rule of thumb, with one core function in an OPW, one must penetrate to about $\frac{1}{3}\sigma_{\text{max}}$. With more than one core function in an OPW, one must penetrate to about $\frac{1}{5}\sigma_{\text{max}}$. The Γ_{1v} convergence can be judged from the free-atom anion bottom valence state maximum in σ. The Γ_{15v} convergence depends more strongly on the anion core size, with some dependence on the cation size. The Γ_{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.[3,13,16,17]

ACKNOWLEDGMENTS

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

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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[1] oxides have long received intense interest. The recent identification[2] 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 ($\epsilon = 173$)[3] 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[4] ~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.[5] The reduced rutile is an n-type semiconductor with an activation energy[6] ranging between 10^{-1} and 10^{-3} eV depending on the sample condition and the temperature. The charge carriers have been found[7] to hop from one ion site to the other at temperature $\gtrsim \frac{1}{2}\Theta_D$ (Θ_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.[7] 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[8] have investigated the complex dielectric constant $\epsilon \equiv \epsilon_1 - i\epsilon_2$ at different frequencies and temperatures (mostly above 77 °K). Both ϵ_1 and ϵ_2 are real, and the latter can be related to the ac conductivity σ 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.*[8] 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,[9] a systematic investigation of the temperature and frequency dependences of ϵ with various degrees of reduction is useful.

In the present work we have measured the temperature dependence of ϵ_1 and σ 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[10] was observed to appear *abruptly* at ~17 or ~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, ϵ_1 drops suddenly and σ 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 ϵ_1 and σ 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 ~500 V/cm. And Chynoweth's dynamic technique[11] 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^2 were cut and polished. The samples weighed ~80 mg. The change in weight[12] 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 ~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 ϵ 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 ϵ 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 ϵ_1 and σ 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 σ^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 ϵ_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^4 cryostat. By varying the current through a W-Pt heater and pumping on the He^4 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[11] 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 ϵ_1 and σ 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 σ and the 400-Hz ϵ_1 are, respectively, $\sim 8\times10^{-3}$ $\mu\Omega^{-1}$ cm^{-1} and 140 for the as-grown rutile B. The quoted values[12,3] for pure stoichiometric rutile are $\sim 10^{-6}$ $\mu\Omega^{-1}$ cm^{-1} and 173. The difference is attributed to the oxygen deficiency in our starting rutile boule.

The T dependences of ϵ_1, σ, and $\tan\delta$ at 400 cps are shown in Figs. 1–5. ϵ_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 ϵ_1 at ~17 °K. The amplitude of this drop increases with T_r when 270 °C $\lesssim T_r \lesssim$ 300 °C. Further reduction, i.e., 310 °C $\lesssim T_r \lesssim$ 330 °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 °C $\lesssim T_r \lesssim$ 400 °C only one sharp decrease in ϵ_1 appears, e.g., sample 7. No anomaly is detected in ϵ_1 for T_r = 1000 °C as demonstrated by sample 8. With a peak in σ replacing the drop in ϵ_1, similar behavior in σ to that in ϵ_1 is observed. It is interesting to note that there are two σ peaks for sample 8 in the temperature range where a sluggish ϵ_1 decrease takes place. The general behavior of loss tangent $\tan\delta \equiv 4\pi\sigma/\epsilon_1$ is the same as that of σ, except that for the unreduced sample another peak, broad and weak, appears around 70 °K. No thermal hysteresis in ϵ_1 or σ near or below T_m can be found in spite of the large effect existing above T_m. Oxidation in air at temperature > 600 °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 Shocktty barrier with the rutile, we also used silver-paste electrodes. The same anomalies in ϵ_1 as well as in σ were found although the values of ϵ_1 and σ 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 ω. σ at different ω versus T for sample 5 is shown in Fig. 6. The absolute values of σ at

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

Sample no.	Reduction treatment	dc $\sigma(\mu\Omega^{-1}\text{cm}^{-1})$ [a]	400 Hz $\sigma(\mu\Omega^{-1}\text{cm}^{-1})$	ϵ_1
1	$B0(0)$ [b]	8.4×10^{-3}	3.4×10^{-1}	1.4×10^{2}
2	$B270(6\frac{1}{2})$	6.66×10^{0}	6.87×10^{0}	1.0×10^{2}
3	$B270(2\frac{1}{2})270(20)$	1.95×10	1.97×10	6.7×10^{2}
4	$C270(6\frac{1}{2})$	1.25×10	1.22×10	5.37×10^{2}
5	$B310(2\frac{1}{2})$	8.36×10^{-1}	2.54×10^{0}	1.64×10^{3}
6	$C270(6\frac{1}{2})300(2\frac{1}{2})330(2)$	5×10^{3}	3.5×10^{3}	9.54×10^{3}
7	$B400(2\frac{1}{2})$	4.95×10	5.0×10	5.1×10^{3}
8	$C1000(\frac{1}{2}hr)$ [c]	1.18×10^{4}	1×10^{4}	5.1×10^{3}

[a] The dc conductivity was measured by a two-lead technique using a Simpson Ohm meter.

[b] $XY(Z)$: X denotes the source, Y denotes reduction temperature in °C, and Z denotes reduction time in days unless specified otherwise.

[c] Reduced in hydrogen.

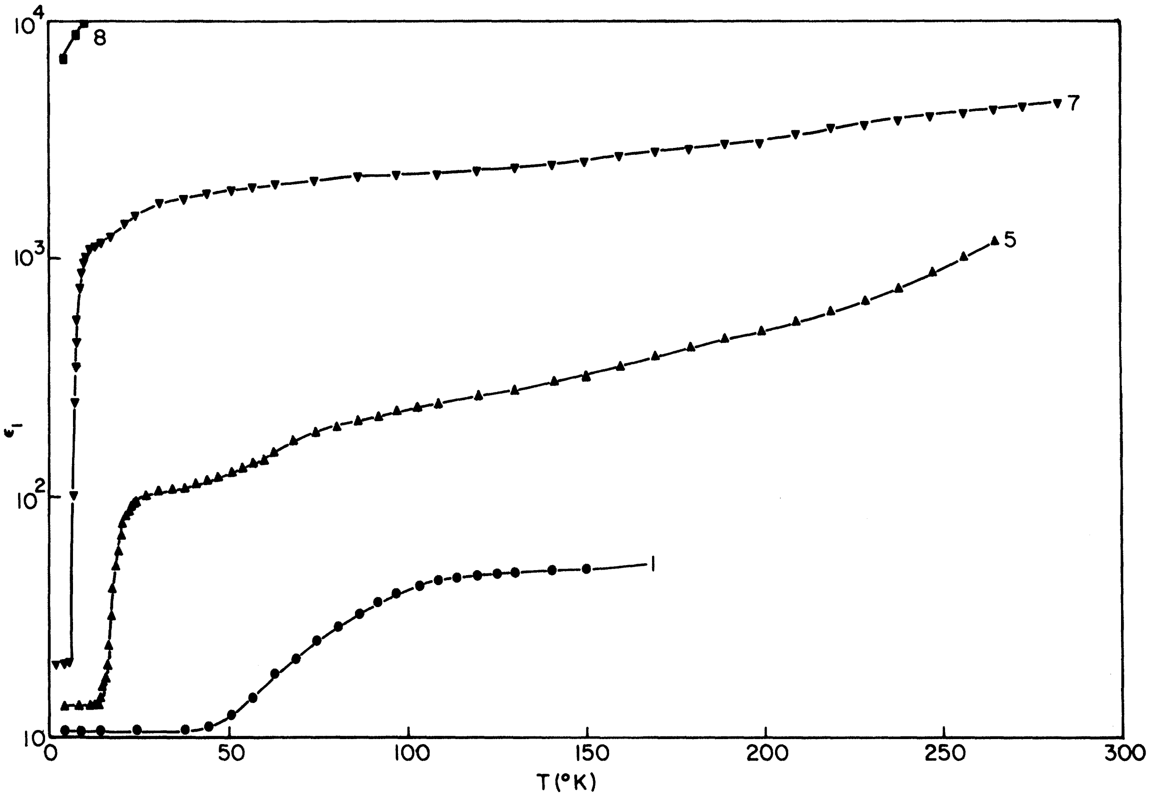

FIG. 1. Temperature dependence of ϵ_1 at 400 Hz for the slightly reduced single rutile crystals, 1: as grown, 5: phase I, 7: phase II, and 8: more reduced.

$\omega \lesssim 4$ 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 ϵ_1 and σ are presented in Fig. 8 for sample 5. Above T_m, σ is largely enhanced by E_B and this enhancement will mask the peak in σ for $E_B \gtrsim 550$ V/cm. Below T_m, σ is hardly affected by E_B. E_B increases ϵ_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 ϵ_1 and σ 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 ϵ_1, σ, or tanδ takes place is not shifted continuously by gradual reduction. Instead, the amplitude of the ϵ_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 ϵ_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 ϵ_1 decrease and of two σ peaks marks the onset of a second ordered phase II. With 340 °C $\lesssim T_c \lesssim$ 400 °C, the ϵ_1 drop and the σ 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 ϵ_1 or σ 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.*[9] led to the suggestion of the existence of a family of ordered phases indexed as Ti_nO_{2n-1} ($n = 15, \ldots \sim 36$). 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 ϵ_1 and σ 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

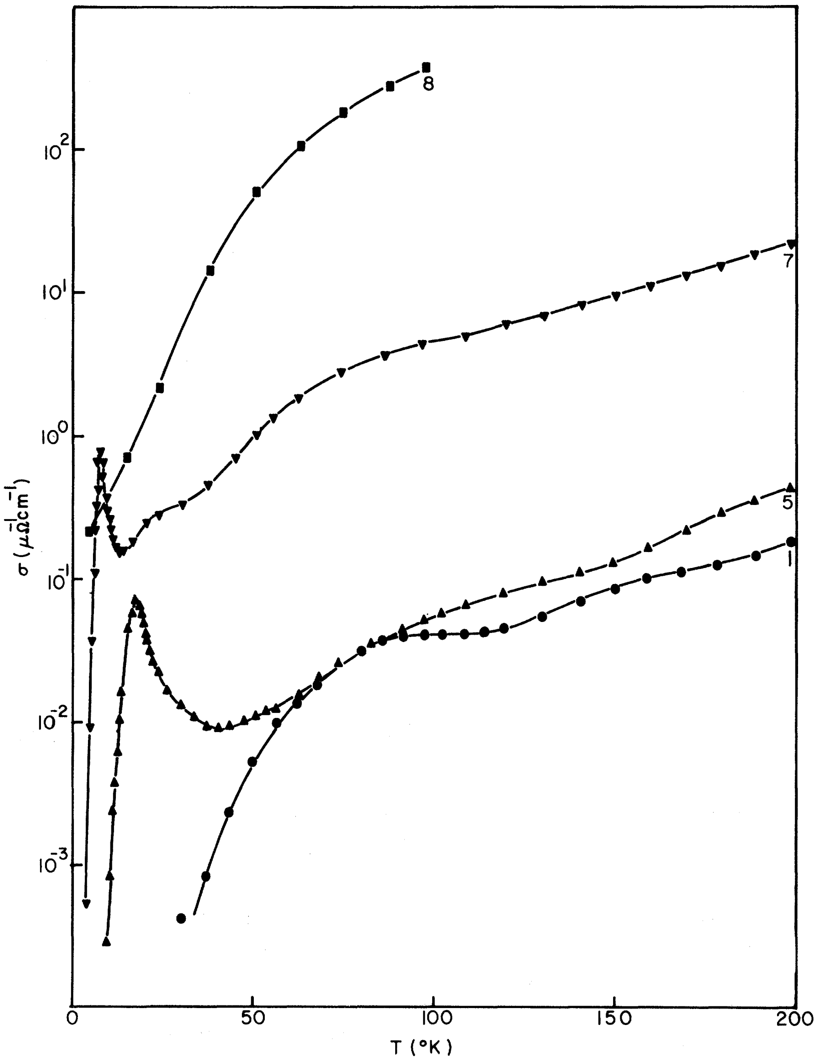

FIG. 2. Temperature dependence of σ at 400 Hz for the slightly reduced single rutile crystals 1, 5, 7, and 8.

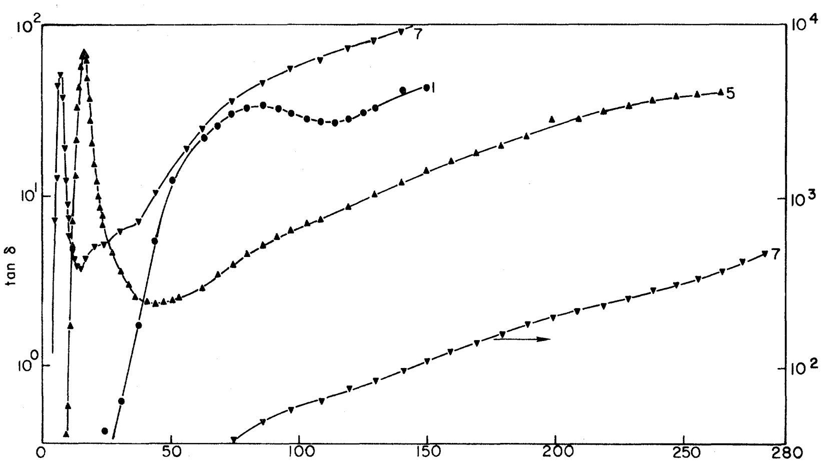

FIG. 3. Temperature dependence of tanδ at 400 Hz for the slightly reduced single rutile crystals 1, 5, and 7.

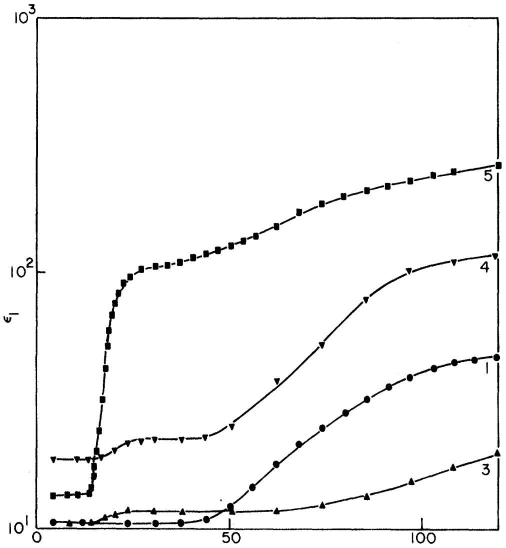

FIG. 4. Temperature dependence of ϵ_1 at 400 Hz for samples 1, 3, 4, and 5.

existence of ordered phases in slightly reduced transition-metal oxides, e.g., MoO_3, WO_3, 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 tanδ at 7 and 17 °K as well as a broad weak peak at ~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 ω.

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

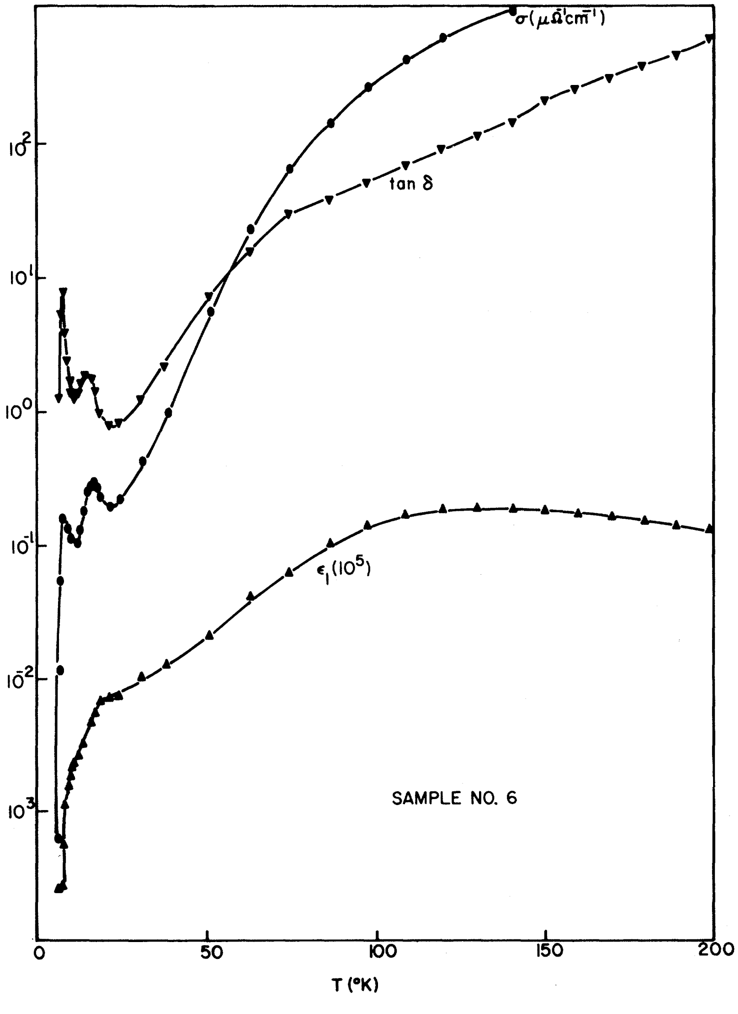

FIG. 5. Temperature dependence of ϵ_1, σ, and tanδ for sample 6.

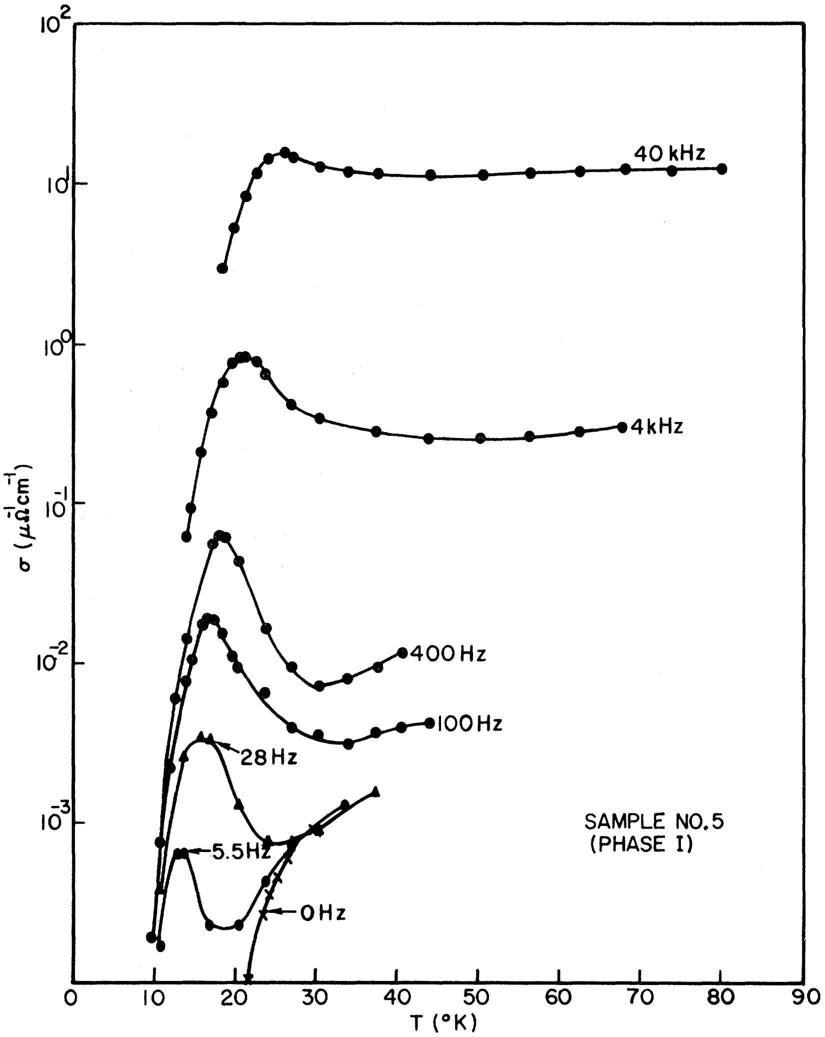

FIG. 6. Temperature dependence of σ at different frequencies for sample 5 (phase I). The dc σ was determined by a vacuum-tube voltmeter (VTVM).

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 ω at which the experiment is carried out can easily be obtained by detailed balance

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

ω_0 is the oscillation frequency of the carrier about an ion site and k is the Boltzmann's constant. Usually ω_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 ω_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 ω. 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

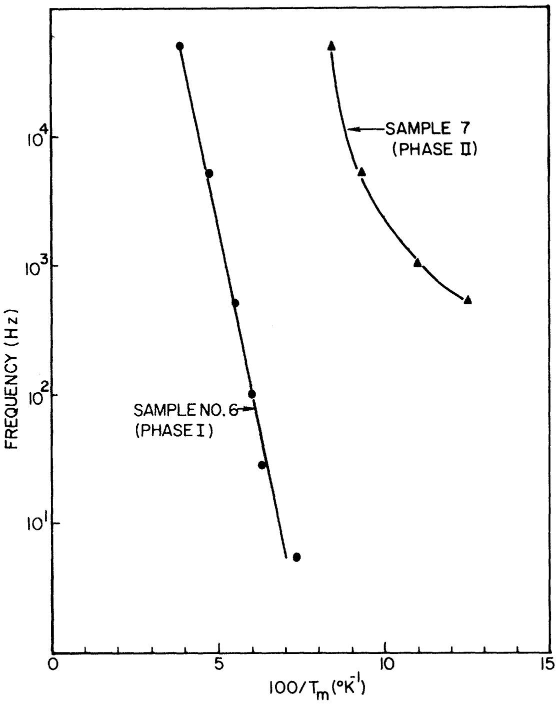

FIG. 7. Frequency dependence of T_m for the two ordered phases.

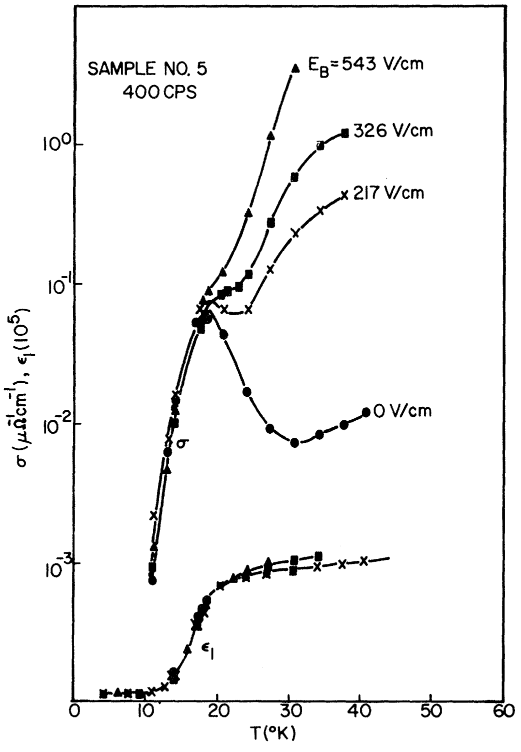

FIG. 8. Electric field effect on ϵ_1 and σ near T_m for sample 5 at 400 Hz. Same symbols were used in ϵ_1 as in σ to denote each specific E_B.

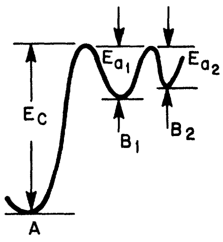

FIG. 9. Potential exerted on a hopping charge carrier by its surroundings.

found that it was difficult for the slightly reduced rutile sample to attain its thermodynamically equilibrium reduced states. For instance, the room temperature σ and ϵ_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 σ and ϵ_1 depend on T_r and t_r in a very complex way. When t_r is fixed, ϵ_1 decreases initially with T_r if $T_r \lesssim 270$ °C and then increases in contrast to the monotonic increase of σ with T_r. However, with T_r fixed, increase of t_r results in a large σ increase but only a small ϵ_1 increase. And these t_r-induced enhancements in σ and ϵ_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.[13] One is the formation of oxygen vacancies and the other the creation of 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 ϵ_1 and σ. We also observed that samples with same room temperature σ need not have same low-temperature behavior of both σ and ϵ_1 if they received different reduction treatment. Therefore the room temperature σ 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 ϵ_1 and σ over a wide temperature range. Of course, for a sample which reaches a thermodynamically equilibrium reduced state, the room temperature σ may still be good measure. Unfortunately, most reduced rutile samples previously studied did not fall into this second category[14] and yet the state of the sample was labeled by the room temperature σ. 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 ϵ_1 and σ 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[15] that the field enhanced σ was due to the migration of Ti or H ions can not account for the present observation.

(c) σ of the ordered phases changes rapidly several orders of magnitude near T_m. T_m can be shifted by the measuring frequency. In addition σ 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.

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