

## Pressure and Temperature Dependence of the Dielectric Properties of the Perovskite Barium Titanate

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The reduction in Curie constant of single-crystal barium titanate under hydrostatic pressure has been explained by a weak temperature dependence of the electrostrictive constant  $Q_{11}+2Q_{12}$ . The magnitude of the temperature coefficient of  $Q_{11}+2Q_{12}$  computed from Samara's data is  $1.2 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ .

A WEALTH of data is available in the literature on the dependence of the dielectric properties of  $\text{BaTiO}_3$  under hydrostatic pressure.<sup>1-4</sup> In all these papers there is a general agreement that the Curie point of  $\text{BaTiO}_3$  decreases with pressure. Using a phenomenological thermodynamic approach, Goswami<sup>5</sup> satisfactorily explained these data.

More recently, Samara<sup>6</sup> has extended the range of dielectric measurements to significantly higher pressure. While in general agreement with the previous work, his data also show that the Curie constant, as deduced from the behavior in the paraelectric phase, decreases significantly with increasing pressure.

In the following, it is shown that this reduction in Curie constant may be explained by a weak temperature dependence of the electrostrictive constant  $Q_{11}+2Q_{12}$ . The magnitude of this temperature dependence is too small to be observed in the rather imprecise measurements of the  $Q$ 's by direct methods, and thus Samara's data provide the first direct proof of this phenomenon.

The elastic Gibbs free energy for barium titanate may be written in the form

$$\begin{aligned}
 G_1 - G_{10} = & -\frac{1}{2}s_{11}(X_x^2 + Y_y^2 + Z_z^2) \\
 & -s_{12}(X_x Y_y + Y_y Z_z + Z_z X_x) \\
 & -\frac{1}{2}s_{44}(X_y^2 + Y_z^2 + Z_x^2) \\
 & + (Q_{11}X_x + Q_{12}Y_y + Q_{12}Z_z)P_x^2 \\
 & + (Q_{12}X_x + Q_{11}Y_y + Q_{12}Z_z)P_y^2 \\
 & + (Q_{12}X_x + Q_{12}Y_y + Q_{11}Z_z)P_z^2 \\
 & + Q_{44}(X_y P_x P_y + Y_z P_y P_z + Z_x P_z P_x) \\
 & + A(P_x^2 + P_y^2 + P_z^2) \\
 & + B(P_x^4 + P_y^4 + P_z^4) + C(P_x^6 + P_y^6 + P_z^6) \\
 & + D(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2) \\
 & + G(P_x^2 P_y^4 + P_x^4 P_y^2 + P_y^2 P_z^4 \\
 & \quad + P_y^4 P_z^2 + P_z^2 P_x^4 + P_z^4 P_x^2), \quad (1)
 \end{aligned}$$

where  $X_x, Y_y, Z_z$  are the normal stress components,  $Y_z, Z_x, X_y$  are the shear stress components,  $s_{11}, s_{12}, s_{44}$  are the elastic compliances,  $P_x, P_y, P_z$  are the components of polarization, and  $Q_{11}, Q_{12}, Q_{44}$  are the electrostrictive coefficients.  $A, B, C, D, G$  are the constants of the free energy function and  $G_{10}$  is the free energy of the unstressed, unpolarized crystal.

For hydrostatic stress,

$$\begin{aligned}
 X_x = Y_y = Z_z = & -\sigma, \\
 X_y = Y_z = Z_x = & 0, \quad (2)
 \end{aligned}$$

where  $\sigma$  is the stress in dyn/cm<sup>2</sup>.

The isothermal dielectric inverse susceptibility (dielectric stiffness) may be deduced from Eq. (1) for any stressed or polarized state since

$$\begin{aligned}
 \chi_{xx} = (\delta^2 G_1 / \delta P_x^2)_T, \quad \chi_{yy} = (\delta^2 G_1 / \delta P_y^2)_T, \\
 \chi_{zz} = (\delta^2 G_1 / \delta P_z^2)_T, \quad \chi_{xy} = (\delta^2 G_1 / \delta P_x \delta P_y)_T. \quad (3)
 \end{aligned}$$

For the cubic paraelectric phase, under a constant hydrostatic stress, the crystal is dielectrically isotropic, and it is clear from Eqs. (1)-(3) that

$$\begin{aligned}
 \chi_{xx} = \chi_{yy} = \chi_{zz} = \chi = 4\pi/\epsilon = 2A + 2(Q_{11} + 2Q_{12})\sigma, \\
 \chi_{xy} = \chi_{yz} = \chi_{zx} = 0. \quad (4)
 \end{aligned}$$

With zero stress, the crystal is known to follow a Curie-Weiss law in the paraelectric phase, i.e.,

$$\epsilon = C_0 / (T - T_0),$$

so that

$$2A = (4\pi/C_0)(T - T_0), \quad (5)$$

where  $\epsilon_0$  is the value of  $\epsilon$  corresponding to zero stress. If the combination of electrostrictive constants  $Q_{11}+2Q_{12}$  is weakly temperature-dependent, Eq. (3) may be rewritten in the form

$$\chi = 4\pi/\epsilon = (4\pi/C_0)(T - T_0) + 2\sigma(Q_{11} + 2Q_{12})_0(1 + \alpha T), \quad (6)$$

<sup>1</sup> W. J. Merz, Phys. Rev. **77**, 52 (1950).

<sup>2</sup> J. Klimowski and J. Pietrzak, Acta Phys. Polon. **19**, 369 (1960).

<sup>3</sup> J. Klimowski, Phys. Status Solidi **2**, 456 (1962).

<sup>4</sup> G. Shiran and A. Takeda, J. Phys. Soc. Japan **7**, 1 (1952).

<sup>5</sup> A. K. Goswami, J. Phys. Soc. Japan **21**, 1037 (1966).

<sup>6</sup> G. A. Samara, Phys. Rev. **151**, 378 (1966).

where  $(Q_{11}+2Q_{12})_0$  is the value of the striction constants at zero temperature and  $\alpha$  is the temperature coefficient.

Equation (6) has the form of a Curie-Weiss law, i.e.,

$$\epsilon = C / (T - T_\theta),$$

with

$$C = \frac{4\pi C_0}{4\pi + 2\sigma\alpha(Q_{11} + 2Q_{12})_0 C_0} \quad (7)$$

and

$$T_\theta = \frac{4\pi T_0 - 2\sigma(Q_{11} + 2Q_{12})_0 C_0}{4\pi + 2\sigma\alpha(Q_{11} + 2Q_{12})_0 C_0} \quad (8)$$

From Eq. (7),

$$(1/C^2)(\delta C/\delta\sigma) = -(1/4\pi)2\alpha(Q_{11} + 2Q_{12})_0$$

or

$$\alpha = -2\pi(Q_{11} + 2Q_{12})_0^{-1}(1/C^2)\delta C/\delta\sigma.$$

Using Samara's tabulated data for  $1/C^2$  and  $\delta C/\delta\sigma$  for single crystals (Table I of Ref. 6), we may deduce a value of  $\alpha \approx +1.2 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ .

This temperature dependence is much too weak to detect from direct measurements of the striction constants, which are at best accurate to  $\pm 10\%$ , but provides a very simple explanation for the observed change in Curie constant with hydrostatic stress.

The dependence of the dielectric properties of BaTiO<sub>3</sub> under hydrostatic pressure. In all papers there is a general agreement that the Curie point of BaTiO<sub>3</sub> decreases with pressure. Using a phenomenological thermodynamic approach, Goswami and Cross have explained these data. More recently Samara has extended the range of dielectric measurements to significantly higher pressures. While in general agreement with the present work, his data also show that the Curie constant as deduced from the behavior in the paraelectric phase decreases significantly with increasing pressure. In the following it is shown that this reduction in Curie constant may be explained by a weak temperature dependence of the electrostrictive constant  $Q_{11} + 2Q_{12}$ . The magnitude of this temperature dependence is too small to be observed in the latter temperature measurements at the O<sub>2</sub> pressure methods, and this Samara's data provide the first direct proof of this phenomenon.

$$\chi_{11} = \chi_{22} = \chi_{33} = \chi_{12} = \chi_{13} = \chi_{23} = 0 \quad (3)$$

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$$\epsilon = C_0 / (T - T_\theta) \quad (5)$$

$$\chi_{11} = \chi_{22} = \chi_{33} = \chi_{12} = \chi_{13} = \chi_{23} = 0 \quad (6)$$

The dielectric Gibbs free energy for domain II can be written in the form  $G - G_0 = \frac{1}{2}(\epsilon_{11}X_1^2 + \epsilon_{22}X_2^2 + \epsilon_{33}X_3^2) + \frac{1}{2}(\chi_{11}X_1^2 + \chi_{22}X_2^2 + \chi_{33}X_3^2) + \frac{1}{2}(\chi_{12}X_1X_2 + \chi_{13}X_1X_3 + \chi_{23}X_2X_3) + \frac{1}{2}(\epsilon_{12}X_1X_2 + \epsilon_{13}X_1X_3 + \epsilon_{23}X_2X_3) + \frac{1}{2}(\chi_{11}\chi_{22}X_1^2X_2^2 + \chi_{11}\chi_{33}X_1^2X_3^2 + \chi_{22}\chi_{33}X_2^2X_3^2) + \frac{1}{2}(\chi_{12}\chi_{13}X_1^3 + \chi_{12}\chi_{23}X_1^2X_2 + \chi_{13}\chi_{23}X_1X_2^2) + \frac{1}{2}(\chi_{11}\chi_{12}\chi_{13}X_1^4 + \chi_{11}\chi_{12}\chi_{23}X_1^3X_2 + \chi_{11}\chi_{13}\chi_{23}X_1^2X_2X_3 + \chi_{12}\chi_{13}\chi_{23}X_1X_2^2X_3 + \chi_{12}\chi_{23}\chi_{33}X_1X_2^2X_3^2 + \chi_{13}\chi_{23}\chi_{33}X_1^2X_2X_3^2) + \frac{1}{2}(\chi_{11}\chi_{12}\chi_{13}\chi_{23}X_1^5 + \chi_{11}\chi_{12}\chi_{13}\chi_{33}X_1^4X_2 + \chi_{11}\chi_{12}\chi_{23}\chi_{33}X_1^3X_2X_3 + \chi_{11}\chi_{13}\chi_{23}\chi_{33}X_1^2X_2^2X_3 + \chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1X_2^2X_3^2) + \frac{1}{2}(\chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^6 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^5X_2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^4X_2^2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^3X_2^2X_3 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^2X_2^2X_3^2) + \frac{1}{2}(\chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^7 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^6X_2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^5X_2^2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^4X_2^2X_3 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^3X_2^2X_3^2) + \frac{1}{2}(\chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^8 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^7X_2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^6X_2^2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^5X_2^2X_3 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^4X_2^2X_3^2) + \frac{1}{2}(\chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^9 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^8X_2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^7X_2^2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^6X_2^2X_3 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^5X_2^2X_3^2) + \frac{1}{2}(\chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^{10} + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^9X_2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^8X_2^2 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^7X_2^2X_3 + \chi_{11}\chi_{12}\chi_{13}\chi_{23}\chi_{33}X_1^6X_2^2X_3^2) + \dots$