Ferroelectricity in the Ilmenite Structure*

H. C. Schweinler
Massachusetts Institute of Technology, Cambridge, Massachusetts
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The ferroelectricity of the ilmenite structure minerals lithium tantalate and lithium niobate is studied theoretically, using the method recently introduced by Slater for barium titanate. The metal ions are assumed to move in a potential which has small quartic terms as well as the usual quadratic terms, all satisfying the appropriate crystal symmetry requirements. This results in a slight dependence of the ionic-displacement polarizability of each metal ion on both the temperature and the polarization of the crystal. The local electric field strength is computed exactly for each ion by Ewald's method, and the internal field constants are given for a number of positions in a rhombohedral unit cell of axial angle $\alpha = 56°$. The polarizabilities can be estimated from other crystal polarization data, leading to a spontaneous polarization below the upper Curie temperature T_0 of $2(T_0-T)^{\frac{1}{2}}$ microcoulombs cm^{-2} (without electromechanical correction). Whereas in barium titanate all dipole moments are in the direction of the resultant polarization, it is found here that the lower crystal symmetry results in sizeable components of the oxygen dipole moments perpendicular to the total polarization, but these last components produce a large field in the direction of the polarization at other ionic positions.

1. INTRODUCTION

UNTIL recently there were only three groups of ferroelectric crystals known. The prototype of the first to be discovered is Rochelle salt,[1] $KNaC_4H_4O_6 \cdot 4H_2O$, which has a "lower Curie point" at $-18°C$ and an "upper Curie point" at $+24°C$, between which temperatures a spontaneous polarization of maximum value about 0.26 microcoulomb cm^{-2} exists in the crystal. Characteristic of the second group is potassium dihydrogen phosphate,[2] KH_2PO_4, which has an upper Curie point only, at about $-150°C$, and a maximum spontaneous polarization of about 4.7 microcoulombs cm^{-2}. In this group isomorphous replacement of potassium ion by ammonium or phosphorus by arsenic produces a crystal with qualitatively similar properties. The most important member of the third group is barium titanate,[3] which has an upper Curie point at 120°C and two lower Curie points at about 0°C and $-70°C$, and a maximum spontaneous polarization of about 15 microcoulombs cm^{-2}. In this case many sets of substitutions on the cations are possible, such as sodium or potassium and niobium or tantalum, respectively, for barium and titanium; strontium for barium; or lanthanum for barium and iron or gallium for titanium. In all of these the perovskite crystal structure is preserved, and ferroelectric behavior is still found.

In 1949 a new kind of ferroelectric crystal was discovered.[4] The only members of this group which have been investigated up to the present time are lithium tantalate, $LiTaO_3$, and lithium niobate, $LiNbO_3$. Lithium tantalate has a maximum spontaneous polarization of about 23 microcoulombs cm^{-2} in the temperature range studied (-100 to $450°C$); the upper Curie point lies outside of this range, but the shape of the spontaneous polarization curve suggests that it is perhaps two hundred degrees higher. The spontaneous polarization decreases to a value of about 1 microcoulomb cm^{-2} at room temperature, but there is no clear indication of a lower Curie point. The crystals have the ilmenite structure, which is more complicated than that of barium titanate but simpler than Rochelle salt or potassium dihydrogen phosphate.

In this paper the method which Slater[5] first applied in his discussion of the ferroelectricity of barium titanate will be used to discuss the ilmenite structure ferroelectrics. The principal contributions of this method are its careful treatment of the internal field in the crystal and its plausible mechanism for the variation of polarizability with temperature.

The rigorous discussion of the internal field begins with the observation that a crystal structure having n ions in the unit cell may be regarded as consisting of n equal and parallel interpenetrating space lattices, one for each ion of the unit. If the ions are polarized, with a dipole moment $\mathbf{p}_i$ for ion i in the unit cell, then the crystal symmetry guarantees that all corresponding ions in the crystal have the same dipole moment, giving rise to a lattice of equal dipoles. This dipole lattice has a polarization $\mathbf{P}_i = \mathbf{p}_i/v_0$, where v_0 is the volume of the unit cell. The total polarization $\mathbf{P}$ is, of course, just the sum of the partial polarizations $\mathbf{P}_i$. The field can be computed for any point within this lattice of dipoles. In particular, the actual field at the position of any one ion is the external field, plus the sum of the fields from all other lattices of dipoles, plus the field from all other dipoles on the lattice containing the ion in question. The resultant field, however, determines the dipole moment of this ion; and since there are as many such equations as there are ions in the unit cell, we can finally express each partial polarization in terms of the applied field $\mathbf{E}^0$.

The effective polarizability of an ion, the ratio of its

[1] J. Valasek, Phys. Rev. **17**, 475 (1921).
[2] G. Busch and P. Scherrer, Naturwiss. **23**, 737 (1935).
[3] von Hippel, Breckenridge, Chesley, and Tisza, Ind. Eng. Chem. **38**, 1097 (1946).
[4] B. T. Matthias and J. P. Remeika, Phys. Rev. **76**, 1886 (1949).
[5] J. C. Slater, Phys. Rev. **78**, 748 (1950).

TABLE I. Description of ilmenite structure minerals.

Crystal	a_0 (kx)	α	u	v	x	y	z
[a]CdTiO$_3$	5.82	53° 36'	0.342	0.158	0.54	−0.03	0.26
CoTiO$_3$	5.49	54° 42'					
[b]FeTiO$_3$	5.52	54° 49'	0.358	0.142	0.555	−0.055	0.250
LiNbO$_3$	5.47	55° 43'					
[c]LiTaO$_3$	5.49	$56\frac{1}{2}$°					
[d]MgTiO$_3$	5.54	54° 39'					
MnTiO$_3$	5.62	54° 16'					
NiTiO$_3$	5.45	55° 08'	0.353	0.142	0.555	−0.055	0.250

[a] "Low" CdTiO$_3$;   [b] ilmenite;   [c] reference 6;   [d] geikielite.

dipole moment to the local field acting on it, may be a function of both the temperature and the local electric field strength. Slater showed that a very slight dependence of the polarizability on the last two quantities could, when coupled with the above set of equations relating the dipole moment of each ion to the local field acting on it, produce the highly anomalous relationship between polarization and temperature which is characteristic of ferroelectric materials. His method is to introduce into the potential in which the ions can be considered to move, certain fourth-power terms in the displacements from the equilibrium position as well as the usual second-power terms. The potential as a whole must satisfy the requirements imposed by the symmetry of the crystal, and the fourth-power terms are expected to be small compared to the second-power terms. This procedure when carried through provides the right dependence of polarizability (in this case ionic-displacement polarizability) on temperature and field strength to account for the ferroelectric behavior of the crystal.

When the actual details of the interaction of various lattices of ions are considered, it is found that the lithiums and tantalums interact with one another more than three times as strongly as the usual Lorentz correction would indicate. Furthermore, it is found that, in the case of the oxygen ions especially, the component of the dipole moment perpendicular to the applied field produces quite strong fields in the direction of the external field at other ionic positions. This effect is not found in barium titanate because of the high symmetry of the perovskite structure. In the case of the tantalums, for example, more than half of the local field can arise in this way.

The condition for ferroelectricity, of course, is that the crystal have a nonvanishing polarization in zero external field. In terms of our present formulation of the theory, this can be expressed as a relationship between the polarizabilities of the lithium, tantalum, and oxygen ions. It is possible to make a quite good estimate of the oxygen polarizability; the resulting relationship between the polarizabilities of lithium and tantalum ions depends mainly on their sum and only slightly on their ratio. We find that the ionic-displacement polarizability of the metal ions needs to be only

about one-half as great as the electronic polarizability for ferroelectricity to occur. Expressed in terms of the potential in which the metal ion moves, we get quite reasonable and ordinary values for the leading coefficients of the potential function.

Finally, an expression for the free energy of the crystal can be set up, from which we obtain the spontaneous polarization as a function of temperature below the Curie point and the dielectric constant as a function of temperature above the Curie point. The constants in both these expressions can be estimated, and prove to have about the values observed for other dielectrics. Unfortunately, direct experimental evidence for lithium tantalate itself is lacking.

2. THE CRYSTAL STRUCTURE AND PARAMETERS

For definiteness we shall confine the discussion to lithium tantalate. Its space lattice is rhombohedral, with $a_0=5.49kx$ and $\alpha=56\frac{1}{2}$°.[6] The crystal class is hexagonal alternating;[7] the space group is C_{3i}^2; and there are two LiTaO$_3$ per unit cell.[8] The structure is the ilmenite (occasionally: geikielite) structure, which has five parameters, as follows: 2Li at $\pm(uuu)$; 2Ta at
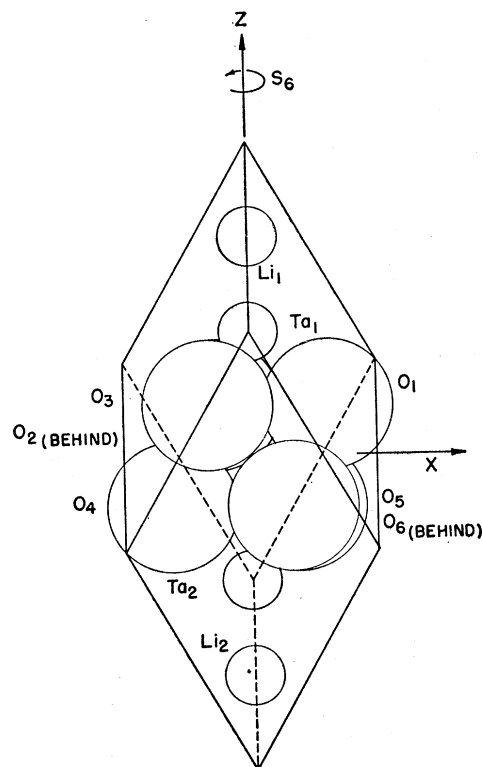

FIG. 1. LiTaO$_3$ unit cell, with ionic size indicated.

[6] E. A. Wood (private communication).
[7] H. A. Miers, *Mineralogy* (Macmillan Company, New York, 1929), second edition, p. 77.
[8] W. H. Zachariasen, Skrifter Norske Videnskans-Akad. Oslo. I. Mat.-Naturv. Klasse No. 4 (1928). The discussion in this reference is of lithium niobate, but Dr. Wood, reference 6, has examined both these substances and has found that the powder photographs are very closely similar.

$\pm(vvv)$; 6O at $\pm(xyz)$, $\pm(yzx)$, $\pm(zxy)$. The isomorphs which have been reported, according to Wyckoff[9] and *Strukturbericht*,[10] are given in Table I.

The so-called "ideal" case of the ilmenite structure arises if the above five parameters can be reduced to two, as follows: $u=\frac{1}{4}+u'$; $v=\frac{1}{4}-u'$; $x=\frac{1}{4}+v'$; $y=\frac{1}{4}-v'$; $z=\frac{1}{4}$. An inspection of the values in Table I shows that these equations are quite well satisfied in all instances for which data are available, and so we shall assume that they hold for lithium tantalate also. In the actual computations described later in this paper the values $u'=1/12$, $v'=1/3$ (i.e., $u=1/3$, $v=1/6$, $x=7/12$, $y=-1/12$, $z=1/4$), $\alpha=56°$, $a_0=5.48kx$ were used. These last parameters are those of the "ideal" corundum structure, the corundum structure being the structure to which the ilmenite structure reduces when the metal ions are the same rather than of two different kinds. A closer examination shows that the use of these values rather than the slightly different ones given in the above table introduces a negligible error.

The unit cell is shown in Fig. 1, with the ions indicated by spheres of the appropriate ionic radius.[11] Both lithium and tantalum ions are small, the former because the nuclear charge is low and the latter because the excess nuclear charge is great enough to pull the orbital electrons in close to the nucleus. The oxygen ions, on the other hand, are relatively large, for the nuclear charge is less than that on the orbital electrons. The structure is best visualized as a slightly distorted hexagonal close packing of the oxygen ions, as shown in
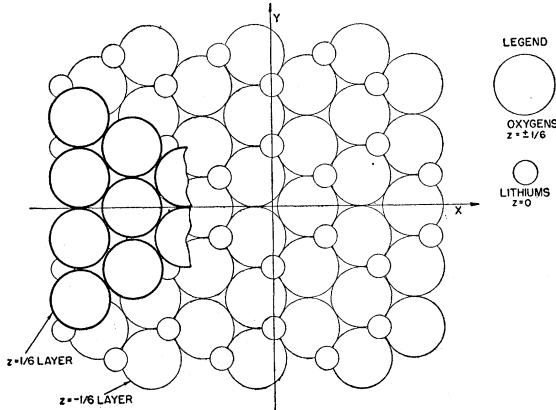

FIG. 2. Detail near the plane $z=0$.

[9] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), first edition, pp. V, a5 and V A , 6.
[10] C. Gottfried and F. Schossberger, *Strukturbericht* (Akademische Verlagsgesellschaft, Leipzig, 1937), first edition, Vol. 3, p. 379.
[11] Linus Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), second edition, p. 346. The conventional crystal radii of the ions are $r(Li^+)=0.60A$, $r(Nb^{+5})=0.70A$, and $r(O^{-2})=1.40A$. Tantalum is not listed, but the practically identical molar volumes of metallic niobium and tantalum make it seem quite likely that the volumes of the ionic cores are approximately equal. (The molar volume of the heavier metal tantalum is, in fact, slightly less than that of the lighter metal niobium.)
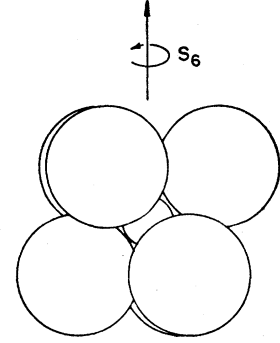

FIG. 3. Oxygen environment of tantalum at $(\frac{111}{666})$.

Fig. 2, with one-third of the interstices occupied by lithium ions, one-third by tantalum ions, and one-third unoccupied. The oxygen environment of the tantalum ion at $(\frac{111}{666})$ is shown in more detail in Fig. 3; that of the lithium ion at $(\frac{111}{333})$ is similar, except for a rotation through an angle of $180°$ about the axis S_6.

3. THE FREE ENERGY OF THE METAL IONS

We begin by considering the crystal at a temperature above the upper Curie point. The temperature motion of the ions then overcomes the tendency for spontaneous polarization, and the average values of the nuclear coordinates are just those of the ideal ilmenite structure, as given above. Each lithium ion is surrounded by six oxygens, located at $\pm(5a_1+a_2-3a_3)/12$, $\pm(-3a_1+5a_2+a_3)/12$, and $\pm(a_1-3a_2+5a_3)/12$ with respect to it, the Li$-$O distance being 2.06A. The tantalum environment is the same except for a rotation of $180°$ about the trigonal axis.

The effect of the oxygen ions on the motion of the metal ion which they surround can be treated by setting up an equivalent potential in which the metal ion moves. Using a rectangular coordinate frame[12] with origin at the metal ion in question, the potential energies of the lithium and tantalum ions (and, for future reference, of the oxygen ions) become

$$\phi_{Li}(x, y, z) = a_1(x^2+y^2)+a_2z^2+b_1(x^2+y^2)^2 \\ +2b_2(x^2+y^2)z^2+b_3z^4+b_4zx(x^2-3y^2), \quad (1)$$

$$\phi_{Ta}(x, y, z) = A_1(x^2+y^2)+A_2z^2+B_1(x^2+y^2)^2 \\ +2B_2(x^2+y^2)z^2+B_3z^4-B_4zx(x^2-3y^2), \quad (2)$$

$$\phi_O(x, y, z) = C(x^2+y^2+z^2). \quad (3)$$

If the electric field strength does not vanish at the position of the ion, the above expressions must be augmented by $-(q\mathbf{r}+\alpha\mathbf{E})\cdot\mathbf{E}+\frac{1}{2}\alpha E^2$, where q is the charge on the ion at $\mathbf{r}$, α is its electronic polarizability, and $\mathbf{E}$ is the local field strength. The term $-(q\mathbf{r}+\alpha\mathbf{E})\cdot\mathbf{E}$ is the energy of a dipole of moment $q\mathbf{r}+\alpha\mathbf{E}$ in the field,

[12] The convention is that of W. Voigt, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, Germany, 1910), first edition, p. 750. The Z axis is in the direction $a_1+a_2+a_3$; the YZ plane contains a_2, with $+Y$ in the same half-plane as a_2; and the X axis completes a right-handed coordinate frame.

$q\mathbf{r}$ being the ionic displacement dipole and $\alpha\mathbf{E}$ the induced dipole, and the term $\frac{1}{2}\alpha E^2$ is the energy of the polarized ion above its unpolarized state. We shall postpone until later a discussion of the dependence of $\mathbf{E}$ on the applied field $\mathbf{E}^0$.

The oxygens are the largest ions in the lattice, and provide, so to speak, the framework with respect to which the other ions move. Equation (3) above is introduced largely as a formality, to allow the oxygens to be treated on the same basis as the metal ions. Ultimately the coefficient C will be made very large, which corresponds to localizing the oxygens; when this is done C drops out of the expression for the free energy of the crystal.

The free energy is obtained by a straightforward application of classical statistical mechanics, and is the sum of three partial free energies, one of N lithium ions, one of N tantalum ions, and one of $3N$ oxygen ions. For example, the first of these has the following form:

$$A_{E\mathrm{Li}} = f_{\mathrm{Li}}(T) - \tfrac{1}{2}N\{[\alpha + q^2/2a_1 - (q^2/2a_1{}^2)(4b_1/a_1$$
$$+ b_2/a_2)kT](E_x{}^2 + E_y{}^2) + [\alpha + q^2/2a_2$$
$$- (q^2/2a_2{}^2)(2b_2/a_1 + 3b_3/a_2)kT]E_z{}^2\}$$
$$+ (Nq^4b_1/16a_1{}^4)(E_x{}^2 + E_y{}^2)^2$$
$$+ (Nq^4b_2/8a_1{}^2a_2{}^2)(E_x{}^2 + E_y{}^2)E_z{}^2$$
$$+ (Nq^4b_3/16a_2{}^4)E_z{}^4$$
$$+ (Nq^4b_4/16a_1{}^3a_2)E_zE_x(E_x{}^2 - 3E_y{}^2) \quad (4)$$

$$f_{\mathrm{Li}}(T) = -NkT \ln[(e\pi^3k^3T^3/Nh^3)(2m_{\mathrm{Li}})^{\frac{3}{2}}/(a_1{}^2a_2)^{\frac{1}{2}}]$$
$$+ N(kT)^2(2b_1/a_1{}^2 + b_2/a_1a_2 + 3b_3/4a_2{}^2). \quad (5)$$

In these equations the local field strengths $\mathbf{E}_i$ have been treated as independent variables, and the total dipole moment of each type of ion is obtained from the thermodynamic equations

$$VP_{xi} = -(\partial A_{Ei}/\partial E_{xi})_T, \quad (6)$$

etc.[13] There is properly, however, only one independent electric field strength, the external field $\mathbf{E}^0$, and the thermodynamic function which is most useful is the free energy expressed in terms of the external field and temperature, A_{E^0}. In particular, the total polarization $\mathbf{P}^0$ is to be derived from A_{E^0} by using the thermodynamic formulas

$$VP_x{}^0 = -(\partial A_{E^0}/\partial E_x{}^0)_T, \quad (7)$$

etc. The total polarization is, however, just the sum of the partial polarizations,

$$\mathbf{P}^0 = \mathbf{P}_{\mathrm{Li}} + \mathbf{P}_{\mathrm{Ta}} + \mathbf{P}_{\mathrm{O}}; \quad (8)$$

and if in the partial polarizations from Eq. (6) the local field strength $\mathbf{E}_i$ is expressed in terms of the external field $\mathbf{E}^0$, we can integrate Eq. (7) directly, thus getting A_{E^0}. It remains, therefore, to express the

local fields $\mathbf{E}_i$ in terms of the external field $\mathbf{E}^0$, and to this we turn our attention in the next two sections.

4. THE LOCAL ELECTRIC FIELD IN A CRYSTAL LATTICE OF EQUAL DIPOLES

Consider an infinite array of dipoles, each of moment $\mathbf{p}$, located at the lattice points of a simple translational space lattice with repeat vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. The electric field strength $\mathbf{E}(\mathbf{r})$ at an arbitrary location $\mathbf{r}$ in the crystal is then obtained in a standard way by differentiating the potential of a similar array of point charges. This latter potential is best computed by Ewald's method,[14] used here in the form given by Born.[15] The resulting expression for the field is

$$\mathbf{E}(\mathbf{r}) = \boldsymbol{\Phi} \cdot \mathbf{p}, \quad (9)$$

where $\boldsymbol{\Phi}$ is a dyadic operator obtained from the Born expression for the potential ϕ_{Born} by applying the gradient operator twice: $\boldsymbol{\Phi} = \nabla\nabla\phi_{\mathrm{Born}}$. After some mathematical manipulation, the dyadic $\boldsymbol{\Phi}$ can be expressed in the following form, which is the form actually used in making the calculations described below:

$$\epsilon_0 v_0 \boldsymbol{\Phi} = \tfrac{1}{3}\mathbf{I} - \tfrac{1}{3}\sum_n{}' \frac{3\mathbf{B}_n\mathbf{B}_n - B_n{}^2\mathbf{I}}{B_n{}^2}$$
$$\times \exp(-\pi^2B_n{}^2/A^2)\cos 2\pi\mathbf{B}_n\cdot\mathbf{r}$$
$$+ \frac{v_0}{4\pi}\sum_n \frac{3(\mathbf{r}-\mathbf{r}_n)(\mathbf{r}-\mathbf{r}_n) - (\mathbf{r}-\mathbf{r}_n)^2\mathbf{I}}{|\mathbf{r}-\mathbf{r}_n|^5}$$
$$\times F(A|\mathbf{r}-\mathbf{r}_n|). \quad (10)$$

In this equation $\mathbf{I} = \mathbf{a}_1\mathbf{b}_1 + \mathbf{a}_2\mathbf{b}_2 + \mathbf{a}_3\mathbf{b}_3$ is the identity dyadic; $\mathbf{b}_i$ is the set of vectors reciprocal to $\mathbf{a}_i(\mathbf{a}_i\cdot\mathbf{b}_j = \delta_{ij})$; $\mathbf{B}_n = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$ is a reciprocal lattice vector; $\mathbf{r}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ is a direct lattice vector, and F is given by

$$F(x) = (8/3\sqrt{\pi})\int_x^\infty t^4 \exp(-t^2)dt,$$

which is easily reducible to a tabulated function.[16] The prime on the first summation sign indicates that the single term $n_1 = n_2 = n_3 = 0$ is to be omitted. MKS units are used here; if gaussian units are desired, the permittivity of empty space, ϵ_0, is to be replaced by $1/4\pi$. A is the "separation constant," upon which the two sums separately depend but $\boldsymbol{\Phi}$ does not depend. The computations were carried out for two values of A, namely $A = \pi/a$ and $A = \pi\sqrt{2}/a$ (a the lattice constant), and the two values differed by no more than 10^{-6} in

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[13] V is the volume of the crystal of N LiTaO$_3$'s and is equal to $\frac{1}{2}Nv_0$ in terms of the volume of the unit cell v_0, the factor $\frac{1}{2}$ entering because there are two LiTaO$_3$ per unit cell.

[14] P. P. Ewald, Ann. Phys. **64**, 253 (1921).
[15] M. Born and M. G. Mayer, *Handbuch der Physik* (Verlag. Julius Springer, Berlin, Germany, 1933), second edition, Vol. 24, p. 710.
[16] *Tables of Probability Functions* (Government Printing Office, Washington, D. C., 1941), first edition, Vol. I.

all cases. Because of the automatic check provided by the method we can have considerable confidence in the results.

Φ is infinite at $r=0$, reflecting the fact that the field E is infinite at each lattice point. It is easy to show that the dyadic which gives the field at a lattice point from dipoles at all *other* lattice points is just Φ with the $r_n=0$ term in the last sum omitted. This dyadic will be called $\Phi'(000)$.

5. THE LOCAL ELECTRIC FIELD IN THE CRYSTAL

Equations (9) and (10) of the preceding section give the local field $E(r)$ at any point in a lattice of dipoles, r being the vector from a point at which a dipole is located to the point at which the field is desired. For the purposes of the present calculation we do not need the field throughout the unit cell, but only at the positions of the ions. Thus if we are considering the dipoles of moment p_j, located on the lattice which has an origin at r_j with respect to the crystal unit cell, and we desire the field at the position of another ion r_i, then this field is given by $E(r_{ij})=\Phi(r_{ij})\cdot p_j$ where $r_{ij}=r_i-r_j$. The total field at position r_i is therefore the sum of $E(r_{ij})$ for all ten lattices j (one for each ion in the unit cell), augmented by the external field E^0. It is desirable to introduce a new dyadic $D_{ij}=\epsilon_0 v_0 \Phi(r_{ij})$ in place of Φ, and the partial polarization of the jth lattice of ions $P_j=p_j/v_0$ in place of the dipole moment p_j; when this is done, the equation for the local field strength reads

$$\epsilon_0 E_i = \epsilon_0 E^0 + \sum_{j=1}^{10} D_{ij}\cdot P_j. \qquad (11)$$

This equation in conjunction with Eq. (6), which gives P_i in terms of E_i, enables each P_i to be expressed in terms of E^0, and hence, gives the total polarization P^0 in terms of E^0.

Equations (11) contain a hundred dyadics $D_{ij}=D(r_{ij})$. The arguments r_{ij} of the dyadics D are given by all sets of differences between the position vectors of the ions in the unit cell. These dyadics are of course, not all independent, and it is found that with the aid of the following two rules, easily derivable from Eq. (10), all dyadics may be obtained from six essentially different dyadics.

Rule I: The dyadic is invariant under inversion: $D(xyz)=D(\bar{x}\bar{y}\bar{z})$.

Rule II: Let $D(x_1 x_2 x_3)=\sum a_i c_{ij}(x_1 x_2 x_3)b_j$. Then $D(x_{P(1)}x_{P(2)}x_{P(3)})=\sum a_i c_{P(i)P(j)}(x_1 x_2 x_3)P_j$. Here P is a permutation operator on three symbols (in this case the subscripts 1, 2, and 3); that is, an operator which replaces 1, 2, and 3, by some rearrangement of them.

The six essentially different dyadics are the following: (a) $D'(000)$, which gives the field in any ion from all other ions on its lattice; (b) $D(\frac{1}{6}, \frac{1}{6}, \frac{1}{6})$, which gives the field on tantalum from neighboring lithium ion, and vice versa; (c) $D(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$, which gives the field on one

TABLE II. Standard dyadics for six essentially different positions in a rhombohedral unit cell with $\alpha=56°$.

$$D(xxx)=\begin{bmatrix} 0.333333 & c(x) & c(x) \\ c(x) & 0.333333 & c(x) \\ c(x) & c(x) & 0.333333 \end{bmatrix}$$

$$D(\tfrac{1}{6}, -\tfrac{1}{6}, \tfrac{1}{2})=\begin{bmatrix} -0.109429 & 0.031833 & 0.027067 \\ 0.031833 & -0.109429 & 0.027067 \\ 0.767171 & 0.767171 & 1.218858 \end{bmatrix}$$

$$D(5/12, -1/4, 1/12)=\begin{bmatrix} 2.029088 & 0.179461 & 1.388216 \\ -1.517674 & -0.596318 & -0.718488 \\ 0.458462 & 0.048894 & -0.432770 \end{bmatrix}$$

In the first matrix $c(x)$ has these values: $c(0)=-0.021317$; $c(1/6)=0.668439$; $c(1/3)=-0.372748$; $c(1/2)=0.042006$. The elements of the above matrices are the coefficients $c_{ij}(x_1 x_2 x_3)$ of the dyadics expressed in the form $D(x_1 x_2 x_3)=\sum a_i c_{ij}(x_1 x_2 x_3)b_j$.

metal ion in the unit cell from the other similar ion, and also the field on an oxygen ion from its two nearest oxygen neighbors in the unit cell; (d) $D(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which gives the field on a lithium from the tantalum which is body-centered with respect to it, and vice versa; (e) $D(\frac{1}{6}, -\frac{1}{6}, \frac{1}{2})$, which gives the field on an oxygen ion from the three oxygens in the unit cell which are next-nearest neighbors; and (f) $D(5/12, -1/4, 1/12)$, which gives the field on any metal ion from any oxygen, and vice versa. These dyadics are given in Table II.

The internal field Eqs. (11) can be simplified and partially solved simply by taking linear combinations suggested by the point-symmetry of the unit cell. Only the results of the solution will be given here, however.[17] When the external field is along the trigonal axis, the lithiums and tantalums interact strongly, with a Lorentz factor 1.044 instead of $\frac{1}{3}$. The lithium-lithium and tantalum-tantalum interactions are small. The oxygens (considered as a group) have about the normal Lorentz factor for their interaction with themselves and with both types of metal ions. When certain details of the oxygen interaction are considered, however, we get large Lorentz factors relating the field at the metal ions in the direction of the applied field to the components of the oxygen polarization perpendicular to the applied field. (This is a different situation from that met in barium titanate, where all polarizations are parallel to the applied field when the latter is along one of the crystal axes.) The most important single factor in the ferroelectricity of lithium tantalate, however, is undoubtedly the high density of oxygen ions (twenty percent greater than that of barium titanate), the oxygens of course being highly polarizable.

For the polarizability of the oxygen ion we have the following estimates: (a) Fajans and Joos,[18] on the basis

[17] The steps in the solution are instructive in that they show the details of the interactions between lithium, tantalum, and oxygen polarizations. A more complete description is found in the author's report, "Ferroelectricity in the Ilmenite Structure" (Technical Report No. 1, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology), obtainable on request from the Department of Physics, Massachusetts Institute of Technology. This report also treats other parts of this paper in greater detail.

[18] K. Fajans and G. Joos, Z. Physik 23, 1 (1924).

of the refractivities of ions in solution, found α_O/ϵ_0 = 34.6A³; (b) Pauling,[19] working from a quantum mechanical formula for the polarizability of a free ion and the observed values of absorption frequencies and oscillator strengths (which enter the formula), found $\alpha_O/\epsilon_0 = 48.7$A³; (c) Slater,[5] assuming polarizabilities of barium and titanium found by Anderson and Shockley from an intercomparison of the refractivities of many crystals, computed the value of the oxygen polarizability needed to reproduce the optical dielectric constant of barium titanate, and found $\alpha_O/\epsilon_0 = 30.0$A³. In addition to these literature values, we have applied Slater's method to crystalline Li₂O, as described in the appendix, and find the value $\alpha_O/\epsilon_0 = 25.1$A³. Considering these values, we have adopted Slater's choice α_O/ϵ_0 = 30.0A³ as the basis for our subsequent calculations. It is convenient also to introduce the dimensionless quantity $X_O = \alpha_O/\epsilon_0 v_0$, the numerical value of which is 0.284, as well as X_{Li} and X_{Ta} defined similarly.

The final step in our procedure is to write Eqs. (6) and (4) in the form $P_{zLi1} = X_{zLi} \cdot \epsilon_0 E_{zLi1} +$ (terms in $E_{zLi1}{}^3$), which gives for the local field strength in second approximation $\epsilon_0 E_{zLi1} = P_{zLi1}/X_{zL} +$ (terms in $P_{zLi1}{}^3$), with similar results for tantalum. Making this substitution for the local field strengths E_{zLi1}, etc., we get the following set of equations:

$$aP_{Li}{}^3 + (X_{Li}{}^{-1} - 1.761)P_{Li} - 3.392P_{Ta} = 4.395\epsilon_0 E^0 \quad (12)$$

$$dP_{Ta}{}^3 + (X_{Ta}{}^{-1} - 1.761)P_{Ta} - 3.392P_{Li} = 4.395\epsilon_0 E^0 \quad (13)$$

$$P^0 = 4.283\epsilon_0 E^0 + 1.198(P_{Li} + P_{Ta}) \quad (14)$$

(a and d are small terms which are given in the technical report referred to earlier).

The condition for ferroelectricity, of course, is that the polarization be nonzero in vanishing external field. In mathematical terms, this means that the determinant of the coefficients of the linear terms P_{Li} and P_{Ta} in the first two equations above must vanish. This gives a relationship between X_{Li} and X_{Ta} which depends primarily on the sum of these two quantities and only slightly on their ratio. As an example of this dependence we present the following table (using the total polarizability α^{tot}):

$\alpha_{zTa}{}^{tot}/\alpha_{zLi}{}^{tot} =$	1	2	4	10	
$(\alpha_{zTa}{}^{tot} + \alpha_{zLi}{}^{tot})/\epsilon_0 =$	40.9	42.1	45.2	50.4	A³

The above equations and table refer to the case of polarization along the trigonal axis. A similar calculation for the perpendicular direction shows that the total polarizability would have to be fifteen percent higher for spontaneous polarization to occur in this perpendicular direction. This indicates that the permanent polarization would be expected to have the direction of the trigonal axis, provided that the coefficients in the potential function for the metal ions are not greatly different for the directions along and perpendicular to

this axis. This is the behavior which might have been expected, but it is gratifying to see that our model predicts this behavior.

Let us now look more closely at the total polarizabilities which enter the above "critical equation" for ferroelectric behavior. This total polarizability consists for each metal ion of an electronic and an ionic part, of course. For lithium the electronic part is small; in Appendix I we adopt the value 0.75A³ for α_{Li}/ϵ_0. The electronic polarizability of tantalum can be estimated in the following way: Guentherschulze and Keller[20] report that $K = 11.6$, $n^2 = 11.6$ for Ta₂O₅ of specified density. The crystal structure is not known, and so the best we can do is use the Clausius-Mosotti equation to obtain the sum of the polarizabilities. (This, of course, is equivalent to adopting a Lorentz factor of one-third throughout.) Subtracting the value of the oxygen polarizability used above, we obtain the result α_{Ta}/ϵ_0 = 28.7A³. This polarizability is all electronic in nature, for the Maxwell relation $K = n^2$ was found experimentally to hold.

Upon subtracting the electronic polarizabilities of tantalum and lithium from the total polarizabilities given in the above table, we find for the sum of the ionic polarizabilities (denoted by a prime) ($\alpha'_{zTa} + \alpha'_{zLi})/\epsilon_0 = 11.5$A³ to 15.8A³. We shall not attempt to break this down further, but merely note that this is a reasonable value to expect for the ionic polarizability. For example, Slater found in his analysis of barium titanate $\alpha'_{Ti}/\epsilon_0 = 12$A³. Furthermore, the displacement of the oxygen ions in lithium tantalate from the hexagonal close packing arrangement discussed in the section on crystal structure is such as to allow greater freedom of motion of the metal ions parallel to the trigonal axis. We conclude, therefore, that the model used in this paper is capable of explaining the ferroelectricity of lithium tantalate with reasonable values of the assumed parameters.

6. THE FREE ENERGY AND SPONTANEOUS POLARIZATION

We are now in a position to integrate the equation for the free energy A_{E^0}, for the special case (of greatest interest) of applied field along the trigonal axis of the crystal. Equation (7) gives

$$A_{E^0}(E_x{}^0 = E_y{}^0 = 0) = -V \int P_z{}^0(E_z{}^0)dE_z{}^0.$$

If P_{Ta} from Eq. (12) is substituted into Eq. (13), we can solve for P_{Li} in terms of E^0, and similarly for P_{Ta} in terms of E^0. Equation (14) then gives P^0 as a function of E^0. These equations are given in more detail in the technical report referred to in an earlier footnote. For the special case of zero external field the equations simplify and the spontaneous polarization can be expressed in terms of the coefficients of the potential

[19] L. Pauling, Proc. Roy. Soc. (London) A411, 191 (1927).

[20] A. Guentherschulze and F. Keller, Z. Physik 75, 78 (1932).

functions for the metal ions. These are not known, but on the assumption that certain of the coefficients are equal the expression for the spontaneous polarization simplifies with the result $P^0 = 0.02(T_0 - T)^{\frac{1}{2}}$ coulomb m^{-2}. Matthias and Remeika[4] found a maximum spontaneous polarization of about 23 microcoulombs cm^{-2}, with which this estimate is in satisfactory agreement, suggesting a critical temperature T_0 in the neighborhood of 600°C or higher. It must be emphasized that we present here little more than an order-of-magnitude estimate, based on the equating of certain coefficients of Eqs. (1) and (2) which are not actually equal, but only of the same order. For the region above the upper Curie point, the same equations give a dielectric constant of the order of $10^6/(T - T_0)$. Experiments have not yet been made in the latter temperature region. Both the spontaneous polarization and the dielectric constant expressions have the expected form, of course, and the coefficients themselves are in the same range of values as have been found for other ferroelectric materials.

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APPENDIX

The Polarizability of Oxygen in Li$_2$O

Lithium oxide, Li$_2$O, has a cubic space lattice with $a_0 = 4.61$A. The space group is O_h^5, and there are four Li$_2$O per unit cell. The structure is the fluorite (CaF$_2$) structure. In this structure all ionic positions are determined from the symmetry alone; that is, there are no free crystallographic "parameters." When equations like Eq. (11) are written, with the dyadics $\mathbf{D}_{ij}$ appropriate to this structure, and the left-hand sides $\epsilon_0 \mathbf{E}_i$ are set equal to $\mathbf{P}_i/X_i$, it is found that the Lorentz factor of $\frac{1}{3}$ is strictly justifiable for the total polarization of both types of ions in the fluorite structure. Using the Maxwell relation $K = n^2$ between the dielectric constant K and the index of refraction n, we find that $8X_{Li} + 4X_O = 3(n^2 - 1)/(n^2 + 2)$ or $(2\alpha_{Li} + \alpha_O)/\epsilon_0 = 3a_0^3(n^2 - 1)/4(n^2 + 2) = 26.6$A^3, where $n = 1.644$ (for visible light) was used in evaluating the constant. The polarizability of the two lithiums is very small, and so this is essentially the polarizability of the oxygen ion alone. Perhaps the best estimate of the lithium polarizability is that of Bragg,[21] who found from the index of refraction of the alkali halide crystals $\alpha_{Li}/\epsilon_0 = 0.75$A^3. This in conjunction with the above leads to the value $\alpha_O/\epsilon_0 = 25.1$A^3.

[21] W. L. Bragg, The Crystalline State (G. Bell and Sons, London, 1949), first edition, Vol. I, p. 182.

Total Cross Sections for 14-Mev Neutrons*†

H. L. Poss,‡ E. O. Salant, G. A. Snow, and Luke C. L. Yuan

Brookhaven National Labratory, Upton, New York

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With deuterons from the electrostatic generator of the Department of Terrestrial Magnetism incident on a tritium-zirconium target, and with the neutrons detected by a terphenylxylene scintillator and photomultiplier, total cross sections of C, H, D, O, and N for 14.10±0.05 Mev neutrons were measured. The effective neutron energy was evaluated from the kinematics of the T(d,n)He^4 reaction, the dependence of the reaction's cross section on energy and angle, and the multiple scattering of the deuterons and their rate of energy loss in the target. A least squares analysis of the transmissions of six thicknesses each of carbon and polyethylene (40 to 85 percent transmissions) yielded, for total cross sections σ in barns: $\sigma_C = 1.279 \pm 0.004$ and $\sigma_H = 0.689 \pm 0.005$. Transmissions of light and heavy water gave $\sigma_D = 0.803 \pm 0.014$ and $\sigma_O = 1.64 \pm 0.04$. Transmission of melamine gave $\sigma_N = 1.7 \pm 0.1$.

I. INTRODUCTION

IF an analysis of neutron-proton interactions is not to be seriously complicated by either relativistic effects or the presence of nonzero angular momentum states, the neutron energy should not greatly exceed 15 Mev. At this energy, capture is negligible, so that the total cross section is purely a scattering cross section.

There have been a number of measurements of total cross sections for 14-Mev neutrons, for a number of

elements,[1-5] and while all of the earlier work shows a neutron-proton cross section of about 0.7 barn, the state of the technique was such as to leave considerable spreads in the values of both the cross section and the relevant energy. The advent of d,T neutrons has made it feasible to reduce these spreads markedly, as appears in the work of Meyer and Nyer[6] and in the work we

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† A brief account of this work was presented at the Chicago meeting of the American Physical Society, October, 1951.
‡ Now at Hudson Laboratories, Columbia University, Dobbs Ferry, New York.

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