

Lorentz Corrections in Rutile

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Equations for calculating the Lorentz corrections in cassiterites (space group D_{4h}^{14}) are derived which take into account the actual crystal structure. The calculation of critical polarizabilities necessary to cause a polarization catastrophe is demonstrated for a few ferroelectric and antiferroelectric polarizations. The Lorentz corrections are evaluated in the case of rutile (TiO_2); they are quite different from the normal value $4\pi/3$. The ionic polarizability of titanium in rutile at 300°K is found to be within 5% of the critical value for a ferroelectric transition. The calculated internal fields and polarizabilities in rutile are similar to the results of corresponding calculations for the case of cubic barium titanate.

INTRODUCTION

MANY compounds of the type MX_2 crystallize in the cassiterite structure: e.g.,¹⁻³ CoF_2 , CrO_2 , FeF_2 , GeO_2 , IrO_2 , MgF_2 , MnO_2 , MnF_2 , NbO_2 , NiF_2 , OsO_2 , PbO_2 , PdF_2 , RuO_2 , SnO_2 , TiO_2 (rutile), and ZnF_2 . A diagram of the unit cell is shown in Fig. 1. The sites in the lattice are numbered in the diagram to correspond to the notation used below. The space group is D_{4h}^{14} . Sites 1 (0,0,0) and 2 ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) are occupied by M ; X occupies sites 3 ($u, u, 0$), 4 ($1-u, 1-u, 0$), 5 ($\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}$), and 6 ($\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}$).

Several cassiterites are antiferromagnetic: e.g.,¹ CoF_2 , FeF_2 , MnO_2 , MnF_2 , and NiF_2 . In the antiferromagnetic state, the magnetic moment on site 1 is in the $+\hat{z}$ direction; that on site 2 in the $-\hat{z}$ direction.

At least two cassiterites have large dielectric constants at room temperature: $\epsilon_c=170$, $\epsilon_a=86$ in rutile^{4,5} (TiO_2); $\epsilon_c=24$, $\epsilon_a=23.4$ in cassiterite (SnO_2).⁶ The local environment of the titanium ion in rutile is very similar to that in perovskite titanates such as barium titanate: Each titanium ion is surrounded by an octahedron of oxygen ions, with a Ti—O separation of about 2 Å. However, the long-range order in the two crystal structures is quite different.

Slater⁷ and Triebwasser⁸ have shown that ionic polarizations in barium titanate are accompanied by large local fields at some of the lattice sites. The local fields are especially large at sites in titanium-oxygen chains parallel to the applied field.

In the present work, equations relating polarizations and applied fields in the cassiterite structure are derived. The point charge, point dipole approximation which is used for the interactions has been described

by Slater⁷ and Cohen.⁹ The calculation of the critical polarizability for spontaneous polarization is also demonstrated for a few ferroelectric and antiferroelectric polarizations.

These equations are solved in the specific case of rutile. The calculated polarizabilities and internal fields in rutile are compared with values in cubic barium titanate which have been calculated by a similar method by Slater,⁷ Triebwasser,⁸ and Cohen.¹⁰

LOCAL FIELD CALCULATIONS

Rutile is used as an example in the following derivation of the local field equations. The results of this section are equally applicable to any cassiterite.

The field \mathbf{E} at a lattice site in a thin slab of dielectric may be written¹¹

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_a + \mathbf{E}_b. \quad (1)$$

\mathbf{E}_0 is the applied field. \mathbf{E}_a and \mathbf{E}_b are fields due to the polarization of the dielectric. It is usually assumed that the dielectric can be divided into two parts for the purposes of this calculation: the immediate environment of the field point i , treated as discrete points, and the remainder, treated as a continuum. \mathbf{E}_a is then the field inside a spherical cavity in the dielectric due to the polarization \mathbf{P} of the dielectric outside the cavity:

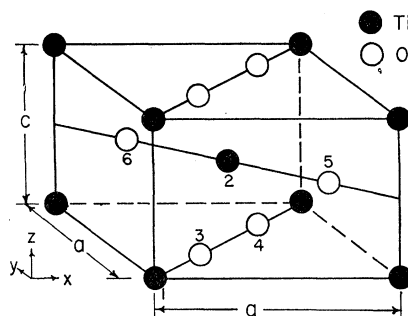


Fig. 1. Unit cell of a cassiterite, drawn for the case of rutile (TiO_2). In the general cassiterite MX_2 , the filled circles represent sites occupied by M ; the open circles sites occupied by X .

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¹ A. B. Lidiard, *Reports on Progress in Physics* (The Physical Society, London, 1954), Vol. 17, p. 201.

² A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1950), 2nd ed.

³ R. W. G. Wyckoff, *Structure of Crystals* (Chemical Catalog Company, Inc., New York, 1931), 2nd ed.

⁴ A. R. von Hippel, *Dielectric Materials and Applications* (John Wiley & Sons, Inc., New York, 1954).

⁵ R. A. Parker, following paper [Phys. Rev. 124, 1719 (1961)].

⁶ N. A. Lange, *Handbook of Chemistry* (Handbook Publishers, Inc., Sandusky, Ohio, 1949), 7th ed.

⁷ J. C. Slater, Phys. Rev. 78, 748 (1950).

⁸ S. Triebwasser, J. Phys. Chem. Solids 3, 53 (1957).

⁹ M. H. Cohen, Phys. Rev. 84, 368 (1951).

¹⁰ M. H. Cohen, Phys. Rev. 84, 369 (1951).

¹¹ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956).

$\mathbf{E}_a = 4\pi\mathbf{P}/3$. \mathbf{E}_b is the field due to sources within the cavity. If the sources are assumed to be point charges and point dipoles located at the lattice sites, this contribution may be written

$$\mathbf{E}_b = \sum'_m \left(\frac{q_m \mathbf{r}_{im}}{r_{im}^3} + \mathbf{p}_m \cdot \frac{3\mathbf{r}_{im}\mathbf{r}_{im} - r_{im}^2 \mathbf{I}}{r_{im}^5} \right), \quad (2)$$

where r_{im} is the distance between the field point i and the source point m , q_m is the effective charge on the m th ion, and \mathbf{p}_m is its dipole moment. The prime after the summation sign in Eq. (2) signifies that the term $i=m$ in the sum is omitted. The first term in Eq. (2) represents the contribution to the local field due to monopole sources; the second, that due to dipole sources; fields due to sources of higher polarity are neglected. If the field point has a cubic environment, $\mathbf{E}_b = 0$. In cassiterites, the environments are not cubic and \mathbf{E}_b may be very different from zero.

The cassiterite structure (Fig. 1) can be thought of as being composed of six simple-tetragonal lattices, one based on each of the numbered sites in the diagram. In any one of these simple-tetragonal lattices, it is assumed that the local fields at all lattice sites are equal and parallel and that the polarization is parallel to the local field. Then, from Eqs. (1) and (2), the field at a particular site in the i th lattice may be written

$$\mathbf{E}_i = \mathbf{E}_0 + \sum_{j=1}^6 (q_j \mathbf{g}_{ij} + \mathbf{P}_j \cdot \mathbf{F}_{ij}), \quad (3)$$

where q_j is the effective charge on ions in the j th lattice, $\mathbf{P}_j = \mathbf{p}_j/V$, and V is the volume of the unit cell,

$$\mathbf{g}_{ij} = \sum'_{j\text{th lattice}} (\mathbf{r}_{in}/r_{in}^3), \quad (4)$$

and

$$\mathbf{F}_{ij} = \frac{4\pi}{3} \mathbf{I} + V \sum'_{j\text{th lattice}} \frac{3\mathbf{r}_{in}\mathbf{r}_{in} - r_{in}^2 \mathbf{I}}{r_{in}^5}. \quad (5)$$

The monopole field,

$$\mathbf{G}_i = \sum_{j=1}^6 q_j \mathbf{g}_{ij},$$

is zero for titanium sites. The z component is zero for oxygen sites; the x and y components are related by

$$\begin{aligned} G_{3x} &= -G_{4x} = G_{5x} = -G_{6x} \\ &= G_{3y} = -G_{4y} = -G_{5y} = G_{6y}. \end{aligned} \quad (6)$$

In rutile, for example, $|\mathbf{G}_3| \approx 5$ v/A. The net polarization caused by these fields is zero.

\mathbf{F}_{ij} is the Lorentz factor for the dipole-dipole interaction between the simple tetragonal lattices i and j . The first term of \mathbf{F}_{ij} in Eq. (5) comes from $\mathbf{E}_a = 4\pi\mathbf{P}/3$. The other term comes from \mathbf{E}_b . If the environment is cubic, $\mathbf{E}_b = 0$ and $\mathbf{F}_{ij} = (4\pi/3)\mathbf{I}$.

TABLE I. Relations between the components $f_{ij\beta\gamma}$ of the Lorentz factors \mathbf{F}_{ij} . $f_{ij\beta\gamma} = f_{ji\beta\gamma} = f_{ij\gamma\beta}$.

\mathbf{F}_{ij}	f_{ijxx}	f_{ijyy}	f_{ijzz}	f_{ijxy}	f_{ijxz}	f_{ijyz}
\mathbf{F}_{11}	f_{11xx}	f_{11xx}	f_{11zz}	0	0	0
\mathbf{F}_{12}	f_{12xx}	f_{12xx}	f_{12zz}	0	0	0
\mathbf{F}_{13}	f_{13xx}	f_{13xx}	f_{13zz}	f_{13xy}	0	0
\mathbf{F}_{14}	f_{13xx}	f_{13xx}	f_{13zz}	f_{13xy}	0	0
\mathbf{F}_{15}	f_{23xx}	f_{23xx}	f_{23zz}	$-f_{23xy}$	0	0
\mathbf{F}_{16}	f_{23xx}	f_{23xx}	f_{23zz}	$-f_{23xy}$	0	0
\mathbf{F}_{22}	f_{11xx}	f_{11xx}	f_{11zz}	0	0	0
\mathbf{F}_{23}	f_{23xx}	f_{23xx}	f_{23zz}	f_{23xy}	0	0
\mathbf{F}_{24}	f_{23xx}	f_{23xx}	f_{23zz}	f_{23xy}	0	0
\mathbf{F}_{25}	f_{13xx}	f_{13xx}	f_{13zz}	$-f_{13xy}$	0	0
\mathbf{F}_{26}	f_{13xx}	f_{13xx}	f_{13zz}	$-f_{13xy}$	0	0
\mathbf{F}_{33}	f_{11xx}	f_{11xx}	f_{11zz}	0	0	0
\mathbf{F}_{34}	f_{34xx}	f_{34xx}	f_{34zz}	f_{34xy}	0	0
\mathbf{F}_{35}	f_{35xx}	f_{35yy}	f_{35zz}	0	0	0
\mathbf{F}_{36}	f_{35yy}	f_{35xx}	f_{35zz}	0	0	0
\mathbf{F}_{44}	f_{11xx}	f_{11xx}	f_{11zz}	0	0	0
\mathbf{F}_{45}	f_{35yy}	f_{35xx}	f_{35zz}	0	0	0
\mathbf{F}_{46}	f_{35xx}	f_{35yy}	f_{35zz}	0	0	0
\mathbf{F}_{55}	f_{11xx}	f_{11xx}	f_{11zz}	0	0	0
\mathbf{F}_{56}	f_{34xx}	f_{34xx}	f_{34zz}	$-f_{34xy}$	0	0
\mathbf{F}_{66}	f_{11xx}	f_{11xx}	f_{11zz}	0	0	0

The components of the second rank tensor \mathbf{F}_{ij} will be denoted by $f_{ij\beta\gamma}$. Here i and j refer to the simple tetragonal lattices which are interacting; β and γ to the coordinates x , y , and z . For example,

$$f_{ijxx} = \frac{4\pi}{3} + V \sum'_{j\text{th lattice}} \frac{3x_{in}^2 - r_{in}^2}{r_{in}^5},$$

$$f_{ijxy} = V \sum'_{j\text{th lattice}} \frac{3x_{in}y_{in}}{r_{in}^5}.$$

Because of the symmetry of the cassiterite structure, there are relations between the various components $f_{ij\beta\gamma}$. These relations are indicated in Table I.

Optical Case

When the frequency of the driving field is sufficiently high that all polarizations are electronic, the equations for the local fields are derived from Eq. (3). There are six such equations, one for each type of site. The polarizabilities α_j are defined by $\mathbf{p}_j = \alpha_j \mathbf{E}_j$.

Consider first the case of an applied field in the z direction. There is no monopole contribution to the field in the z direction. Since f_{ijxz} and f_{ijyz} are both zero for all i and j , the polarizations are all parallel to the z direction. The symmetries of the environments of the sites are such that for the titanium sites $P_{1z} = P_{2z}$ and $\alpha_{1z} = \alpha_{2z}$; and for the oxygen sites, $P_{3z} = P_{4z} = P_{5z} = P_{6z}$ and $\alpha_{3z} = \alpha_{4z} = \alpha_{5z} = \alpha_{6z}$. The six vector equations derived from Eq. (3) may immediately be reduced to two independent scalar equations:

$$\begin{aligned} E_{1z} &= E_{0z} + P_{1z}(f_{11zz} + f_{12zz}) + P_{3z}(2f_{13zz} + 2f_{23zz}), \\ E_{3z} &= E_{0z} + P_{1z}(f_{13zz} + f_{23zz}) \\ &\quad + P_{3z}(f_{11zz} + f_{34zz} + 2f_{35zz}). \end{aligned} \quad (7)$$

Since $P_{1z}/E_{1z}=\alpha_{1z}$ and $P_{3z}/E_{3z}=\alpha_{3z}$, there are only four unknowns. In addition, there is a relation between the total polarization and the optical dielectric constant n_c^2 :

$$n_c^2 E_{0z} = E_{0z} + 8\pi(P_{1z} + 2P_{3z}). \quad (8)$$

When the applied field is in the x direction, the equations corresponding to Eqs. (7) and (8) contain more terms. The monopole fields are not all zero; nor are the cross terms in the Lorentz factors. The symmetries of the two titanium sites are such that $P_{1x}=P_{2x}$ and $P_{1y}=-P_{2y}$; $\mathbf{G}_1=\mathbf{G}_2=0$. By symmetry, the monopole fields at the oxygen sites are related by Eq. (6). Hence, in the absence of an applied field, the oxygen polarizations \mathbf{P}_i^0 are related by

$$\begin{aligned} P_{3x}^0 &= -P_{4x}^0 = P_{5x}^0 = -P_{6x}^0 \\ &= P_{3y}^0 = -P_{4y}^0 = -P_{5y}^0 = P_{6y}^0. \end{aligned} \quad (9)$$

The total polarization of an oxygen site is written $\mathfrak{P}_i = \mathbf{P}_i^0 + \mathbf{P}_i$, where \mathbf{P}_i is the increment in the polarization caused by the applied field. The local fields are written in a similar manner. The polarization increments when a field is applied in the x direction are related by

$$P_{3x} = P_{4x} = P_{5x} = P_{6x}, \quad (10)$$

and

$$P_{3y} = P_{4y} = -P_{5y} = -P_{6y}.$$

It follows from Eqs. (9) and (10) that

$$\begin{aligned} \mathfrak{P}_{3x} + \mathfrak{P}_{4x} &= \mathfrak{P}_{5x} + \mathfrak{P}_{6x} = 2P_{3x}, \\ \mathfrak{P}_{3y} + \mathfrak{P}_{4y} &= -\mathfrak{P}_{5y} - \mathfrak{P}_{6y} = 2P_{3y}. \end{aligned} \quad (11)$$

It is possible to use Eq. (11) to set up the equations for the local fields so that polarization increments due to the applied field may be calculated without evaluating the monopole field at a lattice site.

Then the six vector equations derived from Eq. (3) relating the polarizations and the fields, summed appropriately to remove the monopole field terms, may be reduced to four independent scalar equations:

$$\begin{aligned} E_{1x} &= E_{0x} + P_{1x}(f_{11xx} + f_{12xx}) + P_{3x}2(f_{13xx} + f_{14xx}) \\ &\quad + P_{3y}2(f_{13xy} + f_{23xy}), \\ E_{1y} &= P_{1y}(f_{11xx} - f_{12xx}) + P_{3x}2(f_{13xy} - f_{23xy}) \\ &\quad + P_{3y}2(f_{13xx} - f_{23xx}), \\ E_{3x} &= E_{0x} + P_{1x}(f_{13xx} + f_{23xx}) + P_{1y}(f_{13xy} - f_{23xy}) \\ &\quad + P_{3x}(f_{11xx} + f_{34xx} + f_{35xx} + f_{35xy}) + P_{3y}f_{34xy}, \\ E_{3y} &= P_{1x}(f_{13xy} + f_{23xy}) + P_{1y}(f_{13xx} - f_{23xx}) + P_{3x}f_{34xy} \\ &\quad + P_{3y}(f_{11xx} + f_{34xx} - f_{35xx} - f_{35xy}), \end{aligned} \quad (12)$$

where \mathbf{E}_3 is the increment in the local field at the oxygen sites due to the applied field. Since $P_{1x}/E_{1x}=P_{1y}/E_{1y}=\alpha_{1x}/V$, and $P_{3x}/E_{3x}=P_{3y}/E_{3y}=\alpha_{3x}/V$, these equations contain only six unknowns.

An additional equation relates the polarizations and the optical dielectric constant n_a^2 :

$$n_a^2 E_{0x} = E_{0x} + 8\pi(P_{1x} + 2P_{3x}). \quad (13)$$

There are no terms involving the polarizations in the y direction in Eq. (13) since

$$\sum_{j=1}^6 P_{jy} = 0.$$

Static Case

When the driving frequency is low, there are additional ionic polarization terms in the local field equations. These terms will be due to the shift in location of the various lattices with respect to each other. Cohen⁹ has shown that for small displacements, as in rutile, the appropriate equations are derived from Eq. (3) as before in the optical case, with the addition of terms of the type

$$\sum_{j=1}^6 \left(\mathbf{P}_j' - \frac{q_j}{q_i} \mathbf{P}_i' \right) \cdot \mathbf{F}_{ij}. \quad (14)$$

\mathbf{P}_j' is the ionic polarization of the j th lattice. $\mathbf{p}_j' = q_j \delta_j$, where q_j is the effective charge of the ions in the j th lattice and δ_j is the displacement of the j th lattice from its zero-field position.

In rutile, $q_1=q_2=-2q_3=-2q_4=-2q_5=-2q_6$. As for the ionic polarizations, the equations for the local fields are insoluble unless some assumption is made concerning the relative motions of the various ions. Several modes of motion are possible in rutile. In the cases worked out below, the ionic polarization was assumed to be a displacement of the titanium lattices with respect to the oxygen lattices, with the oxygen lattices held fixed.

When the field is in the z direction, the electronic polarizations are related as before in the optical case. In addition, the ionic polarizations P_i' are in the z direction and are related by $P_{1z}'=P_{2z}'$. The six vector equations derived from Eqs. (3) and (14) for the local fields reduce to

$$\begin{aligned} E_{1z} &= E_0 + P_{1z}(f_{11zz} + f_{12zz}) \\ &\quad + (2P_{3z} + P_{1z}')(f_{13zz} + f_{23zz}), \\ E_{3z} &= E_0 + (P_{1z} + P_{1z}')(f_{13zz} + f_{23zz}) \\ &\quad + P_{3z}(f_{11zz} + f_{34zz} + 2f_{35zz}). \end{aligned} \quad (15)$$

The equation relating the polarizations and the static dielectric constant is

$$\epsilon_c E_{0z} = E_{0z} + 8\pi(P_{1z} + P_{1z}' + 2P_{3z}). \quad (16)$$

The ionic polarizability α_{1z}' is defined by

$$P_{1z}' = \alpha_{1z}' E_{1z}/V.$$

When the field is in the x direction, the electronic polarizations are related as above in the optical case. The ionic polarizations are in both the x and y directions. Assuming as before that the ionic polarization is a displacement of the titanium lattices with respect to

fixed oxygen lattices, symmetry requires that $P_{1x}' = P_{2x}'$, $P_{1y}' = -P_{2y}'$, and $\alpha_{1x}' = \alpha_{1y}' = P_{1x}'/E_{1x} = P_{1y}'/E_{1y}$. Rewriting the local field equations [Eqs. (12)] to include the ionic polarization terms, the six vector equations derived from Eqs. (3) and (14) may be reduced to four scalar equations:

$$\begin{aligned} E_{1x} &= E_{0x} + P_{1x}(f_{11xx} + f_{12xx}) \\ &\quad + (P_{1x}' + 2P_{3x})(f_{13xx} + f_{23xx}) \\ &\quad + (P_{1y}' + 2P_{3y})(f_{13xy} - f_{23xy}), \\ E_{1y} &= (P_{1x}' + 2P_{3x})(f_{13xy} - f_{23xy}) \\ &\quad + P_{1y}(f_{11xx} - f_{12xx}) - 2P_{1y}'f_{12xx} \\ &\quad + (P_{1y}' + 2P_{3y})(f_{13xx} - f_{23xx}), \\ E_{3x} &= E_{0x} + (P_{1x} + P_{1x}')(f_{13xx} + f_{23xx}) \\ &\quad + P_{3x}(f_{11xx} + f_{34xx} + f_{35xx} + f_{35yy}) \\ &\quad + (P_{1y} + P_{1y}')(f_{13xy} - f_{23xy}) + P_{3y}f_{34xy}, \\ E_{3y} &= (P_{1x} + P_{1x}')(f_{13xy} + f_{14xy}) + P_{3x}f_{34xy} \\ &\quad + (P_{1y} + P_{1y}')(f_{13xx} - f_{23xx}) \\ &\quad + P_{3y}(f_{11xx} + f_{34xx} - f_{35xx} - f_{35yy}). \quad (17) \end{aligned}$$

The equation relating the polarizations and the static dielectric constant is

$$\epsilon_a E_{0x} = E_{0x} + 8\pi(P_{1x} + P_{1x}' + 2P_{3x}), \quad (18)$$

since

$$\sum_{j=1}^6 P_{jy} = 0.$$

It will be noted that in the local field equations the unknowns always exceed the number of equations. It is therefore necessary to make some assumption regarding the unknowns in order to solve the equations.

Polarization Catastrophes

The critical value of the ionic polarizability necessary to cause a polarization catastrophe may also be calculated from equations for the local fields. Local field equations are written in terms of the polarizations. A nonzero solution for the polarizations is found in the case of no applied field. (This corresponds to spontaneous polarization without a change in crystal structure.) The critical polarizability is then P_i/E_i .

The critical polarizability for ferroelectric transitions in which the oxygen lattices are held fixed and the titanium lattices are spontaneously displaced may be calculated from Eqs. (15) and (17). It is assumed that the polarizations are related by $P_{1z}' = P_{2z}'$ in the z direction and $P_{1x}' = P_{2x}'$ and $P_{1y}' = -P_{2y}'$ or $P_{1y}' = P_{2y}'$ and $P_{1x}' = -P_{2x}'$ in the xy plane, or any combination of these relations.

A similar calculation can be made for the case of an antiferroelectric polarization in the z direction. It is assumed that $P_{1z}' = P_{2z}'$; hence, by symmetry, $P_{3z} = P_{4z}$

TABLE II. Components of the Lorentz factors in rutile.

\mathbf{F}_{ij}	f_{ijxx}	f_{ijyy}	f_{ijzz}	f_{ijxy}	f_{ijxz}	f_{ijyz}
\mathbf{F}_{11}	0.50361	0.50361	11.55911	0	0	0
\mathbf{F}_{12}	5.92395	5.92395	0.71845	0	0	0
\mathbf{F}_{13}	8.04624	8.04624	-3.52614	9.65294	0	0
\mathbf{F}_{23}	-2.04474	-2.04474	16.65583	9.57433	0	0
\mathbf{F}_{34}	6.97766	6.97766	-1.38898	3.24913	0	0
\mathbf{F}_{35}	14.51841	-4.69007	2.73800	0	0	0

$= -P_{5z} = -P_{6z}$. The resulting equations are

$$\begin{aligned} E_{1z} &= P_{1z}(f_{11zz} - f_{12zz}) - 2P_{1z}'f_{12zz} \\ &\quad + (P_{1z}' + 2P_{3z})(f_{13zz} - f_{23zz}), \\ E_{3z} &= (P_{1z} + P_{1z}')(f_{13zz} - f_{23zz}) \\ &\quad + P_{3z}(f_{11zz} + f_{34zz} - 2f_{35zz}). \quad (19) \end{aligned}$$

Other types of ferroelectric and antiferroelectric transitions in rutile are possible, but appropriate equations have not been derived. As long as the volume of the unit cell remains constant, the calculations will be similar to those outlined above, with the same Lorentz factors. If the transition requires a larger unit cell, the Lorentz factors must be recalculated for the new simple lattices.

All of the calculations outlined in this section are applicable to any crystal with a cassiterite structure. The values of the components of the Lorentz factors to be used in the equations will be different in each case because of the variations in the lattice parameters u and c/a . But otherwise the equations are identical.

LOCAL FIELD CALCULATIONS IN RUTILE

The local field equations derived above for the cassiterite structure [Eqs. (7), (8), (12), (13), and (15)-(18)] were solved in the case of rutile.

Rutile (TiO_2) is a cassiterite with a unit cell characterized by $a = 4.5931 \text{ \AA}$, $c/a = 0.6441$, and $u = 0.3090$.¹² The components of \mathbf{F}_{ij} defined in Eq. (5) have been computed in the case of rutile.¹³ They are listed in Table II. The components of \mathbf{F}_{11} agree with values calculated by Mueller.¹⁴

Polarizabilities in Rutile

Slater⁷ has evaluated the polarizabilities in barium titanate using similar equations for the dielectric constants and local fields. His procedure was first to find reasonable values of the electronic polarizabilities which are compatible with the observed refractive index. Then the ionic polarizability was calculated from the static dielectric constant and these electronic

¹² F. A. Mauer, Constitution and Microstructure Section, this laboratory, (unpublished results).

¹³ L. R. Walker, Bell Telephone Laboratories, Murray Hill, New Jersey (unpublished results).

¹⁴ H. Mueller, Phys. Rev. **47**, 947 (1935).

polarizabilities. The same procedure was followed to deduce the polarizabilities in rutile from the optical and static dielectric constants.

Slater⁷ has explained the refractive index of barium titanate by a titanium polarizability $4\pi\alpha_1 = 2.34 \text{ \AA}^3$ and an oxygen polarizability $4\pi\alpha_3 = 30.0 \text{ \AA}^3$. The volume of the rutile unit cell¹² at 300°K is 62.42 \AA^3 . The values of the refractive indices of rutile calculated from Eqs. (7), (8), (12), and (14) using these polarizabilities are $n_e = 2.617$ and $n_a = 2.776$, compared with the experimental values of 2.903 and 2.616, respectively.¹⁵ On the other hand, if the electronic polarizability of titanium is assumed to be $2.34 \text{ \AA}^3/4\pi$, the electronic polarizabilities of oxygen calculated from the experimental refractive indices are $4\pi\alpha_{3e} = 32.68 \text{ \AA}^3$ and $4\pi\alpha_{3a} = 28.73 \text{ \AA}^3$. These values are listed in Table III.

Cohen¹⁰ has estimated the ionic polarizability of titanium to be $4\pi\alpha_1' = 11.90 \text{ \AA}^3$ in barium titanate at the ferroelectric transition. Using this value and $4\pi\alpha_1 = 2.34 \text{ \AA}^3$ and $4\pi\alpha_3 = 30.0 \text{ \AA}^3$ as before, the static dielectric constants calculated from Eqs. (15), (16), (17), and (18) are $\epsilon_e = 31$ and $\epsilon_a = 76$, compared with the experimental values of 170 and 86, respectively.^{4,5} However, if the electronic polarizabilities deduced from the refractive indices are used in the equations, the ionic polarizabilities calculated from the experimental dielectric constants at 300°K are $4\pi\alpha_{1e}' = 11.47 \text{ \AA}^3$ and $4\pi\alpha_{1a}' = 12.88 \text{ \AA}^3$.

If it is assumed that the electronic polarizabilities per unit volume are constant, the relation between the dielectric constant and the ionic polarizability in titanium dioxide may be written

$$\epsilon_e = -0.823 + \frac{9.259}{1 - 5.150(4\pi\alpha_{1e}'/V)} \quad (20)$$

and

$$\epsilon_a = 2.773 + \frac{4.070}{1 - 4.612(4\pi\alpha_{1a}'/V)}. \quad (21)$$

The denominator in the corresponding equation for barium titanate¹⁰ is $1 - 5.38(4\pi\alpha_1'/V)$. According to Eqs. (20) and (21), the dielectric constant of rutile will be infinite in the c direction if $4\pi\alpha_{1e}' = 12.127 \text{ \AA}^3$ and in the a direction if $4\pi\alpha_{1a}' = 13.542 \text{ \AA}^3$. These values may also be calculated from Eqs. (15) and (17) as the ionic polarizabilities necessary to cause a ferroelectric polarization catastrophe. The critical polarizability in rutile is only a little larger than the value 11.90 \AA^3 which Cohen¹⁰ calculated for a similar transition in barium titanate. All of the polarizabilities in this section are listed in Table III.

Even at 300°K the ionic polarizability in rutile is nearly large enough to cause a ferroelectric polarization catastrophe. The ratio of the ionic polarizability at 300°K to the critical value is 0.946 in the c direction

TABLE III. Polarizabilities at 300°K in rutile.

	Polarizabilities (\AA^3)	
	$4\pi\alpha_e$	$4\pi\alpha_a$
Rutile		
titanium (electronic)	2.34	2.34
oxygen (electronic)	32.68	28.73
titanium (ionic)	11.47	12.88
Critical ionic polarizability		
ferroelectric catastrophe	12.13	13.54
antiferroelectric catastrophe	286	
Barium titanate		
titanium (electronic)	2.34	
oxygen (electronic)	30.00	
barium (electronic)	24.42	
titanium (ionic)	11.90	
Critical ionic polarizability		
ferroelectric catastrophe	11.90	
antiferroelectric catastrophe	9.89	

and 0.951 in the a direction. A temperature coefficient of the polarizability per unit volume

$$\frac{V}{\alpha'} \frac{d(\alpha'/V)}{dT} \gtrsim -\frac{0.05}{300^\circ\text{K}} = -1.7 \times 10^{-4}/^\circ\text{K} \quad (22)$$

would be sufficient to cause a transition at 0°K.

The value of the ionic polarizability necessary to cause an antiferroelectric transition in the z direction was calculated from Eq. (19). If the electronic polarizabilities deduced from the refractive index are used, $4\pi\alpha_{1e}' = 286 \text{ \AA}^3$ is calculated as the critical ionic polarizability. This value is so much larger than that calculated above from the static dielectric constant that this type of antiferroelectric transition seems unlikely.

The critical ionic polarizability to cause a similar antiferroelectric transition in barium titanate¹⁰ is 9.89 \AA^3 . This is somewhat less than the value 11.90 \AA^3 which Cohen calculated was required for ferroelectricity in barium titanate. Hence he concludes that the favoring of ferroelectricity in barium titanate cannot be explained by this simple dipole-dipole interaction model.

Polarizations in Rutile

The equations relating local fields and dielectric constants [Eqs. (15), (16), (17), and (18)] may also be solved for the local fields. The experimental values of the refractive indices and the static dielectric constants were used in the calculations.

By symmetry, there are no net polarizations perpendicular to a field applied in the c or a directions in rutile. However, because of the large off-diagonal elements in some of the Lorentz factors (Table II), there are sizeable individual polarizations perpendicular to a field applied in the a direction. These cross polarizations are zero when the field is applied in the z , $[110]$, or $[\bar{1}\bar{1}0]$ directions. The results of the calculations will therefore be given in these directions.

¹⁵ D. C. Cronmeyer, in Massachusetts Institute of Technology Laboratory for Insulation Research Report No. 46, 1951 (unpublished), p. 19.

TABLE IV. Lorentz corrections in rutile. The Lorentz correction L_i is defined by $\mathbf{E}_i = \mathbf{E}_0 + L_i \mathbf{P}$. $L_i = 4\pi/3 = 4.189$ for cubic environments.

	Lorentz correction	
	Optical case	Static case
Rutile, c direction		
titanium (1 or 2)	6.546	6.548
oxygen (3, 4, 5, or 6)	4.042	4.530
Rutile, $[110]$ direction		
titanium (1)	5.378	11.307
(2)	3.713	5.954
oxygen (3 or 4)	3.500	8.347
(5 or 6)	3.310	0.362
Barium titanate		
titanium	6.02	17.3
barium	3.69	0.39
oxygen (a)	5.45	13.2
(b_1 or b_2)	3.85	2.07

The contribution to the total polarization due to the electronic polarization of titanium is $\lesssim 5\%$ in all cases. Hence, the results of the calculations should not be strongly dependent upon the value assumed for the electronic polarizability of titanium.

The relation between the applied field and the local fields and polarizations may be conveniently represented as an effective Lorentz factor or Lorentz correction.

Lorentz Corrections in Rutile

The increment in the local field \mathbf{E}_i at a site in the lattice due to an applied field \mathbf{E}_0 may be written

$$\mathbf{E}_i = \mathbf{E}_0 + \mathbf{L}_i \cdot \mathbf{P},$$

where \mathbf{P} is the total polarization and \mathbf{L}_i is the Lorentz correction. If the environment of the field point is cubic, it follows from Eq. (3) that $\mathbf{L}_i = 4/3\pi\mathbf{I}$. More generally,

$$\mathbf{L}_i \cdot \mathbf{P} = \sum_{j=1}^6 \mathbf{F}_{ij} \cdot \mathbf{P}_j.$$

As noted above, \mathbf{F}_{ij} is the Lorentz factor for the interaction between the simple lattices i and j . In the effective Lorentz factor \mathbf{L}_i , these factors are weighted by the relative contribution that the associated polarization makes to the total polarization.

The calculated Lorentz corrections in rutile are listed in Table IV. The Lorentz corrections in barium titanate calculated from the results of Slater⁷ and Triebwasser⁸ are also listed. In the optical case, none of these factors is very different from $4\pi/3 = 4.189$. In the static case in the z direction in rutile, the Lorentz corrections are about equal to those in the optical case. In the $[110]$ direction in the static case, the Lorentz corrections are two or three times $4\pi/3$ at sites 1, 3, and 4 and only one-tenth of $4\pi/3$ at sites 5 and 6. In barium titanate in the static case, the Lorentz corrections are

even larger at the titanium and a oxygen sites and about one-half of $4\pi/3$ at the b oxygen sites.

Sites 3 and 4 in rutile and site a in barium titanate correspond to oxygens in a titanium-oxygen chain parallel to the applied field. Sites 5 and 6 in rutile and sites b in barium titanate are in titanium-oxygen chains perpendicular to the field. In barium titanate, chains of the type O-Ti-O-Ti-... extend through the crystal in the x , y , and z directions. In rutile, there are chains of the type O-Ti-O-O-Ti-O-... in the $[110]$ and $[\bar{1}\bar{1}0]$ directions. In both structures, the local fields in the optical case are similar to those for cubic environments. But in the static case, the local fields are 2 to 4 times larger when the field is parallel to the titanium-oxygen chain and 2 to 10 times smaller when the field is perpendicular. The Lorentz corrections in rutile are not quite as large as those in barium titanate.

Effective Charge in Rutile

The effective charge of the ions in the lattice may be estimated from the ionic polarizability¹⁶: $\alpha_1' = q_1^2/K$, where q_1 is the effective charge of the titanium ion and K is the force constant of the vibration of the titanium ion. These force constants have been calculated from the Raman spectrum of rutile.^{17,18} The effective force constant for a vibration of a titanium ion with the rest of the crystal 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.¹⁹ $\alpha_1' \approx 1 \text{ \AA}^3$ has been deduced from the dielectric constants. Hence, $q_1/e \approx 0.7$, compared with the nominal value $+4$. Slater⁷ has estimated a similar effective charge (~ 1) for the titanium ion in barium titanate. According to Pauling,²⁰ the electronegativity of oxygen is 3.5 and that of titanium 1.6; the expected ionicity is then $\sim 40\%$ or $q_1/e \approx 1.6$.

From this effective charge and the Lorentz correction calculated above (Table IV), the displacement of a titanium ion is estimated to be $\sim 10^{-15}$ cm when a 1 v/cm field is applied to the crystal. This is a justification of the assumption of small ionic displacements in the calculations of the local fields in rutile in the static case.

CONCLUSIONS

Local field equations have been derived for the cassiterite structure (space group D_{4h}^{14}). Equations for calculating critical polarizabilities for representative ferroelectric and antiferroelectric polarization catastrophes have also been derived.

These equations have been solved in the specific case of rutile. The Lorentz factors for the interactions

¹⁶ J. H. Barrett, Phys. Rev. **86**, 118 (1952).

¹⁷ B. Dayal, Proc. Indian Acad. Sci. **32A**, 304 (1950).

¹⁸ P. S. Narayanan, Proc. Indian Acad. Sci. **32A**, 279 (1950).

¹⁹ B. Dayal and N. Appalarasimham, J. Sci. Research Benares Hindu Univ. **1**, 26 (1950).

²⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945).

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 (TiO_2), 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. $\epsilon_{300^\circ\text{K}} = 170$ and 86, respectively, and $\epsilon_{1000^\circ\text{K}} = 97$ 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 indices² ($n_c = 2.903$, $n_a = 2.616$) 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 $\sum_i 4\pi\alpha_i/3V \geq 1$, 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 Roberts⁶ and the unit cell volume¹ 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 $\sim 2\text{\AA}$. Slater⁷ and Triebwasser⁸ 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 rutile⁹ show that when the titanium ion is ionically polarized in the [110] or $[\bar{1}\bar{1}0]$ 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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² D. C. Cronmeyer, in Massachusetts Institute of Technology Laboratory for Insulation Research Report No. 46, 1951 (unpublished), p. 19.

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⁴ F. A. Grant, *Revs. Modern Phys.* **31**, 646 (1959).

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⁸ S. Triebwasser, *J. Phys. Chem. Solids* **3**, 53 (1957).

⁹ R. A. Parker, preceding paper [*Phys. Rev.* **124**, 1713 (1961)].