr-doped  $V_2O_3$  is one of its highlights. With this point in view as well and considering the anomalously high dielectric constant ( $\epsilon = 173$ )<sup>3</sup> of rutile ( $TiO_2$ ), the

study of stoichiometric and reduced rutile is instructive in the understanding of the electrical-transport mechanism in rutile.

Stoichiometric rutile is a highly polar insulating crystal with an intrinsic energy gap<sup>4</sup>  $\sim 3$  eV between the filled  $2p$  band of  $O^{2-}$  and the empty  $3d$  band of  $Ti^{4+}$ . Slight reduction of rutile by heating in vacuum

is believed to create charge carriers of different natures.<sup>5</sup> The reduced rutile is an  $n$ -type semiconductor with an activation energy<sup>6</sup> ranging between  $10^{-1}$  and  $10^{-3}$  eV depending on the sample condition and the temperature. The charge carriers have been found<sup>7</sup> to hop from one ion site to the other at temperature  $\geq \frac{1}{2}\Theta_D$  ( $\Theta_D$  is the Debye temperature) and to have very low mobility. This fact, together with the highly polarizable background in rutile, has led to their identification with polarons.<sup>7</sup> At low temperature, the carriers can be considered to move in a very narrow  $d$  band ( $\sim 10^{-1}$  eV) due to the overlap of the  $3d$  orbitals of the titanium ion via the  $2p$  orbitals of the oxygen ion.

To understand the nature of these very immobile carriers, various authors<sup>8</sup> have investigated the complex dielectric constant  $\epsilon \equiv \epsilon_1 - i\epsilon_2$  at different frequencies and temperatures (mostly above 77 °K). Both  $\epsilon_1$  and  $\epsilon_2$  are real, and the latter can be related to the ac conductivity  $\sigma$  by  $\epsilon_2 = 4\pi\sigma/\omega$ . At room temperature, broad and weak relaxations at different frequencies were observed. These relaxations were considered to depend on the prehistory of the samples and on the experimental conditions. Low-temperature data is sparse. Dominik *et al.*<sup>8</sup> have found dielectric relaxation in a slightly reduced rutile sample at temperatures around 2 °K. The study is far from being systematic or complete. Furthermore, in view of the existence of the many ordered phases of titanium oxides,<sup>9</sup> a systematic investigation of the temperature and frequency dependences of  $\epsilon$  with various degrees of reduction is useful.

In the present work we have measured the temperature dependence of  $\epsilon_1$  and  $\sigma$  between 1.5 and 300 °K at frequencies ranging from 5.5 Hz to 40 kHz on pure single rutile crystals from different sources. A sharp absorption at 400 Hz<sup>10</sup> was observed to appear *abruptly* at  $\sim 17$  or  $\sim 7$  °K as the degree of reduction increased *continuously*. This is taken as evidence for the existence of two new ordered phases of the slightly reduced rutile. At temperature  $T_m$  of the absorption peak,  $\epsilon_1$  drops suddenly and  $\sigma$  goes through a sharp peak. This anomalous behavior may be indicative of the presence of cooperative effects near  $T_m$  for the new ordered phases. For the less reduced phase (I)  $T_m$  increases exponentially with frequency with an activation energy  $E_a = (2.4 \pm 0.5) \times 10^{-4}$  eV. This can be described in terms of a one-relaxation process corresponding to the hopping of a heavy charge carrier between two ion sites. However, the frequency dependence of  $T_m$  for the more reduced phase (II) is more complicated. A broad distribution of relaxations may be needed to account for the behavior. The over-all effects of reduction

temperatures  $T_r$  and time  $t_r$  on  $\epsilon_1$  and  $\sigma$  of rutile suggest that room-temperature conductivity alone cannot be taken as a measure of the state of the sample. In addition, preliminary study shows that  $T_m$  is not shifted by a field up to  $\sim 500$  V/cm. And Chynoweth's dynamic technique<sup>11</sup> was applied to look for pyroelectricity, but no such signal was found in these samples down to 1.5 °K.

#### EXPERIMENTAL DETAILS

Single rutile crystals grown by the Verneuil process were obtained from three different sources. Spectrographic analysis shows the following major impurities in %: Si 0.0X, Mg 0.00X, Cu 0.00X low, Al 0.00X, and Fe 0.00X, where  $X$  varies between 1 and 9. Samples with thicknesses 0.1–0.05 cm along the  $c$  axis and with cross-sectional area 0.25 cm<sup>2</sup> were cut and polished. The samples weighed  $\sim 80$  mg. The change in weight<sup>12</sup> due to reduction was too small to be measured. The small thickness of the sample was chosen to reduce the possibility of an inhomogeneous layer structure since this particular structure could result in extrinsic dielectric relaxation.

Reduction in vacuum at different  $T_r$  (270–400 °C) for different  $t_r$  (2 days–3 weeks) was carried out in the following way. A narrow neck of 1–2 mm diam was made at the center of a  $\frac{3}{8}$ -in.-i.d. quartz tube. The bottom end was then sealed off. Some fresh uranium saw chips were let into the lower compartment to act as oxygen getter at low temperature. The rutile sample was later introduced into the upper compartment so that there was no direct physical contact between the samples and the getter. The whole assembly was finally evacuated to  $\sim 10^{-3}$  mm Hg, sealed off, and heated in a furnace at the desired  $T_r$  for a certain period of  $t_r$ . For the  $T_r$  in which we were interested, the uranium has extremely low vapor pressure and its diffusion into rutile is considered very unlikely. Direct reduction in hydrogen was also done at several temperatures and produced the same  $\epsilon$  anomalies as the aforementioned method. The color of the sample changed from pale grey, to light green, then to light blue as the sample was more and more reduced. Powder x-ray patterns did not show any crystal structure change after reduction. After the sample was reduced, gold electrodes were evaporated on both faces perpendicular to the  $c$  axis. Platinum leads were then glued onto the electrodes using silver paste. For samples where successive reduction was desired after the  $\epsilon$  measurement, the electrodes were removed in *aqua regia* solution and rinsed in alcohol before they were rereduced.

A two-electrode method was used to determine  $\epsilon_1$  and  $\sigma$  with two different techniques depending

on frequency. At 400 Hz we used a general radio 1680-A automatic capacitance bridge. At other frequencies we used a Tektronix 3A8 operational amplifier driven by signal from the oscillator of a Princeton Applied Research HR-8 lock-in amplifier. The peak-to-peak voltage across the sample was always kept at 50 mV. Since  $\sigma^3$  depends on the voltage, low voltages are preferable. The method was found to be useful to study the frequency effect on  $T_m$ . However, it did not give accurate quantitative values of  $\epsilon_1$  when the sample was too lossy or the frequency was too high. To achieve the wide range of temperature, the sample was immersed in a helium atmosphere of  $\sim 10^{-2}$  mm Hg in a glass Dewar. This Dewar with a vacuum jacket was installed inside a He<sup>4</sup> cryostat. By varying the current through a W-Pt heater and pumping on the He<sup>4</sup> bath, we could change continuously the temperature between 300 and 1.5 °K. The temperature was determined by a gold-chromel thermocouple situated next to the sample. To check whether there was any pyroelectric effect Chynoweth's dynamic technique<sup>11</sup> was used. White-light pulses of various repetition rates were transmitted to the sample through a quartz light pipe. The signal was amplified and detected by a PAR HR-8 lock-in amplifier.

#### EXPERIMENTAL RESULTS

A large number of differently reduced rutile single crystals were examined along the  $c$  axis. The general features of  $\epsilon_1$  and  $\sigma$  can be illustrated by results of only a few samples. In Table I we have listed the reduction treatments and the room-temperature data of these samples in order of increasing oxygen vacancies. The dc  $\sigma$  and the 400-Hz  $\epsilon_1$  are, respectively,  $\sim 8 \times 10^{-3} \mu\Omega^{-1} \text{cm}^{-1}$  and 140 for the as-grown rutile  $B$ . The quoted values<sup>12,3</sup> for pure stoichiometric rutile are  $\sim 10^{-6} \mu\Omega^{-1} \text{cm}^{-1}$  and 173. The difference is attributed to

the oxygen deficiency in our starting rutile boule.

The  $T$  dependences of  $\epsilon_1$ ,  $\sigma$ , and  $\tan\delta$  at 400 cps are shown in Figs. 1–5.  $\epsilon_1$  decreases monotonically with decreasing  $T$  until it becomes  $T$  independent at lower temperature except for the longest reduced samples, e.g., sample 6. It is clear from Fig. 4 that slightly reduced samples start showing a sudden drop in  $\epsilon_1$  at  $\sim 17^\circ \text{K}$ . The amplitude of this drop increases with  $T_r$  when  $270^\circ \text{C} \lesssim T_r \lesssim 300^\circ \text{C}$ . Further reduction, i.e.,  $310^\circ \text{C} \lesssim T_r \lesssim 330^\circ \text{C}$ , makes the drop very broad between 17 and 7 °K as shown in Fig. 5. For this sample, it still can be recognized that the drop is a superposition of two separate drops. At  $340^\circ \text{C} \lesssim T_r \lesssim 400^\circ \text{C}$  only one sharp decrease in  $\epsilon_1$  appears, e.g., sample 7. No anomaly is detected in  $\epsilon_1$  for  $T_r = 1000^\circ \text{C}$  as demonstrated by sample 8. With a peak in  $\sigma$  replacing the drop in  $\epsilon_1$ , similar behavior in  $\sigma$  to that in  $\epsilon_1$  is observed. It is interesting to note that there are two  $\sigma$  peaks for sample 8 in the temperature range where a sluggish  $\epsilon_1$  decrease takes place. The general behavior of loss tangent  $\tan\delta \equiv 4\pi\sigma/\epsilon_1$  is the same as that of  $\sigma$ , except that for the unreduced sample another peak, broad and weak, appears around 70 °K. No thermal hysteresis in  $\epsilon_1$  or  $\sigma$  near or below  $T_m$  can be found in spite of the large effect existing above  $T_m$ . Oxidation in air at temperature  $> 600^\circ \text{C}$  for only a few minutes will remove all these anomalies. To make sure that this anomalous behavior is not a characteristic of the electrode material which may form a Shockley barrier with the rutile, we also used silver-paste electrodes. The same anomalies in  $\epsilon_1$  as well as in  $\sigma$  were found although the values of  $\epsilon_1$  and  $\sigma$  were smaller.

We have investigated the frequency dependence of  $T_m$  for samples 5 and 7 which represent ordered phases I and II, respectively.  $T_m$  increases with frequency  $\omega$ .  $\sigma$  at different  $\omega$  versus  $T$  for sample 5 is shown in Fig. 6. The absolute values of  $\sigma$  at

TABLE I. Room-temperature data of the samples shown in the figures.

Sample no.	Reduction treatment	dc	400 Hz	$\epsilon_1$
		$\sigma(\mu\Omega^{-1} \text{cm}^{-1})^a$	$\sigma(\mu\Omega^{-1} \text{cm}^{-1})$	
1	B0(0) <sup>b</sup>	$8.4 \times 10^{-3}$	$3.4 \times 10^{-1}$	$1.4 \times 10^2$
2	B270( $6\frac{1}{2}$ )	$6.66 \times 10^0$	$6.87 \times 10^0$	$1.0 \times 10^2$
3	B270( $2\frac{1}{2}$ )270(20)	$1.95 \times 10$	$1.97 \times 10$	$6.7 \times 10^2$
4	C270( $6\frac{1}{2}$ )	$1.25 \times 10$	$1.22 \times 10$	$5.37 \times 10^2$
5	B310( $2\frac{1}{2}$ )	$8.36 \times 10^{-1}$	$2.54 \times 10^0$	$1.64 \times 10^3$
6	C270( $6\frac{1}{2}$ )300( $2\frac{1}{2}$ )330(2)	$5 \times 10^3$	$3.5 \times 10^3$	$9.54 \times 10^3$
7	B400( $2\frac{1}{2}$ )	$4.95 \times 10$	$5.0 \times 10$	$5.1 \times 10^3$
8	C1000( $\frac{1}{2}hr$ ) <sup>c</sup>	$1.18 \times 10^4$	$1 \times 10^4$	$5.1 \times 10^3$

<sup>a</sup>The dc conductivity was measured by a two-lead technique using a Simpson Ohm meter.

<sup>b</sup>XY(Z): X denotes the source, Y denotes reduction temperature in °C, and Z denotes reduction time in days unless specified otherwise.

<sup>c</sup>Reduced in hydrogen.

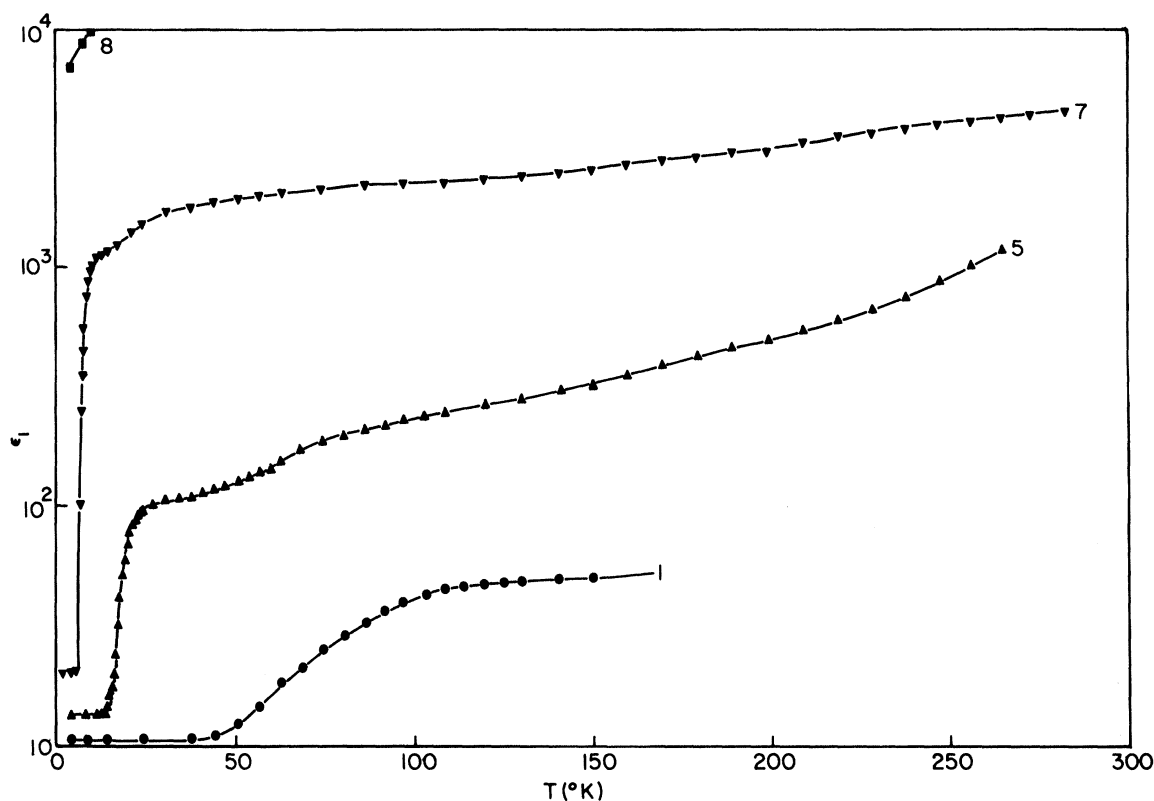


FIG. 1. Temperature dependence of  $\epsilon_1$  at 400 Hz for the slightly reduced single rutile crystals, 1: as grown, 5: phase I, 7: phase II, and 8: more reduced.

$\omega \lesssim 4$  kHz or  $\omega \lesssim 50$  Hz should not be considered with numerical emphasis for the reason mentioned previously.  $T_m$  obtained from these curves are plotted as a function of  $1/T$  in Fig. 7. It is a straight line for sample 5 but not for sample 7.

Effects of dc bias field  $E_B$  up to 500 V/cm on  $\epsilon_1$  and  $\sigma$  are presented in Fig. 8 for sample 5. Above  $T_m$ ,  $\sigma$  is largely enhanced by  $E_B$  and this enhancement will mask the peak in  $\sigma$  for  $E_B \gtrsim 550$  V/cm. Below  $T_m$ ,  $\sigma$  is hardly affected by  $E_B$ .  $E_B$  increases  $\epsilon_1$  very slightly only above  $T_m$ .  $T_m$  is not shifted by  $E_B$  at all. In the absence of  $E_B$ , no pyroelectric current was detected. With nonzero  $E_B$ , a signal peaked near  $T_m$  was observed. Analysis of the signal waveform indicated that it was associated with change in  $\epsilon_1$  and  $\sigma$  caused by the light pulse near  $T_m$  and therefore was not pyroelectric in nature.

#### DISCUSSION AND CONCLUSION

(1) The existence of two ordered phases in slightly reduced rutile: It is clear from Figs. 1–5 that  $T_m$  at which the anomaly in  $\epsilon_1$ ,  $\sigma$ , or  $\tan\delta$  takes place is not shifted continuously by gradual reduction. Instead, the amplitude of the  $\epsilon_1$  drop at 17 °K increases continuously with reduction as

$T_r \lesssim 310$  °C. This is indicative of the growth of ordered phase I with increasing reduction since  $\epsilon_1$  is well known to be a measure of the dielectric properties of a *bulk* material. For  $310$  °C  $< T_r$   $< 340$  °C, the appearance of a sluggish  $\epsilon_1$  decrease and of two  $\sigma$  peaks marks the onset of a second ordered phase II. With  $340$  °C  $\lesssim T_r \lesssim 400$  °C, the  $\epsilon_1$  drop and the  $\sigma$  peak observed only at 7 °K indicates that ordered phase I is replaced completely by ordered phase II. Further reduction removed both phases and therefore no anomalies in  $\epsilon_1$  or  $\sigma$  can be observed. The removal of these anomalies by oxidation shows that they can not be caused through impurities introduced by reduction. In fact, recent electron microscope study of reduced rutile by Bursill *et al.*<sup>9</sup> led to the suggestion of the existence of a family of ordered phases indexed as  $\text{Ti}_n\text{O}_{2n-1}$  ( $n=15, \dots, \sim 36$ ). However, the new ordered phases we observed are estimated to be less reduced with  $n > 36$ .

Therefore we conclude that there are two new ordered phases existing in slightly reduced rutile. The anomalies in  $\epsilon_1$  and  $\sigma$  may be associated with some cooperative phenomena near  $T_m$ . It is further suggested that the present method is a very sensitive technique for the study of the possible

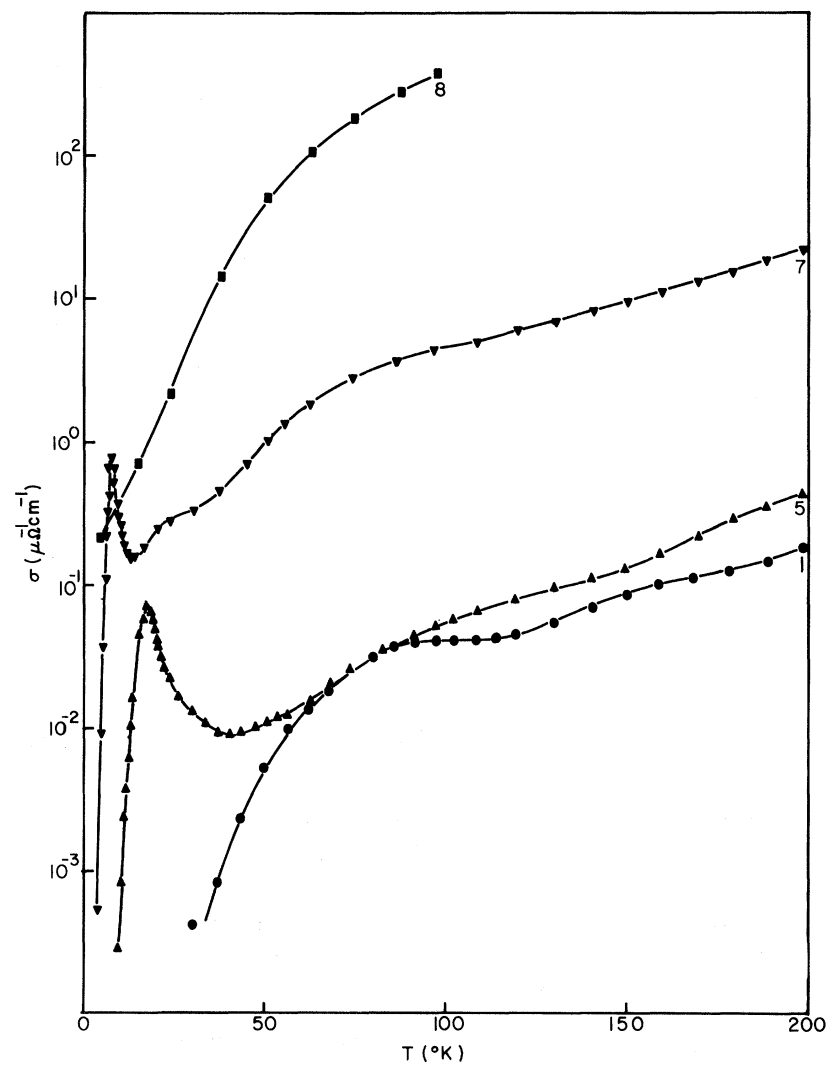


FIG. 2. Temperature dependence of  $\sigma$  at 400 Hz for the slightly reduced single rutile crystals 1, 5, 7, and 8.

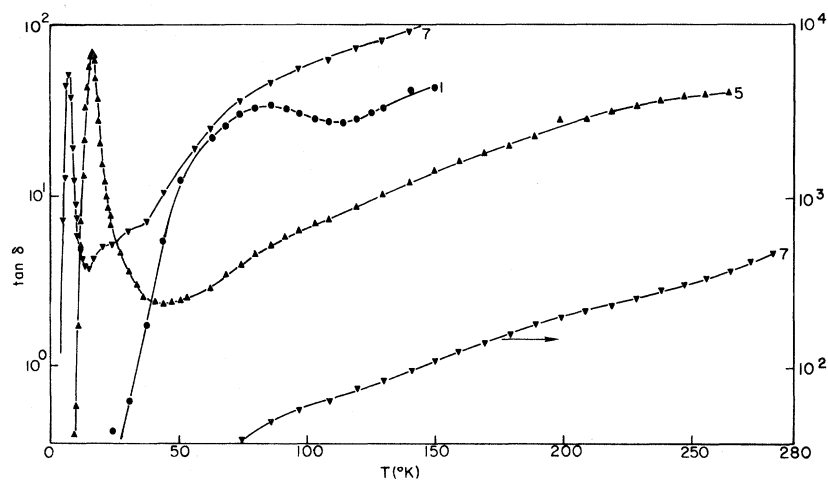


FIG. 3. Temperature dependence of  $\tan \delta$  at 400 Hz for the slightly reduced single rutile crystals 1, 5, and 7.

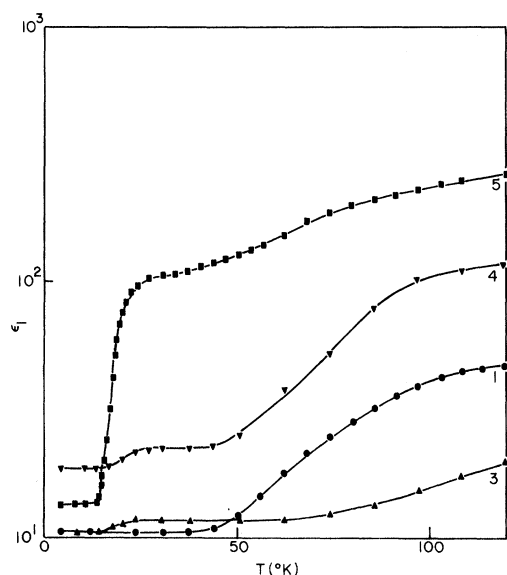


FIG. 4. Temperature dependence of  $\epsilon_1$  at 400 Hz for samples 1, 3, 4, and 5.

existence of ordered phases in slightly reduced transition-metal oxides, e.g.,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{VO}_2$ , etc.

(2) Sharp dielectric absorptions in the ordered phases of slightly reduced rutile: In Fig. 3 one easily finds two sharp maxima in  $\tan\delta$  at 7 and 17 °K as well as a broad weak peak at  $\sim 70$  °K for  $\omega = 400$  Hz. The last peak is attributed to the inhomogeneity of the starting material. The sharp peak at 17 °K is considered to be characteristic of the ordered phase I and the other of the ordered phase II.  $T_m$  increases with  $\omega$ .

These resonance absorptions can be described by the following simple model. Because of the special crystal structure of rutile, charge carriers moving between two ion sites will tunnel through the barrier formed by its surroundings. The form of the potential seen by a charge is depicted in Fig. 9. At low temperatures all charge carriers are frozen in position A. They are thermally excited at higher temperature to position B where the charge carriers can hop adiabatically between two ion sites, i.e., equivalent to dipolar

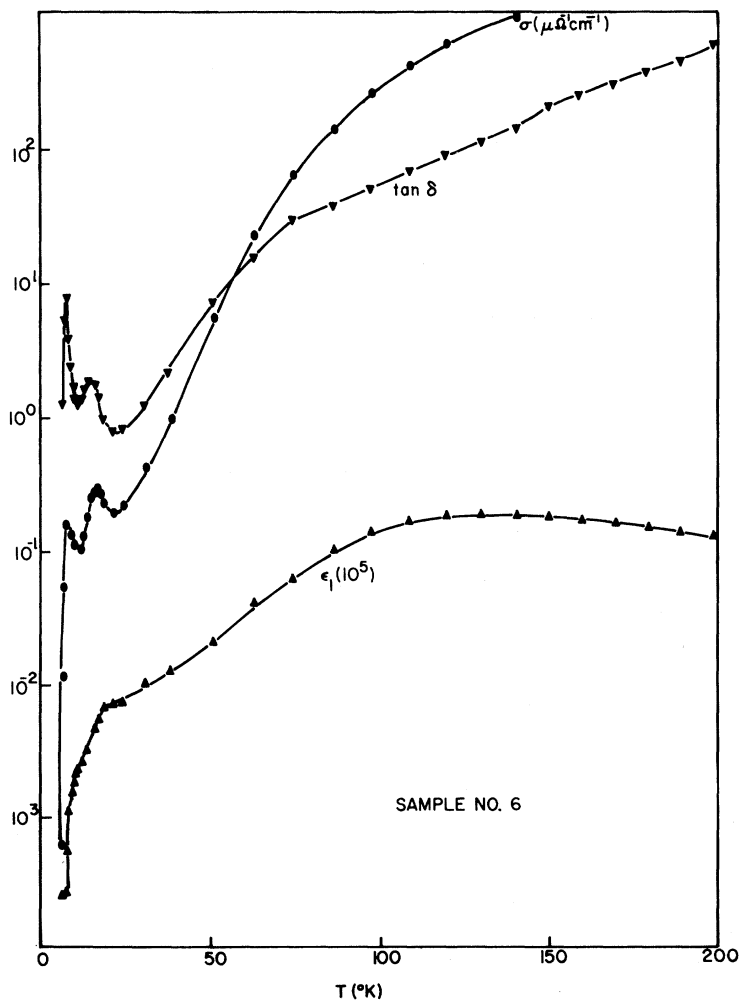


FIG. 5. Temperature dependence of  $\epsilon_1$ ,  $\sigma$ , and  $\tan\delta$  for sample 6.

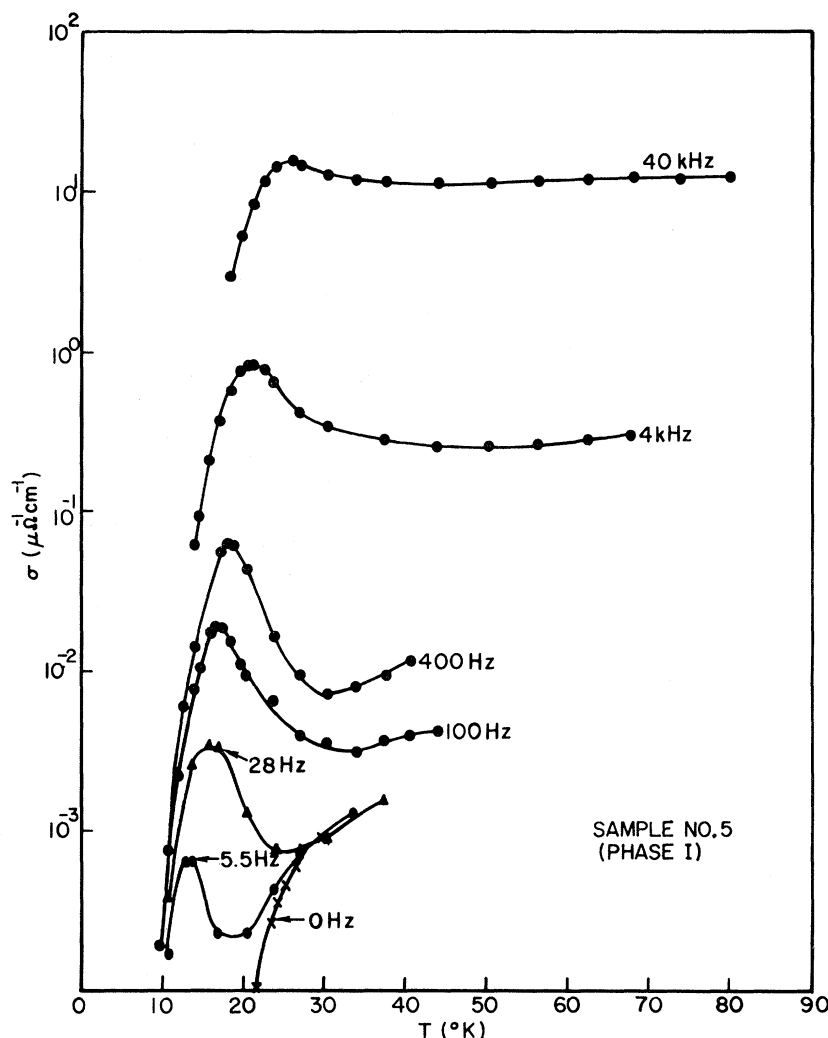


FIG. 6. Temperature dependence of  $\sigma$  at different frequencies for sample 5 (phase I). The dc  $\sigma$  was determined by a vacuum-tube voltmeter (VTVM).

reorientation with two equilibrium directions.  $E_c$  is different for different phases. For the simpler case of phase I, we can assume that two sites are identical, i.e.,  $E_{a1} = E_{a2} \equiv E_a$ . These sites may be associated with the oxygen vacancies along the  $c$  axis for reasons given in the next section. The following relation between  $T_m$  and the frequency  $\omega$  at which the experiment is carried out can easily be obtained by detailed balance

$$\omega = \omega_0 \exp(-E_a/kT_m).$$

$\omega_0$  is the oscillation frequency of the carrier about an ion site and  $k$  is the Boltzmann's constant. Usually  $\omega_0$  is of the order of the Debye frequency  $\sim 10^{13}$  Hz. From Fig. 7 we deduced that  $\omega_0 = (1.0 \pm 0.05) \times 10^9$  Hz and  $E_a = (2.4 \pm 0.05) \times 10^{-4}$  eV for ordered phase I. The deviation of the experimental value of  $\omega_0$  from  $\sim 10^{13}$  Hz may be explained in terms of the possible linear  $T$  dependence of  $E_a$ .  $E_a$  is about an order of magnitude smaller than

the thermal energy. This indicates that the adiabatic assumption used implicitly in deriving the  $\omega - T_m$  relation is justified. While for phase II,  $T_m$  does not vary exponentially with  $\omega$ . This may be caused by the differences between two ion sites or the existence of correlation between sites and hence the activation energies can not be simply represented by  $E_a$ . If this is the case a broad distribution of relaxations will be required to account for the absorption in phase II.

Hence the sharp dielectric absorptions in the new ordered phases can be attributed to hopping of a heavy charge carrier between two ion sites. Study of Ohmic mobility of these phases as a function of frequency would be very interesting. Acoustic attenuation investigation near  $T_m$  will be helpful for the further understanding of the relaxation mechanism in these phases.

(3) Charge carriers created by heating in vacuum and at high temperature: In this study we

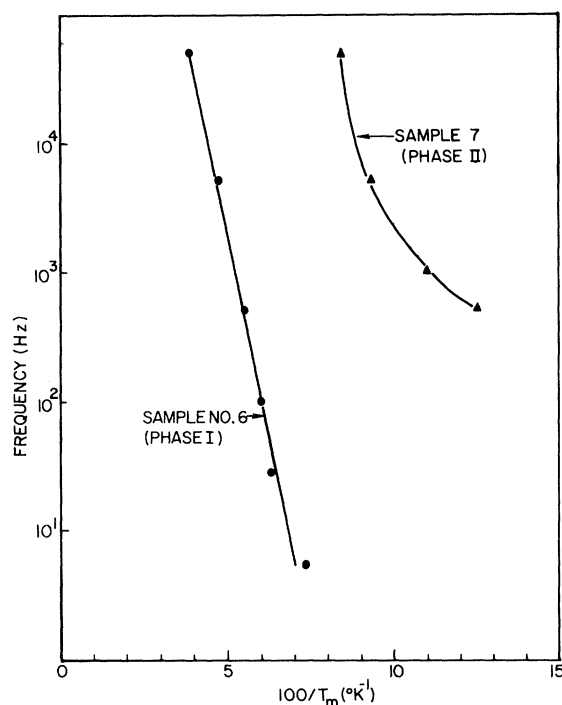


FIG. 7. Frequency dependence of  $T_m$  for the two ordered phases.

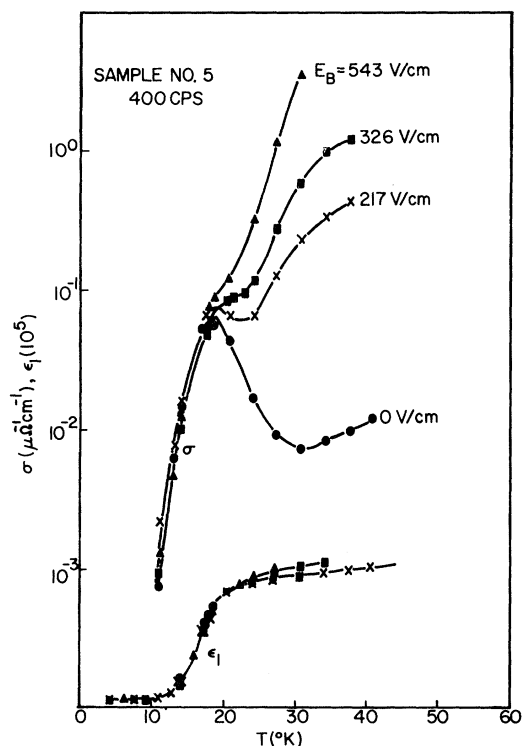


FIG. 8. Electric field effect on  $\epsilon_1$  and  $\sigma$  near  $T_m$  for sample 5 at 400 Hz. Same symbols were used in  $\epsilon_1$  as in  $\sigma$  to denote each specific  $E_B$ .

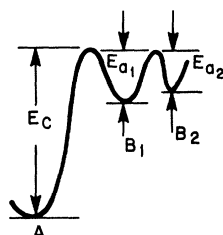


FIG. 9. Potential exerted on a hopping charge carrier by its surroundings.

found that it was difficult for the slightly reduced rutile sample to attain its thermodynamically equilibrium reduced states. For instance, the room temperature  $\sigma$  and  $\epsilon_1$  of the sample continued to vary with  $t_r$ , even after being heated in vacuum for 3 weeks at a fixed temperature 270 °C. According to results shown in Table I and Figs. 1–5, it is clear that  $\sigma$  and  $\epsilon_1$  depend on  $T_r$  and  $t_r$  in a very complex way. When  $t_r$  is fixed,  $\epsilon_1$  decreases initially with  $T_r$  if  $T_r \lesssim 270$  °C and then increases in contrast to the monotonic increase of  $\sigma$  with  $T_r$ . However, with  $T_r$  fixed, increase of  $t_r$  results in a large  $\sigma$  increase but only a small  $\epsilon_1$  increase. And these  $t_r$ -induced enhancements in  $\sigma$  and  $\epsilon_1$  usually have little effect on the occurrence of the two ordered phases of rutile. Taking the presence of the ordered phases I and II as a measure of oxygen content in reduced rutile, it leads to the following conclusion: There are two processes taking place in rutile by our heat treatment in agreement with the proposition by previous workers.<sup>13</sup> One is the formation of oxygen vacancies and the other the creation of  $\text{Ti}^{+3}$  interstitials. The former is more sensitive to  $T_r$  than to  $t_r$ , while the latter is to both. The charge carriers associated with these two kinds of defects seem to have different effects on  $\epsilon_1$  and  $\sigma$ . We also observed that samples with same room temperature  $\sigma$  need not have same low-temperature behavior of both  $\sigma$  and  $\epsilon_1$  if they received different reduction treatment. Therefore the room temperature  $\sigma$  alone can not be taken as a good measure of the state of a slightly reduced rutile. Instead the reduced state should be specified by the behavior of  $\epsilon_1$  and  $\sigma$  over a wide temperature range. Of course, for a sample which reaches a thermodynamically equilibrium reduced state, the room temperature  $\sigma$  may still be good measure. Unfortunately, most reduced rutile samples previously studied did not fall into this second category<sup>14</sup> and yet the state of the sample was labeled by the room temperature  $\sigma$ . This may be the cause for the existence of many inconsistent results in the work of reduced rutile.

(4) Miscellaneous: (a) The results of the field effect on  $T_m$  and the pyroelectric study suggest that there is no antiferroelectric, ferroelectric, or piezoelectric ordering taking place in these new



ordered phases of reduced rutile down to 1.5 °K.

(b) As shown in Fig. 8, the electric field effect on  $\epsilon_1$  and  $\sigma$  above  $T_m$  is different from that below  $T_m$ . This indicates that induced electronic process may have been involved in the presence of the field and the field effect seems to be intrinsic in nature. The previous suggestion<sup>15</sup> that the field enhanced  $\sigma$  was due to the migration of Ti or H ions can not account for the present observation.

(c)  $\sigma$  of the ordered phases changes rapidly several orders of magnitude near  $T_m$ .  $T_m$  can be shifted by the measuring frequency. In addition  $\sigma$  does not show any thermal hysteresis near and below  $T_m$ . All these special properties of the

ordered phases of reduced rutile make it a very sensitive low-temperature thermometer over a large temperature range.

#### ACKNOWLEDGMENTS

The author is grateful to A. M. Glass, A. Jayaraman, B. T. Matthias, J. P. Remeika, T. M. Rice, and P. H. Schmidt for many helpful and stimulating conversations. In particular, thanks are due to E. Corenzwit for his supreme skill in reducing the samples. The author also wants to thank L. G. Van Uitert for the rutile boules and A. S. Cooper for the x-ray studies.

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