two and three electron pairs, respectively. He therefore concluded that in liquid lead two pairs of electrons are shared between neighboring atoms, while in tin three pairs are shared. The value for liquid germanium then indicates that four electron pairs are being shared between neighbors. Moreover, the fact that the structural parachor of liquid silicon does not exhibit any appreciable additional increase over that of germanium is consistent with the fact that four is the maximum number of available electrons which can be shared. These results are not in disagreement with the metalic conductivity of liquid germanium[3] and the presumably metallic conductivity of liquid silicon, since only a small fraction of free electrons is sufficient to explain the conductivity in the liquid state.

The values in parentheses for carbon must be considered a speculative extrapolation.

The results derived from the parachors do not give any answer as far as the geometrical arrangement of the atoms in the liquid state is concerned. Hendus[4] has shown that in germanium the coordination number changes from four to eight upon melting. The same result should be expected for silicon. No immediate connection between these results and the values of the parachor can be expected.

TABLE I. Surface tension and parachor of the elements of group IVb.

IVb elements	Surface tension in the liquid phase dynes/cm	Atomic volume[a]	Parachor of the elements in the liquid phase	Atomic parachor from compounds[b]	Structural parachor	Sugden's values
C	(2100)	5.41	(36.8)	4.8	(32)	
Si	720	12.0	61	33–35	28–36	
Ge	600	13.5	67	38–36	29–31	
Sn	530	16.2	79–84[b]	58	21–26	23.3
Pb	450	18.3	84–91.4[b]	76.2	8–15	11.6

[a] H. D. Hubbard and W. F. Meggers, *Periodic Chart of the Atoms* (W. W. Welch Scientific Company, Chicago, 1950).
[b] See reference 2.

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[3] R. W. Keyes, Phys. Rev. **84**, 367 (1951).

[4] H. Hendus, Z. Naturforsch. **2a**, 505–521 (1947).

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Double Hysteresis Loop of $BaTiO_3$ at the Curie Point

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It is known that the Curie point θ of the ferroelectric $BaTiO_3$ shifts to higher temperatures when a dc bias field is applied. If the crystal shows a sharp transition, we expect by applying an ac field at the Curie temperature that the crystal would become alternately ferroelectric and nonferroelectric in the cycle of the ac field. This can be seen in the shape of the hysteresis loop at temperatures slightly above θ. In the center of the polarization P *versus* field E plot, we observe a linear behavior corresponding to the paraelectric state of $BaTiO_3$ above θ. At both high voltage ends, however, we observe a hysteresis loop corresponding to the ferroelectric state. A change in temperature causes a change in size and shape of the double hysteresis loops, ranging from a line with curves at the ends (higher temperature) to two overlapping loops (lower temperature). The results obtained allow us to calculate the different constants in the free-energy expression of Devonshire and Slater. One of the results shows that the transition is of the first order since the P^4 term turns out to be negative. The properties of the hysteresis loops are discussed, especially the large spontaneous electrical polarization and the low coercive field strength.

I. INTRODUCTION

SEVERAL investigators[1–3] have shown that the Curie point θ of $BaTiO_3$ and some other ferroelectrics[4] is displaced to higher temperatures by application of a biasing field. Having available some unusually good crystals, it has been possible to investigate their behavior at the Curie point more carefully. The crystals used had simple, well-defined domain patterns; i.e., they had only parallel and antiparallel domains.[5] They also showed very sharp transitions and were good insulators even at elevated temperatures.

By working at temperatures a few degrees above the Curie temperature, it has been possible to study the $BaTiO_3$ crystals as they change from nonferroelectric to ferroelectric and back during each cycle of a strong 60 cycle field. At zero or low values of field, the crystal is not ferroelectric, since its temperature is above the normal Curie point. But at the peak values of the field, the Curie temperature is shifted by the field, so that the crystal there is below its Curie point and displays the properties of a ferroelectric.

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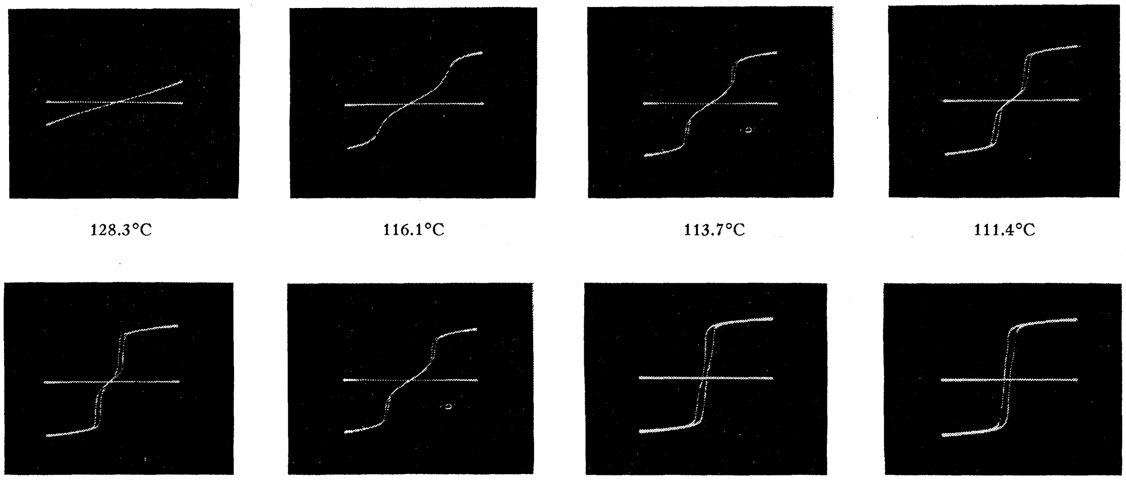
[1] A. F. Devonshire, Technical Report L/T 185 British Electrical and Allied Industries Research Associates, 1948 (unpublished).

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

[3] M. E. Caspari and W. J. Merz, Phys. Rev. **80**, 1082 (1950).

[4] G. Shirane, Phys. Rev. **86**, 219 (1952).

[5] W. J. Merz, Phys. Rev. **88**, 421 (1952).



128.3°C 116.1°C 113.7°C 111.4°C

110.5°C 109.1°C 108.2°C 107.0°C

FIG. 1. Double hysteresis loops of $BaTiO_3$.

II. MEASUREMENTS

The experimental data have been obtained from a series of hysteresis loops which are plots of electrical polarization P *versus* applied field E. The loops shown in Fig. 1 at several different temperatures are typical.

At higher temperatures, we observe a straight line: the crystal is paraelectric and at no part of the cycle is the field high enough to shift θ enough to make it ferroelectric. At lower temperatures, we find at the peak values of the field two small hysteresis loops: the crystal becomes ferroelectric when under the influence of a high electrical field. Near the Curie point these two loops overlap. At and below θ, we observe the regular hysteresis loop. If we plot the Curie temperature *versus* electric field at which the crystal becomes ferroelectric, we obtain a linear behavior (Fig. 2).

III. COMPARISON WITH THEORY

For comparison with theory, we express the free energy per cm^3 of $BaTiO_3$ as a function of electrical polarization and stress with the stress equated to zero, as proposed by Devonshire[1,6] and Slater:[7]

$$F=A(T-T_0)P^2-BP^4+CP^6+F_0(T), \qquad (1)$$

where P = electrical polarization; T = temperature; T_0 = extrapolated temperature of the $1/\epsilon(T)$ plot; A, B, C = constants. $F_0(T)$ = free energy of the unpolarized state.

The derivative of F with respect to P gives, for the electrical field strength E,

$$\partial F/\partial P=E=2A(T-T_0)P-4BP^3+6CP^5. \qquad (2)$$

In order to get dimensionless units, we normalize this equation by multiplying it with a constant K:

$$KE=2AK(T-T_0)P-4BKP^3+6CKP^5. \qquad (3)$$

We then obtain a normalized dimensionless polarization p by setting

$$\begin{aligned} 4BKP^3&=4p^3,\\ 6CKP^5&=2p^5, \end{aligned} \qquad (4)$$

with

$$K=(3C/B^{5/3})^{3/2}\ \text{cm/volt}. \qquad (5)$$

In a similar way, we introduce a normalized dimensionless electrical field e,

$$KE=e, \qquad (6)$$

and a normalized dimensionless temperature t,

$$2AK(T-T_0)P=2pt. \qquad (7)$$

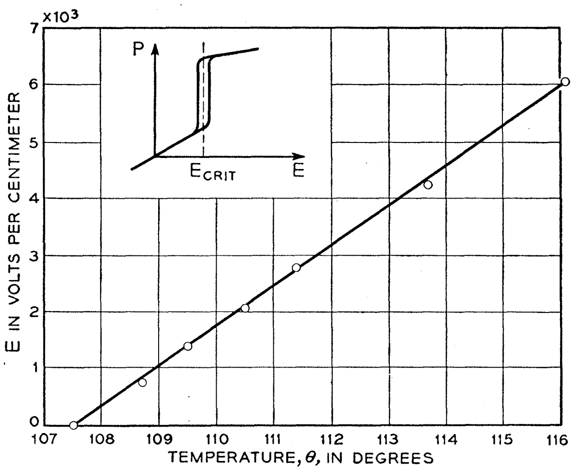


FIG. 2. Shift of Curie temperature θ *versus* applied field E.

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[6] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949).

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

TABLE I. Values for constants B and C.

Crystal	$(3C/B)^{\frac{1}{2}}$ cm²/coulomb	$(27C^3/B^5)^{\frac{1}{2}}$ cm/volt	B volt cm⁵/coulomb³	C volt cm⁹/coulomb⁵
I	7.8×10^4	3.6×10^{-4}	1.3×10^{18}	2.7×10^{27}
II	7.8×10^4	3.4×10^{-4}	1.4×10^{18}	2.8×10^{27}

TABLE II. Values for constants A, B, and C.

	A (cgs)	B (cgs)	C (cgs)
Our results	3.7×10^{-5}	1.7×10^{-13}	3.8×10^{-23}
Devonshire's results	5×10^{-5}	11×10^{-13}	61.6×10^{-23}
Corrected Devonshire's result	5×10^{-5}	2.7 to 3.1×10^{-13}	4.7 to 5.9×10^{-23}

With Eq. (5) we get, for Eqs. (4), (6), and (7),

$$p=(3C/B)^{\frac{1}{2}}P, \tag{8a}$$

$$e=(27C^3/B^5)^{\frac{1}{2}}E, \tag{8b}$$

$$t=(3AC/B^2)(T-T_0). \tag{8c}$$

Equation (2) can now be written in the form

$$e=2p^5-4p^3+2pt, \tag{9}$$

and is plotted in Fig. 3 for different values of t. Whenever dp/de becomes negative, which corresponds to an unstable condition, we replace the curve by a vertical line until it crosses the curve at a point where dp/de is positive again. We can now compare this figure with our experimentally obtained curves (Fig. 1).

IV. RESULTS

Experimentally, we can determine the expression $x=2pt-e$ of Eq. (9) from Fig. 1 for different values of p and t (related to temperature T) as indicated in Fig. 4, using just the smooth parts of the double loop curves where we have stable conditions. The results obtained are plotted as points in Fig. 4. For comparison, we also plot in Fig. 4 a solid line which represents the theoretical expression $(-2p^5+4p^3)$ as a function of p, which, according to Eq. (9), is equal to $2pt-e$. The agreement is quite good.

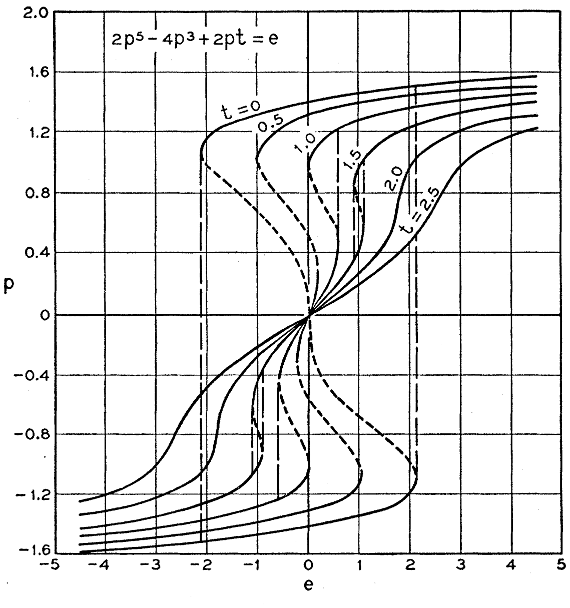

FIG. 3. Plot of function $2p^5-4p^3+2pt=e$.

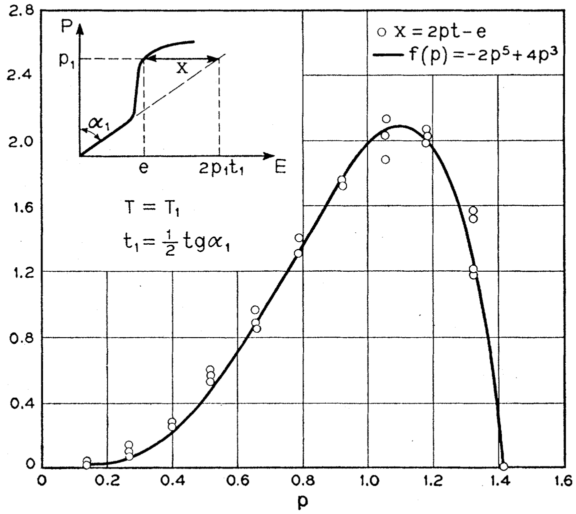

FIG. 4. Plot of values $x=2pt-e$ and function $f(p)=-2p^5+4p^3$.

In order to fit the experimental points (P,E) to the theoretical curve (p,e), we multiply polarization P and electrical field E of Fig. 1 (x is measured in terms of E) with calibration constants. We then get with Eqs. (8a) and (8b) values for $(3C/B)^{\frac{1}{2}}$ and $(27C^3/B^5)^{\frac{1}{2}}$ from which we can calculate the constants B and C (Table I).

In order to get a value for the constant A, we plot the reciprocal dielectric constant $1/\epsilon_c$, as measured with a bridge, *versus* temperature T (Fig. 5). Since, according to Eq. (2), $1/\chi=2A(T-T_0)$ in first approximation, we

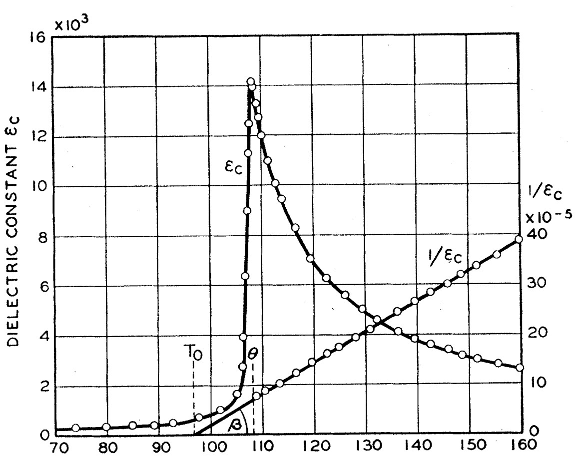

FIG. 5. Dielectric constant ϵ_c and reciprocal dielectric constant $1/\epsilon_c$ *versus* temperature T.

get for A from the slope β of Fig. 5

$$A=2\pi\beta=3.7\times10^{-5}\text{ cgs.} \tag{10}$$

As a check we can compare the temperature T of our curves (Fig. 1) with the t values of the corresponding curves (Fig. 3). Using the corresponding value for T_0 and Eq. (8c), we then get an expression for AC/B^2 which can be compared with the values A, B, and C obtained before. The agreement is good. Table II gives the average values for A, B, and C for the 2 crystals in cgs units with an accuracy of about 5–10 percent. If we compare these values with the values obtained by Devonshire[6] [his Eqs. (7.12), (7.14), (7.16)], where

$$A=\tfrac{1}{2}(\chi'_0/T_1-T_0);\quad B=\xi_{11}'/4;\quad C=\zeta'/6\quad\text{(Table II)},$$

we find that the values for A agree fairly well. This is to be expected, because A is determined in both cases by measuring the slope of the $1/\epsilon$ *versus* T curve above θ in the nonferroelectric region, where the quality of the crystal is not too important (no domain influence). The difference $\theta-T_0$ is found to be about 11°C, similar to Devonshire's[6] value.

However, our values for B and C differ greatly from Devonshire's results. In order to understand this, we measured the spontaneous electrical polarization. Whereas the dielectric constant as a function of temperature agrees fairly well with old measurements,[8] we find that the value of the spontaneous electrical polarization P_s differs greatly from old measurements.[8,9] We find that the jump of P_s at the Curie point θ is very much steeper because of the fact that the transition is much sharper. The most important difference, however, is that the absolute value of P_s is much bigger, $P_s\sim26\times10^{-6}$ coulomb/cm² at room temperature compared with $P_s\sim15.5\times10^{-6}$ coulomb/cm² before (Fig. 6). Furthermore, the value of P_s after the jump at the Curie point is $P_s\sim18\times10^{-6}$ coulomb/cm² compared with $P_s\sim10\times10^{-6}$ coulomb/cm²; that means that the new P values are 1.7 to 1.8 times bigger than the old ones.

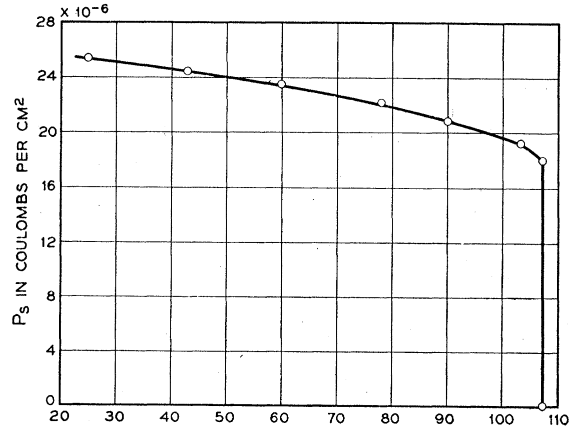

FIG. 6. Spontaneous electrical polarization P_S *versus* temperature T.

Since just the small values for P were available to Devonshire, our constants B and C must be smaller than his. According to Eqs. (6.9) and (6.10) in Devonshire's paper,[6] we have to divide his values B by $[P_s\text{ new}/P_s\text{ old}]^2=(1.7)^2$ to $(1.8)^2$ and C by $[P_s\text{ new}/P_s\text{ old}]^4=(1.7)^4$ to $(1.8)^4$. Furthermore, we change the value χ_0' in Eqs. (6.9) and (6.10) of Devonshire's paper, because our T_1-T_0 value is not 10°C but about 11°C (Fig. 5). Taking our value for $\chi_0'/(T_1-T_0)=2A=0.74\times10^{-4}\text{ degree}^{-1}$, we then get for $\chi_0'=8.1\times10^{-4}$ instead of 10×10^{-4}, which means that we also have to multiply B and C with 0.81. The corrected values of Devonshire's constant B and C are listed in Table II and give a fairly good agreement with our values.

Devonshire[1] calculated the shift of the Curie point, when an electric field E is applied, to be

$$\Delta T=(1/A)[2C/B]^{\frac{1}{2}}\times E. \tag{11}$$

Using our values for A, B, and C, we find

$$\Delta T=1.9\times10^{-3}\times E, \tag{12}$$

when E is measured in volts/cm.

The observed temperature shift is, according to Fig. 2,

$$\Delta T=1.43\times10^{-3}\times E. \tag{13}$$

Kaenzig and Maikoff[2] measured $\Delta T=1.2\times10^{-3}\times E$, and, using Devonshire's original values, we get $\Delta T=2.2\times10^{-3}\times E$.

V. ELECTROCALORIC EFFECT

Up to now, we have assumed that the electrocaloric effect near the Curie point can be neglected. It can be calculated in the following way from Eq. (1):

$$S=-(\partial F/\partial T)=-AP^2-(\partial F_0)/(\partial T)_P$$
$$=-AP^2+S_0(T). \tag{14}$$

For adiabatic conditions $S=$ constant. Since all temperature changes will be small, we can write

$$S_0(T)=S_0(T_1)+(c_P\rho/T)\Delta T, \tag{15}$$

where T_1 is the temperature where $P=0$, c_P is the specific heat at constant P, and ρ is density of the crystal.

We then find

$$\Delta T=(AT/c_P\rho)P^2=T-T_1, \tag{16}$$

which is equivalent to the well-known form:[10,11]

$$\Delta T=fP^2/2c_P, \tag{17}$$

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[8] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

[9] J. K. Hulm, Nature **160**, 127 (1947).

[10] E. T. Jaynes, *Ferroelectricity* (Princeton University Press, Princeton, 1953).

[11] Blattner, Kaenzig, and Merz, Helv. Phys. Acta **17**, 35 (1949).

where $f=\theta\beta$ is the Lorentz factor and β is the reciprocal Curie constant.

The crystal will take on an average temperature change ΔT somewhere between zero and $(AT/c_P\rho)P_{\max}^2$. The correction in temperature resulting the electrocaloric effect will be large just in case of intermediate loops, because at high temperatures (flat line) $P_{\max}$ is small and because at low temperature (well-developed loops) P actually never goes through zero and the measured temperature will be the same as the temperature at near the maximum P. The value $(AT/c_P\rho)\times P_{\max}^2$ turns out to be about 1.0°, if we use $P_{\max}=16\times10^{-6}$ coulomb/cm^2 ($P_{\max}$ for intermediate loop), $c_P=0.16$ cal/g degree,[11] and $\rho=6.04$ g/cm^3.

That means that the actual temperature correction in the worst case (intermediate loops) will be of the order of half a degree. From Eq. (16), we get

$$T=T_1+(AT/c_P\rho)P^2, \tag{18}$$

so that Eq. (1) can be written as

$$F=A(T_1-T_0)P^2-(B-A^2T/c_P\rho)P^4+CP^6, \tag{19}$$

which shows that, besides the uncertainty in T_1, the electrocaloric effect gives us a change of B which is never larger than about 10 percent. Since our accuracy is not much better than 10 percent, we neglect these corrections. (See also remarks of Kaenzig and Maikoff.[2])

VI. DISCUSSION

Since the BP^4 term is negative, there seems to be no doubt any more that the transition at the Curie point is of the first order, as discussed by others.[1,2,6,10] The extremely sharp jump of P_S at the Curie point (Fig. 6) substantiates this argument.

However, there is one interesting point of difference. This is the fact that the spontaneous electrical polarization P_S is much larger than previous results indicated. There are two ways to explain this result. Either our new crystals are different crystals, or we are able to switch and align more domains than before. Though the crystals contain a certain amount of impurities to make them nonconductive and bigger, the x-ray pictures show about the same $c/a(\Delta a/a$ or $\Delta c/c)$ ratio as the old crystals. We therefore think that we have probably not changed the crystal appreciably. This is also indicated by the fact that the behavior of the dielectric constant is very similar to the old measurements. It is obvious that the dielectric constant at room temperature is slightly smaller (160), because we have no a domains, whereas before we always had a few. Furthermore, the peak value at the Curie temperature is a little higher because the transition is sharp and not smeared out any more. It therefore seems that the high value of P_S has to be explained by the fact that, because of the better quality of the crystal, we can switch all or almost all parallel and antiparallel c domains. Because we have just parallel and antiparallel domains, all the domain movements are much smoother and faster and require smaller field strengths, as can be seen from the hysteresis loop. The coercive force is much smaller than before; we get $E_{\text{coercive}}\cong500$ volts/cm, or slightly more at 60 cps. The jump at E_c is very sharp, and the hysteresis loop is extremely steep. (Fig. 7.) This means that all the domains switch at almost the same time. Furthermore, we find an almost perfect saturation. We can increase the field to many times the value of E_c and get very little additional change in P because of domain movements (Fig. 7). However, we still feel that even here we have a few domains which do not change orientation from antiparallel to parallel, especially at higher frequencies.

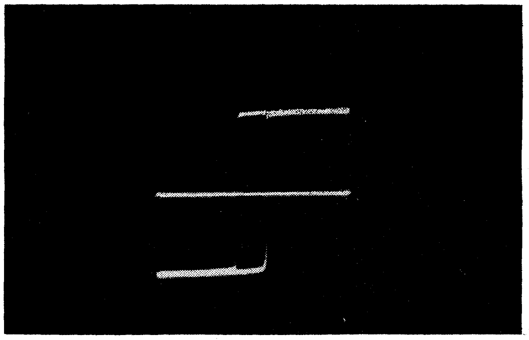

FIG. 7. Hysteresis loop of BaTiO$_3$ at 60 cps.

The flat part of these rectangular loops corresponds to a dielectric constant of about 150–200, whereas the steep part corresponds to a value of the order of a few hundred thousand to almost a million.

Shirane[4] observed similar double hysteresis loops on (Pb-Ba)ZrO$_3$ ceramics. However, in that case, the ceramics go from an antiferroelectric to a ferroelectric state when an electric field is applied, whereas, in our case, the BaTiO$_3$ crystals go from a paraelectric to a ferroelectric state.

I wish to thank Dr. P. W. Anderson for many helpful discussions and suggestions, Dr. Elizabeth A. Wood for measuring the crystallographical properties of our BaTiO$_3$ crystals, and Mr. J. Remeika for the preparation of the very good single crystals.