Effect of Hydrostatic Pressure on the Ferroelectric Properties of Tri-Glycine Sulfate and Selenate

F. Jona* and G. Shirane

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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The transition temperatures T_c of tri-glycine sulfate and isomorphous tri-glycine selenate are raised by the application of hydrostatic pressure. Up to 2700 atmos, the dependence of T_c on pressure is linear with a slope of 2.6×10^{-3} degrees/atmos for the sulfate and 3.8×10^{-3} degrees/atmos for the selenate. The Curie-Weiss law, $\epsilon_b \cong C/(T-T_c)$, is unaffected by pressure except for the shift in transition temperature. The curve of the spontaneous polarization is shifted accordingly along the temperature axis; in the vicinity of the transition point, the square of the spontaneous polarization depends linearly on temperature and pressure. The results are discussed in terms of the thermodynamic theory of ferroelectrics.

INTRODUCTION

THE description of the experimental facts observed in ferroelectric crystals has been most successful in terms of a thermodynamic theory. Such a theory was developed in detail by Devonshire[1] for the case of ferroelectric barium titanate and, earlier, by Mueller[2] for the case of Rochelle salt. The foundation of the theory is the postulate of the existence of a unique free-energy function of a number of variables, for which Devonshire proposed a polynomial expression. The most convenient free-energy function used is the elastic Gibbs function, expressed in terms of temperature, stress, and polarization. Normally, the stress is assumed to be zero, and then the free-energy function is expanded in powers of the polarization, the coefficients being functions of temperature.

Only a few terms of this expression need be considered in order to describe the general features of the properties of ferroelectric crystals. In the case of barium titanate[1] and, generally, a transition of the first order, as in some alums,[3] some of the terms in the sixth power of the polarization must be taken into account, while in the case of Rochelle salt[2] and, generally, second-order transitions,[4] it is sufficient to consider only the terms up to the fourth power of the polarization. The temperature dependence of the coefficients appearing in the free-energy polynomial can be determined experimentally.

The use of a power-series representation of the free-energy function, however, always involves the problem of convergence. It was pointed out by Forsbergh[5] that this problem can be avoided by using information such as stress phase diagrams to establish the geometrical features of an isotherm of the free-energy function. This geometrically constructed thermody-

namic potential can be used to confirm whether or not a given polynomial representation of an isotherm of the free-energy function is approximately complete in the domain of interest. To date, only a few stress phase diagrams involving ferroelectric crystals are available.

The effects of stresses on the dielectric properties of Rochelle salt was first investigated by Eremeev[6] and by David,[7] and later in greater detail, using hydrostatic pressures, by Bancroft.[8] Similar investigations were carried out by Merz on single crystals of barium titanate[9] and guanidinium aluminum sulfate hexahydrate (GASH),[10] while Forsbergh[11] studied the effect of two-dimensional pressure on the tetragonal-cubic transition of barium titanate.

The main purpose of these investigations, with exception of Merz's study of GASH, was to determine the shift of the transition temperature due to the application of hydrostatic or two-dimensional pressure. This shift is governed by the Clausius-Clapeyron equation, in the case of a first-order transition, and by Ehrenfest's relations in the case of a second-order transition. Forsbergh[11] showed, on the other hand, how the same effect can be computed for a transition of the first order from the polynomial expression of the free energy, predicting a linear dependence of the extrapolated Curie temperature on the hydrostatic pressure.

Little attention was devoted to the effect of pressure on the spontaneous polarization P_s of ferroelectric crystals, except for Merz's investigation of GASH. This experiment was carried out only at room temperature and indicated a linear increase of P_s with pressure.[10]

The purpose of the present investigation is to study the effect of hydrostatic pressure on the transition temperature and the spontaneous polarization of ferroelectric tri-glycine sulfate and the isomorphous

* Now at IBM Research Laboratory, Poughkeepsie, New York.
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selenate,[12] for which the transition is of the second order,[4,18] and to check the prediction of the thermodynamic theory for this class of ferroelectric crystals.

Tri-glycine sulfate, $(CH_2NH_2COOH)_3 \cdot H_2SO_4$, has the Curie point at 49°C and the isomorphous tri-glycine selenate, $(CH_2NH_2COOH)_3 \cdot H_2SeO_4$, at 22°C.[12] The crystals are monoclinic, space group $P2_1/m$ above, $P2_1$ below the Curie temperatures, the lattice parameters at room temperature being $a=9.42$ A, $b=12.64$ A, $c=5.73$ A, $\beta=110°23'$ for the sulfate and $a=9.54$ A, $b=12.92$ A, $c=5.86$, $\beta=110°$ for the selenate.[14]

EXPERIMENTAL

The pressure apparatus built for the present experiment was capable of developing hydrostatic pressures up to 40 000 psi≅2700 atmos. A Dow Corning 200 fluid with 20 centistokes viscosity was used as the hydrostatic-pressure fluid. The insulation and the seal of the electrical lead into the pressure bomb were achieved by means of a small cone of pipestone, which had sufficiently low capacitance and dielectric loss in the temperature range covered by the present measurements. A simple spring holder was used to support the crystal within the pressure bomb, one of the two silver-painted surfaces of the crystal plate being connected to ground.

Control of the temperature was achieved by immersing the pressure bomb in a silicone-oil bath and using a thermistor device which allowed regulation within ±0.1°C.

The dielectric constant of the crystal plates was measured with a General Radio Bridge 716C with a field of approximately 20 v/cm and a frequency of 1 kc/sec. The hysteresis loops were displayed on an oscilloscope by means of a hysteresis bridge built especially for the measurement of crystals having one of the electrodes grounded, and the value of the spontaneous polarization was read on a Ballantine peak-to-peak voltmeter.

RESULTS

The behavior of the dielectric constant ϵ_b of tri-glycine sulfate as a function of temperature for different values of the hydrostatic pressure shows that the transition temperature T_c is displaced toward higher temperatures with increasing hydrostatic pressure p. The dependence of T_c on p is linear and is depicted in Fig. 1(a) for tri-glycine sulfate and Fig. 1(b) for tri-glycine selenate. The rate of increase of the transition temperature T_c with pressure p can be written in the form:

$$T_c = Kp + T_c^0, \qquad (1)$$

where T_c^0 is the transition temperature at atmospheric

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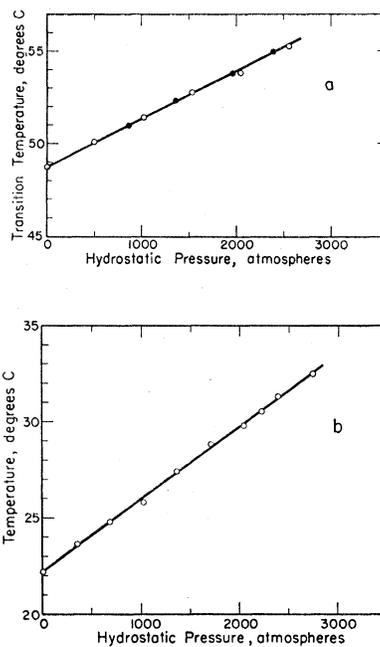
FIG. 1. Transition temperature as a function of hydrostatic pressure: (a) Tri-glycine sulfate (open and closed circles refer to different specimens); (b) Tri-glycine selenate.

pressure, $K=2.6\times10^{-3}$ degree/atmos for tri-glycine sulfate and $K=3.8\times10^{-3}$ degree/atmos for tri-clycine selenate.

The effect of hydrostatic pressure is to displace the whole dielectric constant curve toward higher temperatures. The peak value of the dielectric constant seems to depend on the applied pressure in that it becomes larger with increasing pressure but the experimental accuracy is not sufficient to establish a reliable relationship. The Curie-Weiss law

$$\epsilon \cong C/(T-T_c), \qquad (2)$$

is obeyed by the crystals investigated.[4] Figure 2 shows that the Curie constant C is practically unaffected by the application of hydrostatic pressure p within a range of accuracy of about 5%. C equals 2900 degrees for tri-glycine sulfate and about 4000 degrees for the selenate salt.

An immediate consequence of (1) and (2) is that the behavior of the dielectric constant as a function of pressure at constant temperature should also follow a law of the Curie-Weiss type:

$$\epsilon = C'/(p_c - p), \qquad (3)$$

where $p_c = (T - T_c^0)/K$ is the "transition pressure" and $C' = C/K$. Equation (3) is satisfied by our experimental data, which allow direct determination of C'; for tri-glycine sulfate, for example, the value of C', determined from a plot of $1/\epsilon_b$ vs p at constant temperature $T=54.7°C$ is 1.16×10^6 atmos, while the value of C/K,

determined from Figs. 1(a) and 2 is 1.13×10^6 atmos, showing good agreement within the experimental accuracy.

The spontaneous polarization P_s of tri-glycine sulfate was also measured as a function of temperature and pressure. Again, the application of hydrostatic pressure results in a simple translation of the P_s curve along the temperature axis. Figure 3 shows a plot of P_s vs the reduced temperature $T-T_c$ for different values of applied pressure p. It appears that within the experimental accuracy the displacement of the P_s curve due to pressure is not accompanied by distortion of the shape of the curve.

The behavior of tri-glycine selenate is analogous ($P_s=3.2$ microcoulomb/cm^2 at 0°C and 1 atmos).

DISCUSSION

The present case of tri-glycine sulfate (and selenate) differs from that of barium titanate, treated by Forsbergh,[1i] insofar as the former crystal undergoes a second order transition, while barium titanate exhibits a phase change of the first order. But the two cases are similar to each other in that, above the Curie point, both tri-glycine sulfate and barium titanate belong to a centrosymmetrical (nonpiezoelectric) point group. The thermodynamic treatment of tri-glycine sulfate will therefore only be complicated by the lower symmetry of the nonpolar phase (monoclinic) with respect to that of the nonpolar phase of barium titanate (cubic), but is otherwise similar to Forsbergh's treatment. The polynomial expression for the free energy of tri-glycine sulfate above the transition temperature can be written in terms of the stress components X_{ik} and the polarization components P_i

FIG. 3. Spontaneous polarization P_s of tri-glycine sulfate as a function of reduced temperature $T-T_c$ for different values of hydrostatic pressure p.

in the following way:

$$A(X,P)=\tfrac{1}{2}\sum_1^3 s_{ikjl}X_{ik}X_{jl}+\sum_1^3 q_{ikjl}P_iP_kX_{jl}$$

$$+\tfrac{1}{2}\sum_1^3 X_{ik}P_iP_k+\tfrac{1}{4}\sum_1^3 \xi_{ikjl}P_iP_kP_jP_l+\cdots, \quad (4)$$

where the s_{ikjl} are the elastic compliances, the q_{ikjl} the electrostrictive constants, and X_{ik}, ξ_{ikjl} the coefficients of the second and fourth powers of the polarization, well-known from Devonshire's theory.[1] Since the polarization is directed along the monoclinic b axis, we put $P_1=P_3=0$, $P_2=P$, and since we apply hydrostatic pressures, we put $X_{11}=X_{22}=X_{33}=p$, all other $X_{ik}=0$. We then can write the free energy (4) in a simpler way, thus

$$A(p,P)=Sp^2+KpP^2+A_p+\cdots,$$

where S and K are functions of the elastic and electrostrictive constants and A_P is the free energy in terms of polarization P for zero stress:

$$A_P=\tfrac{1}{2}\chi P^2+\tfrac{1}{4}\xi P^4+\cdots,$$

χ represents the reciprocal susceptibility of the unpolarized crystal; $\chi\cong4\pi/\epsilon=4\pi(T-T_c{}^0)/C$ (the values of the Curie constant C are given above for both tri-glycine sulfate and selenate); ξ equals 0.93×10^{-9} (esu/cm^2)$^{-2}$ for tri-glycine sulfate[4,13] and 0.47×10^{-9} (esu/cm^2)$^{-2}$ for tri-glycine selenate.

Collecting terms, we obtain the following expression for the free energy:

$$A(p,P)=Sp^2+\frac{2\pi}{C}[T-(T_c{}^0+Kp)]P^2+\tfrac{1}{4}\xi P^4+\cdots.$$

It follows from this expression that:

(1) The reciprocal dielectric susceptibility of the unpolarized crystal, $(\partial^2 A/\partial P^2)_{P=0}$, is a linear function

FIG. 2. Temperature dependence of the reciprocal dielectric constant, $1/\epsilon_b$, of tri-glycine sulfate at different hydrostatic pressures p.
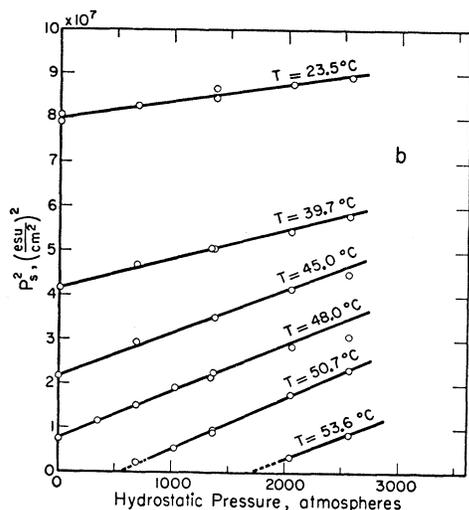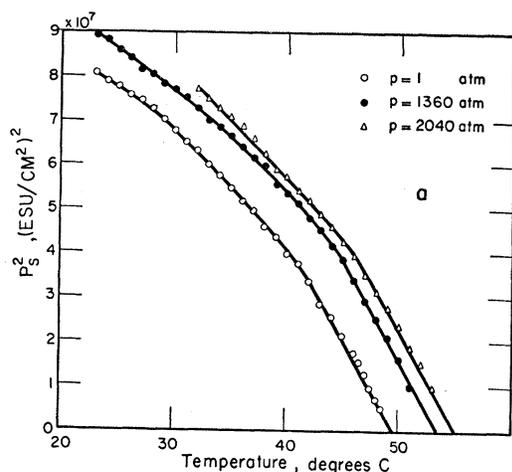
FIG. 4. Square of the spontaneous polarization of tri-glycine sulfate: (a) as a function of temperature for three different values of the hydrostatic pressure p; (b) as a function of pressure for different values of temperature T.

of the temperature even when a hydrostatic pressure p is applied. The Curie-Weiss law is satisfied and the Curie constant is unaffected by the pressure (Fig. 2).

(2) The transition temperature T_c depends linearly on the applied pressure [Fig. 1 (a), (b)].

(3) In the vicinity of the transition temperature the spontaneous polarization P_s is given by:

$$P_s^2 = -\frac{4\pi}{C\xi}[T-(T_c^0+Kp)],$$

i.e., if we assume that ξ is independent of temperature and pressure, the square of the spontaneous polarization is a linear function of temperature for constant pressure and a linear function of pressure for constant temperature. Both these theoretical predictions are verified, in the immediate vicinity of the transition, by the experimental results reported in Fig. 4(a), (b). The slope of the initial straight lines in Fig. 4(a) is determined as 0.46×10^7 (esu/cm^2)^2 deg^{-1}, while the quantity $4\pi/C\xi$, as computed from the values of C and ξ reported above is: $4\pi/C=0.47\times10^7$ (esu/cm^2)^2 deg^{-1}. Actually, this means only that the value of ξ as computed from the present data would agree satisfactorily with previous determinations,[4,13] and also that our assumption about the pressure independence of ξ is verified by the experiment within an accuracy estimated at 5%. Similarly, the slope of the isotherm for 48°C in Fig. 4(b) is determined as 1.1×10^4 (esu/cm^2)^2 atmos^{-1}, while the quantity $4\pi K/C\xi=1.2\times10^4$ (esu/cm^2)^2 atmos^{-1}.

Thus, the experimental results, in addition to verifying the pressure independence of the constants C and ξ within the limits imposed above, confirm that the polynomial representation of the free energy gives a sufficiently accurate picture of the experimental facts in the vicinity of the transition temperature.

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