CONCLUSION

The annealing of copper-gold alloys produces a large change in the residual resistance in those alloys that show order, and little or no change in the other compositions. The values of Debye temperature obtained from the electrical resistance are strongly temperature-dependent, and show no appreciable difference between the quenched and annealed states. Most of the change in electrical resistance on annealing appears to be due to structural changes rather than to changes in the phonon spectrum.

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Dielectric Behavior of Barium Titanate in the Paraelectric State

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The coefficients in the equation of state of $BaTiO_3$ proposed by Devonshire can be considered as describing the polarization and temperature dependence of the dielectric constant. This dependence has been studied by a dynamic method. The polarization is developed by a large-amplitude af field and the dielectric constant is measured by means of a small rf signal.

This method provides an accurate measurement of the coefficient of the P^4 term in Devonshire's equation for the free energy of $BaTiO_3$. This coefficient has been studied as a function of temperature, and, contrary to previous assumptions, has been found to have a strong temperature dependence, decreasing linearly, with temperature. The fields which can be applied without breaking the samples are not high enough to detect any contribution due to the P^6 term at temperatures as low as only 4°C above the transition to the cubic state.

I. INTRODUCTION

In a paper published in 1949,[1] Devonshire developed a phenomenological theory of ferroelectricity in barium titanate. He expanded the free energy of the unit volume[2] of a stress-free crystal as

$$\begin{aligned}\mathfrak{A}=A(P_x^2+P_y^2+P_z^2)+B(P_x^4+P_y^4+P_z^4)\\ +B_1(P_y^2P_z^2+P_z^2P_x^2+P_x^2P_y^2)\\ +C(P_x^6+P_y^6+P_z^6)+\cdots+\mathfrak{A}_0(T),\quad(1)\end{aligned}$$

where P_x, P_y, and P_z are components of the polarization along the a, b, and c axes respectively, and computed the values of A, B, and C from the experimental data that were available to him. In order to account for the Curie-Weiss law behavior of the dielectric constant, A was taken to be a linear function of temperature, namely $A=\alpha(T-T_0)$. All the other coefficients were assumed to be independent of temperature. The three phase transitions were accounted for by taking B to be negative and B_1 and C positive.

More recently,[3] Merz has shown that the double hysteresis loop of barium titanate around 120° (the upper Curie point) can be easily explained by Devonshire's theory. Merz measured the values of the polarization as a function of field, obtained at different temperatures, and computed the coefficients A, B, and C. Merz found that B was actually negative, which means that the transition must be of the first order.

Several investigators[4–7] have also observed that the transition from the ferroelectric to the paraelectric state occurs at higher temperatures than the converse transition. Here again the thermodynamic theory[5] predicts the possibility of such a temperature hysteresis for a first-order transition. The agreement is only qualitative, however; the thermodynamic treatment leaves deliberately aside some factors (nucleation processes, particularly) that probably play an important part.

We have felt it would therefore be of interest to investigate the validity of Devonshire's treatment in a

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[1] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949), see also A. F. Devonshire, Advances in Phys. **3**, 85 (1954).

[2] Strictly speaking, we are not interested in the free energy of a unit volume, but in the free energy of a fixed amount of barium titanate. These are not the same, since the volume involved changes with polarization and temperature. Since it is the free energy $\mathfrak{A}$ of the whole crystal with which we are concerned, we have $\partial\mathfrak{A}/\partial Q=V$, where Q is the total charge on the electroded area and V is the applied voltage. Since Q and V rather than P and E are the fundamental variables, it is not necessary to correct for dimensional changes due to the polarization. For purposes of comparison, however, our values of charge have been divided by the approximate area of the crystal at room temperature and our values of voltage have been divided by the crystal thickness at room temperature. This point has been brought to our attention through a set of mimeographed lecture notes for which we are indebted to Conyers Herring.

[3] W. J. Merz, Phys. Rev. **91**, 513 (1953).

[4] L. E. Cross, Phil. Mag. **44**, 1161 (1953).

[5] P. W. Forsbergh, Phys. Rev. **93**, 686 (1954).

[6] S. Roberts, Phys. Rev. **85**, 925 (1952).

[7] W. Känzig and N. Maikoff, Helv. Phys. Acta **24**, 343 (1951).

wider range of temperature. In the ferroelectric state, however, the range of variation of polarization is quite narrow, and we have limited our work to the paraelectric state, from about 120°C to 150°C. We performed our experiments on single crystals of pure barium titanate grown in our laboratory by C. Karan and B. Skinner. The samples were very thin plates with gold electrodes evaporated on their faces. They were prepared by H. Dunn and E. Davin. They are characterized by a dielectric constant of about 200 at room temperature with a very high peak (16 000) at the Curie point.[8] The saturation polarization at room temperature is 0.26 coul/m^2.

II. METHODS

Above the Curie point, the only polarization that can exist is that developed by the field applied to the electrodes, perpendicular to the faces of the plate. We can then write

$$\begin{aligned} &P_x=P_y=0, \quad P_z=P, \\ &\mathfrak{A}=AP^2+BP^4+CP^6+\cdots+\mathfrak{A}_0(T), \end{aligned} \tag{2}$$

and by differentiating Devonshire's equation we obtain

$$\partial\mathfrak{A}/\partial P=E=2AP+4BP^3+6CP^5.$$

Above the Curie point, the dielectric constant is so large that we can neglect the term E in comparison to $4\pi P$. Hence

$$\partial E/\partial P\cong 4\pi/\epsilon=2A+12BP^2+30CP^4, \tag{3}$$

where E is the externally applied field and ϵ is the permittivity of the material (equal to the dielectric constant if we use the cgs system, which we will do from now on).

Since the dielectric constant is the physical variable that can be measured most accurately, our method consists of studying the polarization dependence of the capacitance of a sample. The polarization is developed by a low-frequency (60 cps) field of variable amplitude and a very-small-amplitude radio-frequency field is superposed on the low-frequency field to allow the measurement of the capacitance. Measurements taken at different temperatures will thus show the temperature dependence of the coefficients under study.

Merz[3] has already pointed out a slight difficulty due to the electrocaloric effect. Devonshire was primarily concerned with phase transitions and limited himself to equilibrium conditions, with no field applied. His work therefore involves the Helmholtz free energy $\mathfrak{A}$, the minimum of which determines the stable state. Since we are using an ac method, the conditions are much more nearly adiabatic. Therefore the temperature T is a function of the applied polarization P. Let T_i be the temperature at zero polarization. Then if $T-T_i=\Delta T$ is small,

$$E(P,T)=\left(\frac{\partial\mathfrak{A}}{\partial P}\right)_T=\left(\frac{\partial\mathfrak{A}}{\partial P}\right)_{T_i}+\frac{\partial^2\mathfrak{A}}{\partial P\partial T}\Delta T; \tag{4}$$

and since we are studying adiabatic phenomena,

$$dS=d\left(-\frac{\partial\mathfrak{A}}{\partial T}\right)=\frac{\partial S_0}{\partial T}dT -\left[2\frac{dA}{dT}P+4\frac{dB}{dT}P^3+6\frac{dC}{dT}P^5\right]dP=0.$$

S_0 is the entropy of the unpolarized state. This shows that the temperature of the crystal varies along the polarizing cycle according to the equation

$$\Delta T=\frac{T_i}{c_P\rho}\left[\frac{dA}{dT}P^2+\frac{dB}{dT}P^4+\frac{dC}{dT}P^6\right], \tag{5}$$

where T_i is the temperature of the crystal at zero polarization, c_P is the specific heat at constant polarization, and ρ is the density. Substituting this value of ΔT in Eq. (4) and differentiating, we find

$$\left(\frac{dE}{dP}\right)_S=\frac{4\pi}{\epsilon}=2A+12\left[B+\frac{T_i}{2c_P\rho}\left(\frac{dA}{dT}\right)^2\right]P^2 +30\left[C+\frac{T_i}{c_P\rho}\frac{dA}{dT}\frac{dB}{dT}\right]P^4. \tag{6}$$

If we use the values $c_P=0.16$ cal/g deg, $\rho=6.04$ g/cm^3, and $dA/dt=3.7\times10^{-5}$, the corrective term to B,

$$\tfrac{1}{2}(T_i/c_P\rho)(dA/dT)^2,$$

appears to be of the order of 5×10^{-15} cgs, which turns out to be negligible.

Above the Curie point, barium titanate crystals are electrostrictive and exhibit an induced piezo-effect which leads to a more serious difficulty. (The piezoelectric effect is induced by polarizing the crystal.)

In order to evaluate the importance of this effect, we can consider the two cases of a free crystal (denoted by the subscript F) and that of a crystal (denoted by the subscript LC) which is clamped in one direction parallel to the faces of the plates, and cannot change its dimensions in this particular direction. We have

$$\begin{aligned} 4\pi/\epsilon_F&=2A+12B_FP^2+\cdots, \\ 4\pi/\epsilon_{LC}&=2A+12B_{LC}P^2+\cdots. \end{aligned}$$

If we now denote by $\epsilon_F{}^{LC}$ the longitudinally clamped dielectric constant of a free crystal (this is a crystal which is constrained only with respect to small dimensional changes in one direction, such as occur in a dielectric constant measurement; this crystal is not constrained for large and slow changes in polarization),

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[8] M. E. Drougard and D. R. Young, Phys. Rev. **95**, 1152 (1954).

it is shown in the Appendix that

$$B_{LC}-B_F=\frac{\pi}{3P^2}\left[\frac{1}{\epsilon_{LC}}-\frac{1}{\epsilon_F}\right]=\frac{\pi}{2P^2}\left[\frac{1}{\epsilon_F{}^{LC}}-\frac{1}{\epsilon_F}\right].$$

The quantity $\epsilon_F{}^{LC}$ can be calculated from piezoelectric measurements taken in our laboratory by E. J. Huibregtse. At 120°C, using a dc field of 12 cgs units, he found a longitudinal coupling coefficient[9] $k=0.54$. The corresponding dielectric constant was $\epsilon_F=3.3\times10^4$, while the zero field dielectric constant, ϵ_0, was 13 000. The polarization developed by the dc field is approximately

$$P\cong\epsilon_0E/4\pi E\cong1.3\times10^4 \text{ cgs units},$$

and the dielectric constant $\epsilon_F{}^{LC}$ is given by

$$\epsilon_F{}^{LC}=\epsilon_F(1-k^2)\cong23\,000,$$

and we can now compute the difference:

$$B_{LC}-B_F\cong\frac{\pi}{2(1.3)^2 10^8}\left[\frac{1}{13\,600}-\frac{1}{23\,000}\right]$$

$$\cong1.2\times10^{-13} \text{ cgs units}.$$

As will be seen later, this correction is about one-half of B, and this is in the case of a crystal clamped in only one direction perpendicular to the polarization. It is therefore quite likely that the free energy of a completely clamped crystal would have a positive P^4 term, leading to a second-order rather than a first-order transition, as has been predicted by Devonshire.

It is therefore necessary to avoid clamping the samples, which would happen to some extent if we were using a small electrode area evaporated on a much larger crystal. The best measurements should be obtained on plates having their faces entirely coated. We have used several such plates, of either a rectangular or a circular shape.

III. EXPERIMENTAL ARRANGEMENT

Temperature Regulation

The quite drastic temperature dependence of the dielectric constant in the paraelectric region, and especially near the Curie point, necessitates a very accurate stabilization of the temperature of the sample. Our system, shown in Fig. 1, is capable of holding the temperature constant to within 0.01°C for a period of 10 minutes or more.

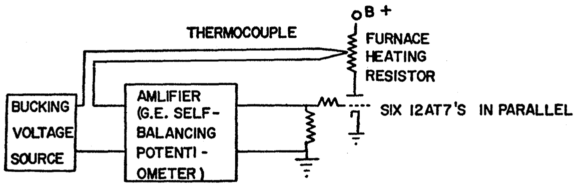

Fig. 1. Temperature stabilization arrangement.

The stabilization is accomplished by having the heating resistor in the plate circuit of a parallel arrangement of tubes. A control thermocouple in contact with the furnace is placed in series with an adjustable bucking voltage source, and the very small differential emf is, after amplification in a General Electric Self Balancing Potentiometer, applied to the grids of these tubes.

In order to measure the dielectric constant as a function of polarization we have used the same basic arrangement that was already described in an earlier paper.[10] This arrangement is shown in Fig. 2.

The very-small-amplitude radio-frequency field is added in a mixer to a large amplitude 60-cps driving sine wave, obtained from an ac regulator. The resulting wave is fed into the "Detector" terminals of a G.R. 716 bridge. The sample is housed in a very small furnace. A large capacitor is in series with it, and the combination is connected to the "Unknown" terminals of the bridge, the output of which is taken at the "Generator" terminals. The voltage across the series capacitor, which is a measure of the polarization developed across the sample, is applied to the Y axis of the scope. The bridge output is applied to the other axis, so that the unbalance of the bridge is displayed against the polarization, and the bridge can thus be balanced for any value of polarization.

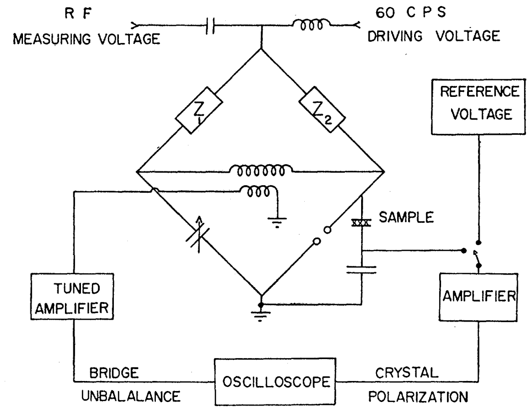

Fig. 2. The capacitor in series with the ferroelectric sample measures the polarization. The voltage developed across this series capacitor is applied to one axis of the oscilloscope. The bridge unbalance is applied to the other axis.

The measurement of the polarization itself is effected by bringing the reticle of a low-power microscope in coincidence with the chosen balance point. The Y input of the scope is then switched to a well-regulated adjustable ac source (60 cps) and the ends of the trace brought to coincidence with the microscope reticle. The measurements are accurate to a few parts in a thousand.

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[9] For a definition of longitudinal coupling coefficient see W. P. Mason, *Piezoelectric Crystals and their Application to Ultrasonics* (D. Van Nostrand Company, Inc., New York, 1950), Chap. 5.

[10] Drougard, Funk, and Young, J. Appl. Phys. **25**, 9 (1954).

IV. RESULTS

From Eq. (1) it is seen that if $\epsilon_0(T)$ and $\epsilon_P(T)$ are the dielectric constants respectively of a nonpolarized sample and of the same sample having a polarization P, the difference,

$$\frac{4\pi}{\epsilon_P(T)}-\frac{4\pi}{\epsilon_0(T)}=12BP^2+30CP^4,$$

is, for small values of P, a linear function of P^2. This is what we experimentally observe, and the slope of the straight line gives the coefficient B.

In agreement with Devonshire's calculations and with Merz's earlier measurements, we find that the coefficient B is negative. Typical results obtained on entirely electroded samples and on samples having an electrode area much smaller than the area of the whole crystal are plotted in Fig. 3, as a function of temperature. For both crystals, the coefficient A can be expressed as

$$A=3.8\times10^{-5}(T-T_0)\text{ cgs units,}\quad (T_0\cong105°\text{C})$$

in agreement with other authors.

The two kinds of samples differ most strikingly in the magnitude of B. The temperature dependence of B for the case of a free crystal is very nearly linear. If this linear law still holds at higher temperatures, the coefficient B should change sign in the vicinity of 175°C. This fact has not been checked experimentally.

No good data on the coefficient of the P^6 term can be presented as yet, because the accuracy of the measurements is slightly affected by a small frequency-independent hysteresis phenomenon which we have not been able to explain.

We have thought that it would be of interest to check our conclusions as to the variation of the temperature of the crystal during the polarizing cycle. The temperature of the crystal is as indicated by Eq. (5), an increasing function of P^2, and the average temperature of the crystal must, at equilibrium, be equal to the temperature of the furnace. Thus, if we vary the polarization at 60 cps, the zero-polarization temperature of the crystal should be slightly lower than the temperature of the furnace. Correspondingly, the dielectric constant at the zero-polarization point of the cycle should be larger than the dielectric constant we would find if only the small amplitude measuring field were applied to the crystal. This is actually what we observe on a completely electroded sample. From the capacitance readings we can compute the temperature difference due to the application of the driving field, and this turns out to be about one-half of the first term of our Eq. (5), which is the expected deviation.

V. DISCUSSION

We can compare our results to both Devonshire's and Merz's results. As pointed out by Merz,[2] the first comparison can only be fair if we replace the values of dielectric constant and polarization used by Devonshire, by those observed on our own crystals. According to the theory, our coefficient B should be given by

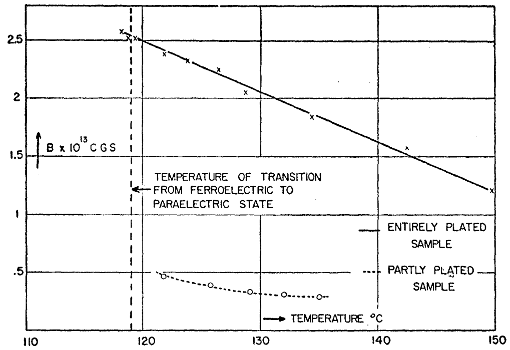

FIG. 3. Measured values of Devonshire's B coefficient *versus* temperature. The magnitude of B is larger for the entirely plated sample.

$$B=4\pi/\epsilon_c P_c^2,$$

where ϵ_c is the dielectric constant in the paraelectric state at what Devonshire calls the critical temperature (this is the temperature at which $\mathfrak{A}(P)$ has three equal minima), and P_c is the spontaneous polarization in the ferroelectric state at the same temperature, which is somewhere in the narrow temperature hysteresis range observed. As a good approximation, we can then take

$$\epsilon_c \doteq 16\,000,\quad P_c=0.18\text{ coul/m}^2=5.4\times10^4\text{ cgs units,}$$

and therefore find $B=2.7\times10^{-13}$ cgs units, which is in much better agreement with our observed value of 2.5×10^{-13} cgs at the Curie point than Merz's value of 1.7×10^{-13}.

VI. SUMMARY

We have measured the coefficient of the P^4 term of the free-energy expansion for barium titanate single crystals. We find that our value near the 120° transition is in very good agreement with Devonshire's theory. Such an agreement can be obtained only if one uses samples which have their faces entirely covered by the electrodes. We show by calculations that this coefficient is extremely sensitive to clamping and we have verified this experimentally. The existence of a hysteresis phenomenon above the Curie point has prevented us from making any good measurements of the coefficient of the P^6 term.

VII. APPENDIX. RELATION BETWEEN THE CLAMPED AND FREE DIELECTRIC CONSTANTS OF A FREE CRYSTAL AND THE DIELECTRIC CONSTANT OF A LONGITUDINALLY CLAMPED CRYSTAL

The quantities corresponding to a free crystal will be denoted by the subscript F and those for a crystal which is clamped in one direction perpendicular to the polarization by the subscript LC. The longitudinally clamped dielectric constant of a free crystal will be denoted by $\epsilon_F{}^{LC}$.

In both cases, if we assume that there are no shears and limit ourselves to the P^4 terms, we can write

$$\mathfrak{A}=\tfrac{1}{2}c_{11}(x_1{}^2+x_2{}^2+x_3{}^2)+c_{12}(x_1x_2+x_2x_3+x_3x_1)$$
$$+AP^2+B_cP^4+g_{11}x_3P^2+g_{12}(x_1+x_2)P^2,$$

where c_{11} and c_{12} are stiffness coefficients, and the x's stand for the strains. The polarization is taken to be in the "3" direction. We explicity follow Devonshire[1] and ignore terms of the type x^2P^2.

For the case of a free crystal, we have $\partial\mathfrak{A}/\partial x_i=0$ or explicitly

$$\begin{aligned} c_{11}x_1+c_{12}x_2+c_{12}x_3&=-g_{12}P^2,\\ c_{12}x_1+c_{11}x_2+c_{12}x_3&=-g_{12}P^2,\\ c_{12}x_1+c_{12}x_2+c_{11}x_3&=-g_{11}P^2. \end{aligned}\qquad\text{(I)}$$

Solving these equations gives x_1, x_2, and x_3 as a function of P^2 and we note that x_1, x_2, and x_3 are proportional to P^2.

The field is given as a function of polarization by

$$E=\frac{d\mathfrak{A}}{dP}=\frac{\partial\mathfrak{A}}{\partial x_i}\frac{\partial x_i}{\partial P}+\frac{\partial\mathfrak{A}}{\partial P}=\frac{\partial\mathfrak{A}}{\partial P},$$

since the $\partial\mathfrak{A}/\partial x_i$ are equal to zero, or

$$E=2AP+4B_cP^3+2g_{11}x_3P+2g_{12}(x_1+x_2)P.\qquad\text{(II)}$$

The free dielectric is obtained by differentiating Eq. (II) with respect to P. Since the quantities x_1, x_2, and x_3 are proportional to P^2,

$$dx_1/dP=2x_1/P,\quad dx_2/dP=2x_2/P,\quad dx_3/dP=2x_3/P,$$

and we obtain

$$4\pi/\epsilon_F\cong dE/dP=2A+12B_cP^2+2g_{11}x_3+2g_{12}(x_1+x_2)$$
$$+2g_{11}Pdx_3/dP+2g_{12}P(dx_1/dP+dx_2/dP).$$

That is,

$$4\pi/\epsilon_F=2A+12B_cP^2+6[g_{11}x_3+g_{12}(x_1+x_2)].\qquad\text{(III)}$$

In the case of a longitudinally clamped crystal, if the strains are now denoted by a prime superscript, we have

$$x_1'=0,\quad \partial\mathfrak{A}/\partial x_2'=0,\quad \partial\mathfrak{A}/\partial x_3'=0,$$

or explicitly

$$\begin{aligned} x_1'&=0,\\ c_{11}x_2'+c_{12}x_3'&=-g_{12}P^2,\\ c_{12}x_2'+c_{11}x_3'&=-g_{11}P^2, \end{aligned}\qquad\text{(IV)}$$

and the field is

$$\frac{\partial\mathfrak{A}}{\partial P}=E=\frac{\partial\mathfrak{A}}{\partial x_i}\frac{dx_i}{dP}+\frac{\partial\mathfrak{A}}{\partial P}=\frac{\partial\mathfrak{A}}{\partial P},$$

$$E=2AP+12B_cP^3+2P(g_{12}x_2'+g_{11}x_3').$$

The dielectric constant of this crystal is obtained by differentiating this last equation, and taking for dx_1', dx_2', and dx_3' the differentials of x_1', x_2', and x_3' as given by Eq. (IV). As in the case of a free crystal, we have

$$dx_2'/dP=2x_2'/P,\quad dx_3'/dP=2x_3'/P,$$

and therefore

$$4\pi/\epsilon_{LC}=2A+12B_cP^2+6[g_{11}x_3'+g_{12}x_2'].\qquad\text{(V)}$$

We wish now to compute the longitudinally clamped dielectric constant of a free crystal. This can be done by differentiating Eq. (II), and the corresponding dx's are obtained by differentiating Eqs. (I), but this time we keep x_1 constant, so that if we denote the corresponding differential strains by the symbols $d'x_1$, $d'x_2$, and $d'x_3$,

$$\begin{aligned} d'x_1&=0,\\ c_{11}d'x_2+c_{12}d'x_3&=-2g_{12}PdP,\\ c_{12}d'x_2+c_{11}d'x_3&=-2g_{11}PdP. \end{aligned}\qquad\text{(VI)}$$

We note that we obtain the same expression by differentiating Eqs. (IV). Thus, if we forget the physical significance of the x_i''s and consider them as mere algebraic symbols,

$$d'x_2/dP=2x_2'/P,\quad d'x_3/P=2x_3'/P,$$

and the dielectric constant becomes

$$\left.\begin{aligned} 4\pi/\epsilon_F{}^{LC}&=2A+12B_cP^2+2g_{11}x_3+2g_{12}(x_1+x_2)\\ &\quad+2g_{11}Pd'x_3/dP+2g_{12}Pd'x_2/dP,\\ 4\pi/\epsilon_F{}^{LC}&=2A+12B_cP^2+2[g_{11}x_3+g_{12}(x_1+x_2)]\\ &\quad+4[g_{11}x_3'+g_{12}x_2']. \end{aligned}\right\}\text{(VII)}$$

We have verified that the coefficient of the P^2 term of the free energy is the same in the case of a free or longitudinally clamped crystal. Therefore the dielectric constant at zero polarization is unaffected by clamping. If we now compute the difference,

$$4\pi/\epsilon_F{}^{LC}-4\pi/\epsilon_F=4\{[g_{11}x_3'+g_{12}x_2']-[g_{11}x_3+g_{12}(x_1+x_2)]\},$$

$$4\pi/\epsilon_C-4\pi/\epsilon_F=6\{[g_{11}x_3'+g_{12}x_2']-[g_{11}x_3+g_{12}(x_1+x_2)]\},$$

we see that

$$1/\epsilon_C-1/\epsilon_F=\tfrac{3}{2}[1/\epsilon_F{}^{LC}-1/\epsilon_F].$$

which is the relation we used in the text.