resistance measurements except for the coefficient D in p-type germanium. The coefficient D could probably be evaluated most accurately by the method proposed in Sec. V.

The nonzero values obtained for D indicate that the assumptions of Sec. I are incorrect, i.e., the energy surfaces and/or the relaxation time surfaces are not spherical in $\mathbf{k}$ space.

Threshold Field and Free Energy for the Antiferroelectric-Ferroelectric Phase Transition in Lead Zirconate

A. P. deBretteville, Jr.

Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey

(Received May 20, 1953; revised manuscript received February 9, 1954)

Sawaguchi and Kittaka obtained the threshold field of $PbZrO_3$—that field necessary to change the antiferroelectric to the ferroelectric phase—below the Curie temperature. The free-energy difference is the difference between the area under the ferroelectric portion of the curve and that under the antiferroelectric portion. An expression for free-energy difference has been obtained as a function of voltage, by eliminating the temperature parameter. This experimental relationship is compared with the author's theoretical expression—one that involves the product of the constant spontaneous polarization (16×10^{-6} coulomb/cm^2 in the ferroelectric phase), the threshold voltage, and the molar volume (43 cm^3); the free energy so calculated is small—of the order of 4 calories/mole at 25 kv/cm. Equations are given for calculating the threshold field-strength and free-energy difference as functions of temperature. The equation for threshold field-strength resembles the Clapeyron-Clausius equation, with field strength analogous to pressure and spontaneous polarization analogous to volume. The threshold voltage *versus* the downward shift of the Curie temperature is in good agreement with the experimental results of Sawaguchi and Kittaka.

I. INTRODUCTION

IT is known that pure lead zirconate has an antiferroelectric phase below and a paraelectric phase above 230°C, the Curie point. Sawaguchi and Kittaka have shown that one can apply a field of the order of 10 kv/cm to pure lead zirconate ceramic and cause the ferroelectric phase to appear below the Curie point.[1]

Below the Curie point the sample is normally antiferroelectric; the dielectric constant ϵ_a is approximately 200, and has a positive temperature coefficient. At the Curie point, the dielectric constant increases sharply about twenty-fold.[2]

Figure 1 shows the experimental data obtained by Sawaguchi for the threshold field of the antiferroelectric-to-ferroelectric phase transition, as a function of temperature.[1]

Figure 2(b) shows the point O, from which the threshold field E_t was calculated; the cross-hatched area is proportional, essentially, to the free energy.[1]

The author intends to calculate the value of the threshold field, and the free-energy difference ΔF, between the ferroelectric phase and the more stable or lower free-energy antiferroelectric phase, as a function of temperature and voltage.

CALCULATION[3]

Sawaguchi and Kittaka have derived an expression for the free-energy difference $\Delta F = (F_f - F_a)$ between

the ferroelectric state F_f and the antiferroelectric state F_a, in terms of the internal energy of the antiferroelectric state U_a and the internal energy of the ferroelectric state U_f[1]

$$F_f(T_m) - F_a(T_m) = U_f(T_f) - U_a(T_a). \quad (1)$$

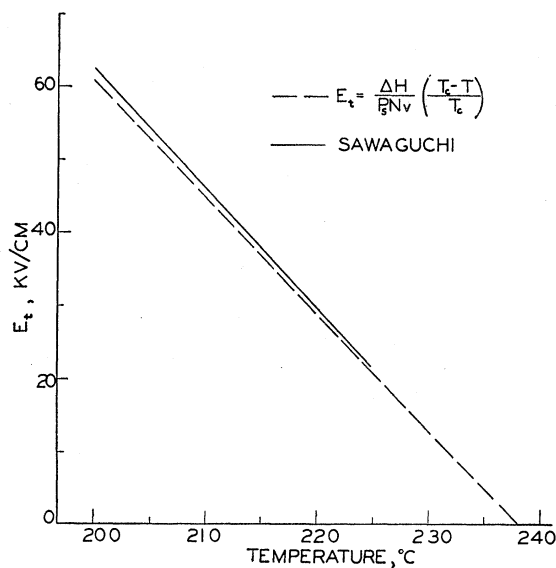The temperatures of the antiferroelectric and ferro-

FIG. 1. Relation between threshold field and Curie temperature.

[1] E. Sawaguchi and T. Kittaka, J. Phys. Soc. Japan 7, 336–337 (1952); E. Sawaguchi, J. Phys. Soc. Japan 8, 615–629 (1953).

[2] Shirane, Sawaguchi, and Takagi, Phys. Rev. 84, 476–481 (1951).

[3] Background for this type of calculation can be found in the field of low-temperature physics. See J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, Inc., New York, 1951), pp. 504–508; E. T. Jaynes, *Ferroelectricity* (Princeton University Press, Princeton, 1953), pp. 70–80.
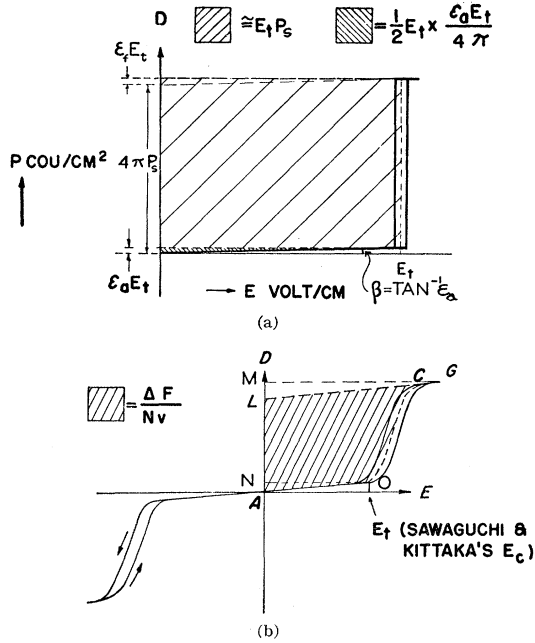
FIG. 2. (a) An idealized hysteresis loop and the method of calculating free-energy difference between the two phases. D is the dielectric displacement; E is the electric field strength. (b) The experimental data on which the free-energy difference can be calculated. Shaded area is that area used by Sawaguchi and Kittaka to calculate free-energy difference.

electric states are T_a and T_f, respectively, while T_m is the mean of the two temperatures. The temperature difference is small and amounts to only 3°C and is obtained by dividing the latent heat by the specific heat for lead zirconate with 3 percent lead titanate. Sawaguchi and Kittaka showed that Eq. (1) is essentially equal to the work done per mole by the electric field, $(Nv/4\pi)\int EdD$, where Nv is the molar volume, E is the electric field, and D is the dielectric displacement.[1,4] They evaluated this term experimentally by integrating the area $AOCL$ surrounded by the loop in Fig. 2(b). The expression

$$\Delta F = \frac{Nv}{4\pi}\int_{P_t}^{P_m} EdD_f - \frac{Nv}{4\pi}\int_0^{E_t} EdD_a, \qquad (2)$$

and will be evaluated below.

The second or negative term in Eq. (2) is the internal energy of the antiferroelectric state. It is shown by the area AON in Fig. 2(b) and is negligible for lead zirconate as will be shown later. Therefore, the author agrees with Sawaguchi and Kittaka that the free energy is essentially the area $AOCL$ in Fig. 2(b).

Furthermore, Sawaguchi and Kittaka showed the free energy due to the temperature difference of the two states could be neglected. This term amounts to only 0.01 calorie compared to several calories for the electrostatic work term.

---

[4] H. Fröhlich, Theory of Dielectrics (Oxford University Press, London, 1949), pp. 160–161.

The internal energy of the antiferroelectric state per unit volume is[4]

$$U_a = \frac{Nv}{4\pi}\int_0^{E_t} E\epsilon_a dE = \epsilon_a E_t^2 Nv/8\pi, \qquad (3)$$

and this energy is shown graphically in Fig. 2. The author has neglected the term

$$\frac{Nv}{4\pi}\int_0^{E_t} E^2 d\epsilon_a = \frac{Nv}{4\pi}\int_0^{E_t} E^2\left(\frac{\partial\epsilon_a}{\partial T}dT + \frac{\partial\epsilon_a}{\partial E}dE\right),$$

because $\partial\epsilon_a/\partial T \approx 1$, and $\partial\epsilon_a/\partial E \approx 0$; therefore it can be neglected compared to (3).

For the ferroelectric state, $dU_f = (E/4\pi)dD_f Nv$, and the limits of integration are derived from Fig. 2(a). The idealized Fig. 2(a) is only an approximation for the purpose of calculation. One is here dealing with a ceramic material, which gives a lower value of the spontaneous polarization, P_s, than the true value which is approached more nearly with single crystals and will be discussed later. The limits will be

$$U_f = \frac{Nv}{4\pi}\int_{E_t}^{E_t} EdE + NvE_t\int_{P_t}^{P_m} dP,$$

where P_m is the maximum polarization namely $P_s + \epsilon_f E_t/4\pi$. P_t is the threshold polarization or $\epsilon_a E_t/4\pi$. The maximum polarization cannot be used, because only values of spontaneous polarization P_s are available. The integrated equation is

$$U_f = E_t P_s Nv + (2\epsilon_f - 2\epsilon_a)E_t^2 Nv/8\pi. \qquad (4)$$

The area $LMCG$ in Fig. 2(b) corresponds to slightly more than half the value of the first part of the second term in Eq. (4). The slope LCG is proportional to ϵ_f, or equal to $4\pi(\partial P/\partial E)$.

Inserting the internal energy difference per mole [Eq. (4) minus Eq. (3)] into the expression for the free energy per mole [Eq. (1)], one obtains

$$\Delta F = P_s E_t Nv + (2\epsilon_f - 3\epsilon_a)E_t^2 Nv/8\pi. \qquad (5)$$

This is the fundamental expression for the free-energy difference. The term due to the internal energy of the antiferroelectric phase, $\epsilon_a E_t^2 Nv/8\pi$, is negligible for the region in which the experimental data were taken, and amounts to only 3 percent of the first term for the maximum threshold field.

The value of ϵ_f is approximately the same as ϵ_a for lead zirconate so that the last two terms in (5) tend to cancel each other out.

Threshold field strength is calculated from (5), by using the relation $S = -\partial F/\partial T$. The new equation then becomes, assuming P_s constant, and $\Delta\epsilon = (2\epsilon_f - 3\epsilon_a)$,

$$\Delta S = -P_s\frac{\partial E_t}{\partial T}Nv - \left(\frac{\partial\Delta\epsilon}{\partial T}\frac{E_t^2}{8\pi} + \frac{\Delta\epsilon E_t}{4\pi}\frac{\partial E_t}{\partial T}\right)Nv. \qquad (6)$$

Substituting the increase of entropy per mole, ΔS

$=\Delta H/T$, Eq. (6) becomes

$$\frac{\partial E_t}{\partial T} = -\left[\frac{\Delta H}{TNv} + \frac{\partial \Delta \epsilon}{\partial T}\frac{E_t{}^2}{8\pi}\right]\bigg/\left[P_s + \frac{\Delta \epsilon}{4\pi}E_t\right]. \quad (7)$$

This is the most general form for the equilibrium slope. For lead zirconate the last two terms in (6) can be neglected; then (7) becomes

$$\partial E_t/\partial T = -\Delta H/P_s TNv. \quad (8)$$

This is equivalent to the familiar Clapeyron-Clausius equilibrium equation, with electric field analogous to pressure and spontaneous polarization analogous to volume. This equation was first pointed out by Shirane, Sawaguchi, and Takagi as being applicable to PbZrO₃ in studying the dc field-dependence of transition temperature from ferroelectric to antiferroelectric state.[5]

Equation (8) expresses the fact that the phase transition is a first order one which is due to the large jump of spontaneous polarization.

In Fig. 2(b) the polarization ordinates are compressed and do not give the reader a true picture of the magnitude of the jump in spontaneous polarization compared to the threshold polarization. The spontaneous polarization is fifteen times greater than the maximum threshold polarization. This ratio was computed by dividing P_s by $\epsilon_a E_t/4\pi$, using $P_s = 16 \times 10^{-6}$ coulomb/cm², $E_t = 60$ kv/cm and $\epsilon_a = 200$. Inserting 135 calories/mole from calorimetric measurements on Pb(Zr₀.₉₇-Ti₀.₀₃)O₃ which is ferroelectric without an applied field, using $T_c = 511°K$ obtained by extrapolating the curve of ΔF versus t to zero, and using the value of $P_s = 16 \times 10^{-6}$ coulomb/cm², we obtain

$$\partial E_t/\partial T = -1.61 \text{ kv/cm°C}.$$

The experimental value obtained from the solid curve of Fig. 1 is -1.65 kv/cm°C.

Integrating (8) with respect to T, assuming that ΔH, P_s, and v are constants, gives

$$E_t = (-\Delta H/P_s Nv) \ln T + \text{constant}.$$

Using $T = T_c$ for $E_t = 0$ to determine the constant, one obtains

$$E_t = (\Delta H/P_s Nv) \ln(T_c/T).$$

To the author's knowledge, this equation has not been published elsewhere. The logarithm is expanded and only the first term is retained. This is justified because the second term amounts to only 3 percent of the first term with respect to a 30°C lowering of the Curie temperature. This gives

$$E_t = \frac{\Delta H}{P_s Nv}\left(\frac{T_c - T}{T_c}\right). \quad (9)$$

Equation (9) is plotted in Fig. 1. The equation is in good agreement with the experimental data.

Equation (9) is plotted in Fig. 1, where 238°C is used for the "ferroelectric" Curie point. In a private communication to the author, Y. Takagi and E. Sawaguchi state that they have investigated the PbZrO₃-PbTiO₃ system. They found the free energies of the antiferroelectric-paraelectric phase became equal at 230°—"antiferroelectric" Curie point; and the free energies of the ferroelectric-antiferroelectric phase became equal at 238°C—"ferroelectric" Curie point. The more stable paraelectric phase actually replaces the ferroelectric phase at 238°C. Hence, the Curie point used in Eq. (9) was determined by extrapolating the temperature-composition line of the ferroelectric-antiferroelectric phase boundary.[1]

DISCUSSION

Sawaguchi and Kittaka[1] estimated the heat of transition from their free energy data by taking the product of the slope and the Curie temperature of pure PbZrO₃ and obtained 80 cal/mole. They then compared this with 130 cal/mole obtained by their calorimetric measurement with Pb(Zr₀.₉₇-Ti₀.₀₃)O₃. They attributed this discrepancy between 130 (135 for Sawaguchi's latest value) and 80 cal/mole to their material, a ceramic.

Some discussion of the E_t versus T graph for pure PbZrO₃ is in order, to explain why the values of ΔH and P_s are not those of PbZrO₃ but those of Pb(Zr₀.₉₇-Ti₀.₀₃)O₃. The phase change for pure PbZrO₃ is from an antiferroelectric state to a paraelectric state, and therefore the value of or 440 cal/mole could not be used.[6] However, when 3 mole-percent PbTiO₃ is added, a ferroelectric phase appears between the antiferroelectric phase and the paraelectric phase. Therefore the value of the heat of transition, 135 cal/mole, ·of this latter antiferroelectric-ferroelectric phase change is used.[1] For a full discussion of the phase diagram and the heats of transition see Sawaguchi.[1]

The value of spontaneous polarization P_s is practically constant and equal to 16×10^{-6} coulomb/cm² from 170 to about 220°C, where it begins to drop slightly. This value was given to the author before publication through the kindness of Y. Takagi and E. Sawaguchi and was obtained by the hysteresis loop method.

Earlier in the paper, it was stated that ϵ_f was approximately equal to ϵ_a or about 200. A calculation of ϵ_f can be made using the expression $4\pi(\partial P/\partial E)$, which can be written as $4\pi(\partial P/\partial T)/(\partial E/\partial T)$. Using Sawaguchi's[1] value of $(\partial P/\partial T)$, or about 3.4×10^{-8} coulomb/cm² °C obtained from Pb(Zr₀.₉₇-Ti₀.₀₃)O₃, and the value 1.65×10^3 v/cm°C for $(\partial E/\partial T)$ in the above expression, one obtains 230 for ϵ_f.

Since the temperature coefficient of polarization is so small, Eq. (9) is unaffected. It was assumed that $\partial P/\partial T$ was zero in the derivation of (9).

[5] Shirane, Sawaguchi, and Takagi, J. Phys. Soc. Japan **6**, 208 (1951), and Sawaguchi, Shirane, and Takagi, J. Phys. Soc. Japan **6**, 337 (1951).

[6] G. Shirane, Phys. Rev. **86**, 226 (1952).

CONCLUSIONS

The fundamental equation for the free energy is given by (5), from which a general equation for other ferroelectrics expressing the equilibrium slope of the threshold field with respect to temperature can be derived.

ACKNOWLEDGMENTS

The author wishes to thank Dr. V. F. Payne of the Chemical Physics Branch, Squier Signal Laboratory, for his constant encouragement, and Ellis L. Manning and Erwin D. Harris for helpful discussion. The author also wishes to thank Professor Y. Takagi of the Tokyo Institute of Technology, Oh-Okayama, Tokyo, Japan, for the reprint of an exceedingly interesting paper by Dr. E. Sawaguchi and his colleague Dr. T. Kittaka of the same institute. The paper served as a foundation for this work; to Professor Takagi and Dr. Sawaguchi go thanks for supplying the author with data pertaining to this work.

Pressure Dependence of the Resistivity of Germanium

WILLIAM PAUL* AND HARVEY BROOKS
Division of Applied Science, Harvard University, Cambridge, Massachusetts
(Received January 26, 1954)

The effect of hydrostatic pressure on the resistivity of a sample of 35 ohm-cm germanium has been investigated up to 30 000 kg/cm² pressure at temperatures between 25°C and 76°C, and up to 7000 kg/cm² pressure at temperatures down to −195°C. The results indicate an increase in the total energy gap to 15 000 kg/cm² at a rate in agreement with earlier experimental determinations at lower pressures. A rapid rise in resistivity above 15 000 kg/cm² that seems to apply to n-type germanium crystals of any purity has also been investigated. Explanations based on the deionization of impurities and on a decrease in electron mobility are discussed.

THE effect of hydrostatic pressure on the electrical properties of germanium has been investigated experimentally by measurements of p-n junction resistance,[1] the resistivity of impure samples,[2] and the resistivity of high-purity material at elevated temperatures.[3,4] It has also been estimated theoretically by a deformation potential method.[5] Both experiment and theory indicated a uniform increase of resistivity with pressure in the intrinsic conduction range, corresponding to a widening of the energy gap between valence and conduction bands. Bridgman's results also showed interesting behavior at pressures above 15 000 kg/cm² where the resistivity of n-type samples of a wide range of purity increased rapidly with increasing pressure. In the present work new measurements are reported at elevated temperature which extend the effective pressure range for intrinsic conduction. New measurements are also reported for temperatures down to liquid nitrogen. An attempt is made to correlate the new and the older measurements and to clarify the behavior above 15 000 kg/cm².

APPARATUS AND METHOD

The pressure apparatus used in the present set of experiments is that developed by Bridgman. The first,

which allowed resistivity determinations up to 30 000 kg/cm², has been sufficiently described already in the literature,[6] so that only a general discussion of it, and of any features peculiar to this experiment, need be set down here. The chamber in which the high pressure is generated is slightly coned on its external surface. As the main moving piston produces high hydrostatic pressure in a central cylindrical hole, this cone is simultaneously thrust into coned receiving sleeves by a second piston; the external support of the chamber compensates the effect of the internal pressure and allows its prolonged operation at pressures higher than a single unsupported cylinder can stand.

The pressure, which was produced in liquid isopentane, was measured by a manganin wire gauge previously calibrated by Bridgman at 30°C and 75°C; sufficient data were therefore available for a determination of the pressure at any of the temperatures of the present set of experiments.

The sample, a germanium single crystal of 35 ohm-cm room temperature resistivity, had been previously investigated by Bridgman,[3] and was originally supplied by Bell Telephone Laboratories through the interest of Dr. W. Shockley. The crystal dimensions were 3 cm × 3 mm², and the contacts to it were soldered with pure tin. The resistance was measured by a potentiometric method for both increasing and decreasing pressure; care was taken that temperature equilibrium had been reestablished after each alteration of pressure. No hysteresis was found, and no variation of resistivity

* Carnegie Research Fellow of the Universities of Scotland.
[1] Hall, Bardeen, and Pearson, Phys. Rev. **84**, 129 (1951).
[2] P. Miller and J. Taylor, Phys. Rev. **76**, 179 (1949).
[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **79**, 139 (1951); **82**, 71 (1953).
[4] W. Paul, Phys. Rev. **90**, 336 (1953).
[5] W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950); **80**, 72 (1950).

[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, 157 (1938).