transition and Fig. 4(b) just above it. A decrease in the value of the polarization is observed with little change in coercive force. Midway between the two transitions, the polarization has increased and the coercive force decreased, as shown in Fig. 4(c). Just below the Curie temperature, Fig. 4(d), the polarization is nearly double its low temperature value. At 472°, Fig. 4(e), the trace is an ellipse and when compensated for dielectric loss becomes a single line. Values of the saturation polarization have been estimated from these photographs and the calibrating data to be 0.9×10^{-6} coulombs/cm^2 at room temperature and 3.8 just below the curie temperature.

It is clear from the work reported here that sodium and potassium niobates are ferroelectric and are comparable with the more thoroughly investigated $BaTiO_3$.

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Theory of Antiferroelectric Crystals

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An antiferroelectric state is defined as one in which lines of ions in the crystal are spontaneously polarized, but with neighboring lines polarized in antiparallel directions. In simple cubic lattices the antiferroelectric state is likely to be more stable than the ferroelectric state. The dielectric constant above and below the antiferroelectric curie point is investigated for both first- and second-order transitions. In either case the dielectric constant need not be very high; but if the transition is second order, ϵ is continuous across the Curie point. The antiferroelectric state will not be piezoelectric. The thermal anomaly near the Curie point will be of the same nature and magnitude as in ferroelectrics. A susceptibility variation of the form $C/(T+\theta)$ as found in strontium titanate is not indicative of antiferroelectricity, unlike the corresponding situation in antiferromagnetism.

I. INTRODUCTION

In the ferroelectric state a crystal exhibits a spontaneous electric polarization. We define the antiferroelectric state as one in which lines of ions in the crystal are spontaneously polarized, but with neighboring lines polarized in antiparallel directions, so that the spontaneous macroscopic polarization of the crystal as a whole is zero. We exclude molecular crystals from the present discussion, and we do not explicitly consider antiferroelectric arrays in which more than two sublattices are involved. It is not yet certain that realizations of antiferroelectrics have been observed,[1] as it has not previously been known how to recognize them correctly.

In ferroelectrics the occurrence of spontaneous polarization is believed at present to be the result of a Lorentz catastrophe in which the constant of proportionality connecting the applied electric field with the polarization exhibits a singularity. Illuminating contributions to the theory of the effect have been made, in particular by Wul,[2] Devonshire,[3] and Slater.[4] It would appear to be quite possible for an antiferroelectric arrangement of dipole moments to be produced by a somewhat generalized form of the Lorentz catastrophe. We shall speak throughout of crystals (such as perovskites) in which specifically quantum-mechanical effects are not of major importance.

We need only consider an arrangement of highly polarizable ions located at the lattice points of a simple tetragonal lattice with an axial ratio[5] $c/a\ll1$, so that the structure may be thought of as constructed of lines of atoms parallel to the c-axis. Because of the geometry of dipolar fields, ions in the same line will tend to be polarized parallel to each other, but the sense of adjacent lines will be opposite.[6]

In looking for realizations of antiferroelectricity in

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[1] Private communication from Professor B. T. Matthias; I am also indebted to Professor P. Scherrer for a discussion of possible realizations. *Note in proof:* Kehl, Hay, and Wahl have recently observed by x-ray methods the occurrence of an antiferroelectric arrangement in tungsten trioxide crystals above 750°C (private communication from G. Jeffrey).

[2] B. Wul, J. Phys. U.S.S.R. **10**, 95 (1946), V. Ginsburg, J. Phys. U.S.S.R. **10**, 107 (1946).

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

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

[5] Actually, as we know from the work of J. A. Sauer and A. N. V. Temperley [Proc. Roy. Soc. (London) **A176**, 203 (1940)] and J. M. Luttinger and L. Tisza [Phys. Rev. **70**, 954 (1946)], even in a simple cubic crystal ($c=a$) the alternating polarized line arrangement of dipoles is the lowest state. This is just our antiferroelectric arrangement. Calculations for barium titanate currently being made by Mr. M. H. Cohen suggest that almost exactly the same polarizabilities as lead to a ferroelectric catastrophe in $BaTiO_3$ would also lead to an antiferroelectric catastrophe. The observed ferroelectricity may be the consequence of short-range interactions.

[6] We may of course discuss by methods similar to those employed in the present paper the case of "quasi-ferroelectricity," in which different types of ions are spontaneously polarized in different directions, but still give a net macroscopic polarization. The ferromagnetic analog of this condition actually occurs in the ferrites and perhaps in other compounds, as suggested by Guillaud and Néel. Jonkers and van Santen [Science **109**, 632 (1949)] have suggested that this situation may obtain in barium titanate.

nature we must inquire first into the signs by which it may be recognized. The present examination of the problem was stimulated by the observation made by Hulm[7] that the dielectric susceptibility of polycrystalline strontium titanate $SrTiO_3$ may be expressed with fair accuracy in the region from 50°K to room temperature in the form

$$\chi = C/(T+\theta) \tag{1}$$

with $\theta = 35°K$ and $C = 6.6\times 10^3$ per °K. Now it is known that above the curie point the ferroelectric crystal barium titanate has a dielectric susceptibility of the form

$$\chi = \text{const.}/(T-\theta) \tag{2}$$

with $\theta = 393°K$. This is, of course, also the form of the Curie-Weiss law

$$\chi = \text{const.}/(T-\theta) \tag{3}$$

for the magnetic susceptibility of ferromagnetic substances above the curie point. It is further known that antiferromagnetic crystals exhibit above the Curie point a magnetic susceptibility of the form[8]

$$\chi = \text{const.}/(T+\theta). \tag{4}$$

It is tempting to grasp at the conclusion that the similarity of Eqs. (1) and (4) implies that in the dielectric case a denominator of the form $T+\theta$ is a sign of antiferroelectricity and in particular that strontium titanate is antiferroelectric. It will be seen below that such a conclusion would be wrong.

II. ANTIFERROELECTRIC LORENTZ CATASTROPHE

We describe first the manner in which the antiferroelectric state may arise. We suppose for simplicity that we have to deal with a lattice of similar atoms or similar unit cells, which may be decomposed into two identical interpenetrating lattices labelled a and b, with polarizations (dipole moment per unit volume) P_a and P_b. The local fields acting on the lattices are

$$F_a = E+\beta_1 P_a - \beta_2 P_b; \quad F_b = E+\beta_1 P_b - \beta_2 P_a. \tag{5}$$

Here E is the applied external electric field; β_1 and β_2 are Lorentz constants which may be calculated from the geometry of the lattice, and in the antiferroelectric case both will be positive.

If we take the polarization as proportional to the local field,

$$\gamma_1 P_a = F_a; \quad \gamma_1 P_b = F_b; \tag{6}$$

where $\gamma_1 = (\Sigma n_i\alpha_i)^{-1}$ in the usual notation, the α_i being the atomic polarizabilities, we have

$$\gamma_1 P_a = E+\beta_1 P_a - \beta_2 P_b; \quad \gamma_1 P_b = E+\beta_1 P_b - \beta_2 P_a. \tag{7}$$

These equations have a non-zero solution for the P's when $E=0$ only if the determinant of the coefficients of the P's is zero:

$$\begin{vmatrix} \gamma_1-\beta_1 & \beta_2 \\ \beta_2 & \gamma_1-\beta_1 \end{vmatrix} = 0, \tag{8}$$

so that

$$\gamma_1 = \beta_1 \pm \beta_2. \tag{9}$$

The root corresponding to the solution $P_a/P_b = -1$ is

$$\gamma_1 = \beta_1 + \beta_2. \tag{10}$$

However, the catastrophe in the dielectric susceptibility is determined by the other root. Adding the two Eqs. (7) together, we have

$$(P_a+P_b)(\gamma_1-\beta_1+\beta_2) = 2E; \tag{11}$$

so that the dielectric susceptibility per unit volume is

$$\chi = (P_a+P_b)/E = 2/(\gamma_1-\beta_1+\beta_2), \tag{12}$$

which has its crisis when

$$\gamma_1 = \beta_1 - \beta_2, \tag{13}$$

at which point $P_a/P_b = 1$, corresponding to ferroelectricity.

We see on substituting Eq. (10) into Eq. (12) that the susceptibility at the antiferroelectric curie point, but on the "high temperature" or unpolarized side, is given by

$$\chi = 1/\beta_2. \tag{14}$$

III. SUSCEPTIBILITY IN THE ANTIFERROELECTRIC STATE WHEN THE TRANSITION IS SECOND ORDER

At this point our interest in the effects of varying temperature makes it expedient to alter our approach to the problem and introduce a phenomenological expansion for the Helmholtz free energy per unit volume:

$$A(P_a, P_b, T) = A_0 + f(P_a^2+P_b^2) + gP_aP_b + h(P_a^4+P_b^4). \tag{15}$$

In this approximation the transition will be second order, as is known from the ferroelectric case. The term in P_a^4 and P_b^4 is introduced to restrict the catastrophe to a finite polarization. The quantities f, g, h are functions of the temperature and are, if we were to neglect entropy changes, simply related to the polarizability and local field constants.

We have

$$\partial A/\partial P_a = E = 2fP_a + gP_b + 4hP_a^3, \tag{16}$$

so that the spontaneous polarization ($E=0$) in the

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[7] J. K. Hulm, Proc. Phys. Soc. (London) **63A**, 1185 (1950). Below 50°K the dielectric constant leveled off, and there was no evidence of a peak down to the lowest temperature reached in the measurements, which was 1.3°K, where the dielectric constant was 1300.

[8] In the antiferromagnetic case θ is not in general equal to the transition temperature T_c, although θ is always positive. For an excellent summary of antiferromagnetism the reader may refer to a forthcoming review article by J. H. Van Vleck to appear in the *Journal de Physique.*

antiferroelectric state ($P_{sa}=-P_{sb}$) is given by

$$P_{sa}^2=(g-2f)/4h. \tag{17}$$

If in the antiferroelectric state we apply a small electric field ΔE the macroscopic polarization $\Delta P=P_a+P_b$ is given by, taking $P_a\cong -P_b$,

$$2\Delta E=2f\Delta P+g\Delta P+12hP_{sa}^2\Delta P,$$

or,

$$\chi=\Delta P/\Delta E=1/2(g-f); \tag{18}$$

at the Curie point $g=2f$, so that

$$\chi(T=T_c)=1/g \tag{19}$$

on the antiferroelectric side. In the unpolarized state we neglect the fourth-power terms in Eq. (15) and find

$$\chi=2/(2f+g), \tag{20}$$

which reduces at the Curie point to

$$\chi(T=T_c)=1/g \tag{21}$$

on the unpolarized side. A comparison of Eqs. (19) and (21) shows that the dielectric constant is continuous across the Curie point, and it does not necessarily have a high value.

We suppose that f, which is related to the atomic polarizabilities, varies with temperature near the curie point as

$$f=\tfrac{1}{2}g+\lambda(T-T_c), \tag{22}$$

where λ is a constant and in $BaTiO_3$ is positive, with a value of the order of 10^{-4} per °K. This expression has as consequences

$$(T<T_c)\quad P_{sa}^2=P_{sb}^2=\lambda(T_c-T)/2h; \tag{23}$$

$$(T<T_c)\quad \chi=1/[g-2\lambda(T-T_c)]; \tag{24}$$

$$(T>T_c)\quad \chi=1/[g+\lambda(T-T_c)]. \tag{25}$$

If λ is positive, the antiferroelectric region lies on the low temperature side of the curie point, and the dielectric constant changes slope slightly and goes through a maximum (which may not always be discernible) at the transition point. If λ is negative the antiferroelectric state lies on the high temperature side of the curie point and the dielectric constant will be a minimum there.

For a simple cubic lattice we find by manipulating the results of Luttinger and Tisza (reference 5) that

$$\beta_1=4.770;\quad \beta_2=0.581; \tag{26}$$

so that an antiferroelectric arrangement is favored, while for body-centered and face-centered cubic lattices, β_2 is negative (when the crystal surfaces are grounded or if domains are formed), favoring ferroelectricity.

Anomalous Heat Capacity

The entropy is given from the Helmholtz free energy by $(\partial A/\partial T)_{P_a}=-S$, so that, supposing that g and h are independent of temperature,

$$\Delta S=-(P_{sa}^2+P_{sb}^2)(\partial f/\partial T)_{P_a} \tag{27}$$

per unit volume. The anomaly in the heat capacity per unit volume at constant pressure p at the curie point is

$$\Delta C_p=T_c\left(\frac{\partial S}{\partial T}\right)_p=\frac{T_c}{h}\left(\frac{\partial f}{\partial T}\right)_p\left(\frac{\partial f}{\partial T}\right)_P, \tag{28}$$

where the derivatives are taken at $T=T_c$. This is essentially the same expression as found in the Wul theory of barium titanate; we may perhaps expect on this account an anomaly in the heat capacity of antiferroelectrics of the same order of magnitude as that found in ferroelectrics, of the order of 5 percent of the normal heat capacity above the Debye temperature.

The spontaneous polarization of each sublattice below the Curie point is related to the excess heat capacity by essentially the same relation as that derived for ferroelectrics.

IV. THEORY FOR FIRST-ORDER TRANSITIONS

Devonshire[3] has suggested that it is possible to give a better account of the transition in ferroelectrics from the polarized to the unpolarized state by treating the transition as first order rather than as second order as we have above. This introduces greater flexibility into the treatment of the dielectric constant near the Curie point, and accounts quite naturally for the rapid drop in saturation polarization near the Curie point, the drop being more rapid than can be accounted for by a second order transition. It is well known that in solids particularly it is rather difficult to decide whether a transition exhibits a latent heat or a discontinuity in the heat capacity. The x-ray evidence of Kaenzig[9] gives strong support to a first-order transition in $BaTiO_3$.

It may be appropriate to comment here on several consequences of the first-order transition theory for ferroelectrics which have escaped common notice. One is that the dielectric susceptibility measured in the direction of the spontaneous polarization may be expected to be about four times as great above the transition in the unpolarized state as below the transition in the polarized state. Writing (reference 3)

$$A=A_0+\alpha P^2+\beta P^4+\gamma P^6, \tag{29}$$

we have at the critical point $A=A_0$ the relations

$$P_c^2=-2\alpha/\beta;\quad P_c^4=\alpha/\gamma;\quad 4\alpha\gamma=\beta^2. \tag{30}$$

The susceptibility just below the transition temperature is found by the usual method to be

$$\chi^{(-)}=1/8\alpha_c, \tag{31}$$

while just above

$$\chi^{(+)}=1/2\alpha_c, \tag{32}$$

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[9] W. Kaenzig, Phys. Rev. **80**, 94 (1950).

so that

$$\chi^{(+)}/\chi^{(-)}=4 \tag{33}$$

in fairly good agreement with the results $\chi^{(+)}=1400$, $\chi^{(-)}\approx 300-500$ of Shirane *et al.*[10] on polycrystalline lead zirconate, although the discrepancy is much greater on the measurements by Roberts.[11]

The second result, as shown by Devonshire, is that it is natural to expect that the principal part of the temperature dependence of the susceptibility above the transition is given by

$$\chi^{(+)}=\frac{1}{2\alpha_c}\frac{T_c-T_0}{T-T_0}, \tag{34}$$

where T_c is the transition temperature, but T_0 is a parameter to be determined. Roberts finds $T_c=234°\mathrm{C}$; $T_0=193°\mathrm{C}$; $\alpha_c\approx 1.2\times 10^{-4}$ for lead zirconate.

We develop now a first-order transition theory for antiferroelectrics, and write

$$A=A_0+f(P_a^2+P_b^2)+gP_aP_b+h(P_a^4+P_b^4)+j(P_a^6+P_b^6). \tag{35}$$

We have

$$\partial A/\partial P_a=E=2fP_a+gP_b+4hP_a^3+6jP_a^5,$$

so that the spontaneous polarization in the antiferroelectric state ($P_{sa}=-P_{sb}$) is given by

$$6jP_{sa}^4+4hP_{sa}^2+(2f-g)=0. \tag{36}$$

At the Curie point the free energy for this solution is equal to that for the unpolarized solution $P_a=P_b=0$ when

$$(2f-g)+2hP_{sa}^2+2jP_{sa}^4=0. \tag{37}$$

The solution of the two Eqs. (36) and (37) gives us

$$(T=T_c)\quad P_{sa}^2=(g-2f)/h, \tag{38}$$

$$(T=T_c)\quad P_{sa}^4=(2f-g)/2j. \tag{39}$$

We find that in the antiferroelectric state just below the transition we have

$$\chi^{(-)}=1/(4f-g), \tag{40}$$

while just above the transition in the unpolarized state we have

$$\chi^{(+)}=2/(2f+g). \tag{41}$$

Thus, if the antiferroelectric transition is first order, there will be a discontinuity in the dielectric constant at the Curie point. The condition for the Curie point is found from Eqs. (38) and (39):

$$2j(2f-g)=h^2. \tag{42}$$

If the transition is second order, a ferroelectric crystal will have a very high dielectric constant at the Curie point, whereas if the transition is first order, the dielectric constant need not necessarily be very high. An antiferroelectric crystal need not necessarily have a high dielectric constant for either first, or second-order transitions. The character of the transition is determined largely by the sign of h in Eq. (35), a negative sign tending to make the transition first order.

V. CONCLUSIONS

From the considerations given above we may suggest, within the limits of the approximations made, the following conclusions:

(1) Antiferroelectric crystals may be expected to occur in nature although a lack of knowledge of what to look for may have handicapped their identification.

(2) The dielectric constant at the antiferroelectric Curie point will not in general be particularly large; if the transition is second order, the dielectric constant will be continuous and nearly constant with temperature at the Curie point, with a small discontinuity in the temperature coefficient. In a first-order transition there will be a discontinuity in the dielectric constant. In ferroelectrics the dielectric constant is very large at the curie point if the transition is second order. The antiferroelectric dielectric constant need not be isotropic.

(3) The antiferroelectric state will not be piezoelectric, as a center of symmetry will exist. In the ferroelectric state one generally finds a large piezoelectric effect. This feature may be the most convenient way to distinguish the two states.

(4) The anomaly in heat capacity at the Curie point should be quite similar in antiferroelectrics to that found in ferroelectrics. The spontaneous polarization should be detectable by x-ray structure determinations above and below the Curie point.

(5) A susceptibility variation of the form $\chi=C/(T+\theta)$ with no apparent transition as found in strontium titanate is *not* indicative of antiferroelectricity. It is suggestive of a crystal which would be ferroelectric "below" 0°K. That is, we have to deal here with the "high temperature" or unpolarized phase of a ferroelectric[12] with a negative Curie temperature.

I wish to thank Mr. Morrel H. Cohen for several valuable discussions and for his kindness in checking the manuscript. Dr. P. W. Anderson has offered helpful suggestions on the manuscript. I am grateful to Prof. G. Jeffrey of the University of Pittsburgh for calling to my attention the x-ray work on WO_3, which has an antiferroelectric structure at high temperatures. I wish here to record also my gratitude to Professor R. T. Birge and the staff of the Department of Physics at Berkeley for their kind hospitality during my stay there on a visiting appointment.

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[10] Shirane, Sawaguchi, and Takeda, Phys. Rev. **80**, 485 (1950).

[11] S. Roberts, J. Am. Cer. Soc. **33**, 63 (1950).

[12] A susceptibility variation of the above form could also, in principle, result from a case in which the polarized ferroelectric state occurs at all temperatures, which could occur if the temperature coefficient of $d\gamma_1/dT$ (see Eq. (6)) had the opposite sign of that observed in $BaTiO_3$ and if the Curie point corresponded to a negative temperature. The two cases could be easily distinguished experimentally by the usual signs of a polarized ferroelectric state —hysteresis, piezoelectricity, and x-ray superstructure.