between pairs of simple tetragonal lattices are quite different from $4\pi/3$ calculated assuming cubic symmetry.

The electronic and ionic polarizabilities in rutile are deduced from the optical and static dielectric constants at 300°K. These are very similar to the polarizabilities used to explain the dielectric constants of barium titanate. The ionic polarizability is within 5% of being large enough to cause a ferroelectric polarization catastrophe in both the c and a directions.

Calculations of the Lorentz corrections in rutile show no large enhancements of the local fields in the z direction over the field which would be predicted assuming cubic symmetry. The local fields in the

[110] direction in rutile are similar to those in barium titanate. The Lorentz corrections show that when ionic polarization occurs, there is a large local field parallel but a small field perpendicular to titanium-oxygen chains in these two crystals, whether the chain is O-Ti-O-Ti-··· as in barium titanate, or O-Ti-O-O-Ti-O-··· as in rutile.

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Static Dielectric Constant of Rutile (TiO₂), 1.6–1060°K

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The static dielectric constant ϵ of rutile has been measured as a function of temperature from 1.6 to 1060°K. Rutile does not appear to be ferroelectric or antiferroelectric in this temperature range. At low temperatures, ϵ approaches a limiting value of 257 in the c direction and 111 in the a direction. $\epsilon_{300°K}=170$ and 86, respectively, and $\epsilon_{1000°K}=97$ and 58. The ionic polarizability of titanium is calculated using the previously derived Lorentz correction in the rutile structure. The polarizability at all temperatures is very close to the critical value for a ferroelectric polarization catastrophe. The temperature variation of the ionic polarizability is explained qualitatively on the basis of other properties of the crystal.

INTRODUCTION

RUTILE is a tetragonal crystal with a c/a ratio of 0.6441.[1] It has large refractive indices[2] ($n_c=2.903$, $n_a=2.616$) and large static dielectric constants[3,4] ($\epsilon_c=170$, $\epsilon_a=86$) at 300°K. There are several reasons for expecting that rutile might undergo a ferroelectric or antiferroelectric transition at a temperature below 300°K.

In crystals in which all of the sites have cubic environments, a polarization catastrophe will occur when $\sum_i 4\pi\alpha_i/3V \geqslant 1$, where α_i is the polarizability, V is the volume of the unit cell, and the summation is performed over the unit cell.[5] According to the polarizabilities of O^{-2} and Ti^{+4} calculated by Roberts[6] and the unit cell volume[1] at 300°K, this sum in the case of

rutile is 1.024. Hence, on the basis of this calculation, rutile would be expected to be ferroelectric at room temperature. The environments of the sites in rutile are not cubic, so this calculation is not entirely appropriate. But the large dielectric constants at room temperature suggest that the polarizability per unit volume is not very far from the value required for a catastrophe.

The local environment of the titanium sites in rutile is similar to that in barium titanate: The titanium site is surrounded by an octahedron of oxygen sites with a titanium-oxygen distance of ~2A. Slater[7] and Triebwasser[8] have shown that when ionic polarizations occur in barium titanate, there are large local fields at some of the lattice sites. Corresponding calculations of local fields in rutile[9] show that when the titanium ion is ionically polarized in the [110] or [1̄10] direction, there are similar large local fields at sites in the rutile lattice. The values of the electronic and ionic polarizabilities deduced from the optical and static dielectric constants at 300°K are very similar to those used by

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Slater[7] and Cohen[10] to explain the dielectric constants of barium titanate. Moreover, the ionic polarizabilities in both the c and a directions in rutile at 300°K are within 5% of the critical value for a ferroelectric transition.[9]

In addition, von Hippel[3] has reported that the dielectric constant of rutile has a relatively large negative temperature coefficient ($\sim -0.18/°K$) at 300°K. This suggests the possibility of a polarization catastrophe at a lower temperature.

In the present work, the possibility of a ferroelectric transition in rutile was investigated. Measurements were made of the dielectric constants in the c and a directions at temperatures between 1.6° and 1060°K. From the experimental results it is concluded that rutile is not ferroelectric or antiferroelectric in this temperature range.

The ionic polarizability as a function of temperature is deduced from the experimental results. This polarizability is at all temperatures within a few percent of the critical value for a ferroelectric polarization catastrophe.[9] The temperature variation of the ionic polarization is explained qualitatively on the basis of other measured properties of the crystal.

EXPERIMENTAL

Sample Preparation

Boules of undoped rutile, grown by the flame fusion technique, were obtained from the Linde Company and from the National Lead Company. The boules were oriented by x-ray back reflection. Samples approximately $1\times5\times5$ mm were cut with a diamond saw. One of the dimensions of the sample corresponded to the c axis and the other two to a axes. The samples were polished on No. 600 corundum paper to remove irregularities in the surface. The dimensions were then measured with a micrometer.

The orientation of the c axis of the samples was checked with polarized light and was in all cases correct within 2°. The samples were not perfect crystals; they seemed highly strained.

Before capacitance measurements were made, the crystals were heavily oxidized in order to eliminate the difficulties with large low-frequency capacitances encountered with oxygen-deficient crystals.[11] The dielectric constants of these oxidized crystals were not a function of frequency for frequencies between 10^2 and 10^6 cps.

Two different types of electrodes were used for the capacitance measurements: soldered indium for measurements below 300°K and fired-on platinum for measurements above 300°K. The electrodes were removed with aqua regia or warm dilute nitric acid. The application of the electrodes and their subsequent removal

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[11] R. A. Parker and J. H. Wasilik, Phys. Rev. 120, 1631 (1960).

with acid had no effect on the measured dielectric constants of the crystals.

Apparatus

For measurements of capacitance, the crystal with metal electrodes applied was held between the plates of a parallel plate capacitor. The two-terminal capacitance of the crystal was measured by a substitution method.[3] The measurements were performed with General Radio 716 and 716-CSL capacitance bridges and a 722-DQ precision variable capacitor. The experimental procedure is described by von Hippel.[3]

Temperatures below 78°K were measured with carbon resistors; above 78°K, with thermocouples.

The usual cryogenic techniques were used to cover the temperature range from 1.6° to 300°K. The sample was kept in a small pressure ($\sim 100\,\mu$) of dry helium. The measurements were primarily made at a frequency of 10^4 cps.

Measurements of the dielectric constant at temperatures above 300°K were made in air in a vertical tube oven. At the higher temperatures, the conductivity of the crystals increases because of two reasons: thermal excitation of intrinsic carriers and the increase in the equilibrium concentration of oxygen vacancies. These capacitance measurements were primarily made at 1–3 $\times 10^6$ cps in order to reduce the difficulties[3] due to the conductivity losses. The corrections to the capacitance due to this effect were too large to allow the accurate measurement of the dielectric constant at temperatures above 1060°K.

In the sample holders used, capacitance differences could be measured to $\pm 0.02\,\mu\mu f$, but the value of the capacitance of the sample could not be determined directly because of the lack of precision in setting the electrode gap for the measurement of the capacitance of the empty holder. Therefore the value of the capacitance of the sample at room temperature was determined to $\pm 1\%$ in a micrometer holder. The temperature variation of the capacitance of the empty holders as a function of temperature was also measured to $\pm 0.02\,\mu\mu f$.

From this information and the capacitance of the sample and holder as a function of temperature, the dielectric constant of the sample was determined to $\pm 3\%$ between 1.6° and 1060°K.

EXPERIMENTAL RESULTS

The measured dielectric constant in these experiments was not a function of frequency ($10^2 - 3\times10^6$ cps), ac field (0.1–30 v/cm), or dc bias (0–4000 v/cm). No significant difference was found in the dielectric constant of rutile cut from boules from the two different sources.

The dielectric constants of rutile in the c and a directions determined in the present experiments are shown as a function of temperature as the solid lines in
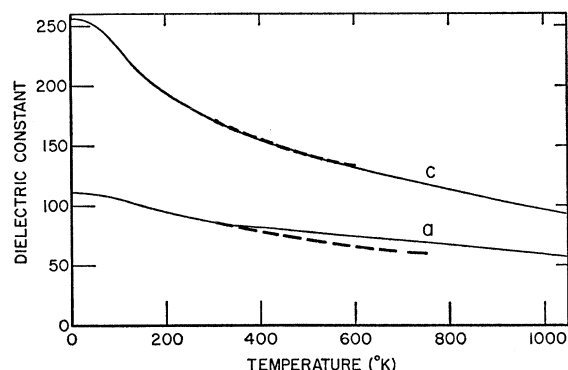
FIG. 1. Static dielectric constants of rutile. The solid lines represent the results of the present experiments; the dashed lines, values given by von Hippel.

FIG. 2. Ionic polarizability of titanium in rutile, compared with the critical value for a ferroelectric polarization catastrophe.

Fig. 1. The dashed lines in Fig. 1 are dielectric constants reported by von Hippel.[3] In the temperature range where the measurements overlap (300–700°K), there appears to be good agreement between the two sets of data in the c direction. The present values are somewhat higher than those quoted by von Hippel in the a direction.

In both the c and a directions, the dielectric constant as a function of temperature has a slope which approaches zero as the temperature approaches zero, as is required by thermodynamics. At temperatures above 30°K, the dielectric constant in both directions begins to decrease with increasing temperature. No discontinuities were found in the dielectric constant. X-ray measurements[1] show no change in the crystal structure in the range of temperatures used in these experiments.

INTERPRETATION

The ionic polarizability in rutile may be calculated from the data for the static dielectric constant by means of the relation between the applied and internal fields. Expressions for the Lorentz corrections in rutile have been derived previously.[9] In order to calculate the ionic polarizability from these expressions, it is necessary to know the electronic polarizabilities of titanium and oxygen, the unit cell volume, the Lorentz factors appropriate to the lattice, and the relative motions of the ions when the ionic polarization occurs.

Of these quantities, only the unit cell volume has been determined[1] as a function of temperature over the temperature range of these experiments. The cell volume at 300°K is 62.42 A^3.

From the optical dielectric constant at 300°K, consistent values of the electronic polarizabilities α_1 and α_3 were deduced previously[9]: $4\pi\alpha_{1c} = 4\pi\alpha_{1a} = 2.34$ A^3, $4\pi\alpha_{3c} = 32.68$ A^3, and $4\pi\alpha_{3a} = 28.73$ A^3. Values of the optical dielectric constants are not available for a large enough range of temperatures that the electronic polarizabilities could be calculated as a function of temperature. Under these circumstances, either the polarizability or the polarizability per unit volume is generally assumed con-
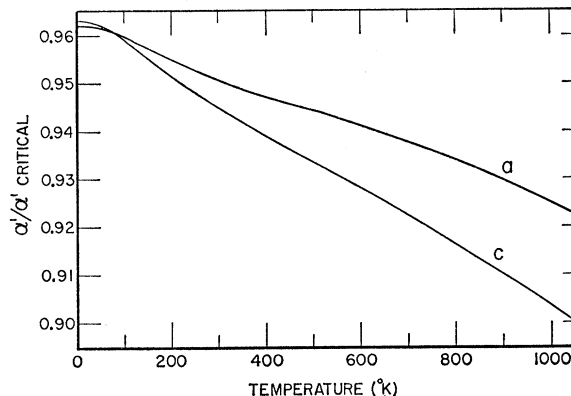
stant as a function of the temperature. For convenience in these calculations, the latter choice was made.

The Lorentz factors for the lattice depend upon the c/a ratio and the relation between a and the titanium-oxygen separation.[9] Measurements of the thermal expansion of rutile[1,12] show that although a changes by ~2.5% in the temperature range of these experiments, c/a varies by 1 part in 600. Data of comparable accuracy for the titanium-oxygen separation are not available. Assuming that this temperature variation is similar, the effect of temperature on the Lorentz factors was neglected in the calculations.

Several modes of ionic polarization are possible in rutile. The equations for the Lorentz corrections are insoluble, however, unless some assumption is made concerning the relative motions of the ions. In these calculations, the ionic polarization was taken to be a motion of the titanium lattices with the oxygen lattices held fixed.

Using the same set of assumptions, the values of $4\pi\alpha'/V$ necessary to cause a ferroelectric polarization catastrophe were calculated to be 0.1942 in the c direction and 0.2168 perpendicular to the c direction.

The calculated ionic polarizability divided by the critical value is shown as a function of temperature in Fig. 2. The ionic polarizability at 300°K is 95.0% of the amount necessary for a ferroelectric polarization catastrophe. The calculated polarizability is close to the critical value at all temperatures, as would be expected from the large dielectric constants of rutile.

An explanation of the temperature dependence of ionic polarizabilities in perovskite structures has been proposed by Barrett.[13] Since the local environment of the titanium site in rutile is very similar to that in barium titanate, his expressions were applied to rutile in order to see whether the temperature dependence of the ionic polarizabilities in rutile could be understood qualitatively on the same basis.

[12] R. K. Kirby, Metrology Division, this laboratory (unpublished results).
[13] J. H. Barrett, Phys. Rev. 86, 118 (1952).

In Barrett's analysis, the limiting value of the ionic polarizability at low temperatures, $\alpha(0)'$, is related to the effective charge of the titanium ion q_1 by the force constant K of the vibration of the titanium ion: $\alpha(0)' = q_1^2/K$. The force constants in rutile have been estimated by Dayal[14] from the Raman spectrum of rutile measured by Narayanan.[15] The effective force constant of a vibration of the titanium ion with the oxygen lattice held fixed is $\sim 1.08 \times 10^5$ d/cm in the c direction and $\sim 1.16 \times 10^5$ d/cm in the a direction.[16] From the present experiments, $\alpha(0)' \approx 1$ A^3. q_1/e is then calculated to be ~ 0.7, compared with the nominal charge of 4. Slater[7] has estimated a similar small charge (~ 1) for the titanium ion in barium titanate. According to Pauling,[17] the electronegativity of oxygen is 3.5 and that of titanium is 1.6; hence the expected ionicity is $\sim 40\%$ or $q_1/e \approx 1.6$.

Barrett has suggested that the saturation of the ionic polarizability at low temperatures is a quantum-mechanical effect which will determine the temperature dependence of the polarizability when $T \lesssim h\nu/k$, where ν is the natural frequency of the vibrations of the ion in the solid. Liebisch and Rubens[18] find strong infrared reflections in rutile for wavelengths between 10 and 120 μ; the temperature range which corresponds to these frequencies is 120–1400°K. The ionic polarizabilities in rutile begin to saturate at about 100°K.

The variation of the ionic polarizability with temperature at constant pressure may be written

$$\left(\frac{\partial(\alpha'/V)}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial\alpha'}{\partial T}\right)_V + \beta\left(\frac{\partial\alpha'}{\partial V}\right)_T - \frac{\alpha'}{V}\beta,$$

where the thermal coefficient of volume expansion $\beta \equiv V^{-1}(\partial V/\partial T)_p$. According to Slater,[7] $[\partial(\alpha'/V)/\partial V]_T > 0$ in barium titanate. If this is the case in rutile also, then $(\partial\alpha'/\partial V)_T \gtrsim \alpha'/V$. $\beta \simeq 2.6 \times 10^{-5}/°$K at 300°K.[1,12] Barrett[13] estimates that in perovskites $\alpha'^{-1}(\partial\alpha'/\partial T)_V \approx -4(3b_1+2b_2)k/K^2$ when the temperature is larger than that at which the ionic polarizability begins to saturate. Slater[7] had earlier proposed $b_1 \approx b_2 \approx K/2r^2$, where r is the titanium-oxygen separation. If this calculation is applied to rutile, $b_1 \approx K/8A^2$; $K \simeq 1.1 \times 10^5$ d/cm; and the estimated value of $\alpha'^{-1}(\partial\alpha'/\partial T)_V$ is $-3.2 \times 10^{-5}/°$K. Then, from the expression for the temperature varia-

tion given above,

$$\frac{V}{\alpha'}\left(\frac{\partial(\alpha'/V)}{\partial T}\right)_p \approx [-3.2+(\gtrsim 2.6)-2.6] \times 10^{-5}/°\text{K}$$
$$\gtrsim -3.2 \times 10^{-5}/°\text{K}.$$

The values of the corresponding terms in barium titanate have been estimated[19] to be $(-2.7+4.8-3.9) \times 10^{-5}/°$K $= -1.8 \times 10^{-5}/°$K. The values of the temperature coefficient of α'/V in rutile calculated from the present experiments are $-6.4 \times 10^{-5}/°$K and $-3.9 \times 10^{-5}/°$K in the c and a directions, respectively, for temperatures above 100°K. Although these temperature coefficients are larger than that in barium titanate, they are still much smaller than $-0.05/300°$K $\approx -17 \times 10^{-5}/°$K which would lead to a ferroelectric polarization catastrophe at 0°K. Moreover, the experimental temperature coefficients in rutile are not constant; they decrease at low temperatures and are essentially zero below $\sim 30°$K.

If $(\partial\alpha'/\partial V)_T$ were known, the temperature and volume effects in the experimentally determined temperature coefficient could be separated. One possible approach to determining this quantity would be to measure the pressure dependence of the dielectric constant since $(\partial\alpha'/\partial V)_T = (\partial\alpha'/\partial p)_T(\partial p/\partial V)_T = -\chi^{-1}(\partial\alpha'/\partial p)_T$, where the isothermal compressibility $\chi \equiv -(\partial V/\partial p)_T$.

CONCLUSIONS

No ferroelectric or antiferroelectric transitions are seen in the dielectric constant of rutile between 1.6° and 1060°K. The ionic polarizability of the titanium ion is calculated from the experimental results using previously calculated values of the Lorentz corrections in rutile. The calculated value of the ionic polarizability is at all temperatures close to the critical value for a ferroelectric polarization catastrophe. The ionic polarizability has a small negative temperature coefficient at 300°K. Below 100°K, the ionic polarizability saturates. The temperature coefficient approaches zero as the temperature approaches zero, as required by thermodynamics. The value of the ionic polarizability and its variation with temperature are explained qualitatively on the basis of other measured properties of the crystal.

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