

USN, and the other officers and men of the USS Norton Sound for the conduct of the expedition and the rocket firing.

Added in proof: A check on the validity of the empirical Eq. (1) above is had by calculating the counting rate of a single G-M

counter with axis vertical above the atmosphere. This rate is $\int_0^{90^\circ} j(\theta) \cdot A(\theta) \cdot 2\pi \sin\theta d\theta$, in which $j(\theta)$ is given by Eq. (1), and $A(\theta)$ is the projected area of the cylindrical counter. The result for the counter used is 8.8 counts/second. The difference between this value and the observed counting rate 9.7 ± 0.2 counts/sec. is reasonably attributable to reason (c) above and perhaps to lack of accuracy in (1).

The Effect of Hydrostatic Pressure on the Curie Point of Barium Titanate Single Crystals*

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The influence of hydrostatic pressure on the Curie temperature of BaTiO₃ single crystals has been investigated. With increasing pressure a linear shift of the Curie point towards lower temperature is observed with a slope of -5.8×10^{-3} degree/atmos. This information allows us to calculate the change of the specific heat and of the compressibility at the Curie point according to Ehrenfest's relation. Thus it is possible to relate the pressure effect to the change of the lattice constant. The decrease of the Curie temperature with shrinking lattice constant is nearly the same as that observed when Sr ions are substituted for Ba in the titanate crystal. In addition, measurements have been made on the influence of pressure on the first order transition point near 0°C.

INTRODUCTION

THE research of this laboratory on the properties of barium titanate¹⁻⁶ has the long-range objective of arriving at an understanding of the mechanism of ferroelectricity. The relatively simple perovskite structure of BaTiO₃ and of the related columbates and tantalates⁷ offers an easier access to this problem than the complex structure of the other two ferroelectric groups, rochelle salt and the alkali phosphates and arsenates.

Barium titanate is cubic above the Curie point (120°C). One question of prime importance is to learn how the Curie temperature, that is, the onset of spontaneous polarization, depends on the lattice parameters. The lattice constant can be reduced by hydrostatic pressure, and a shift of the Curie point would be expected. Arguments can be presented for predicting a shift in either direction. Under pressure, the lattice dimensions prevailing at the normal Curie point are realized at higher temperature, hence the Curie temperature may be raised. *Vice versa*, the successive replacement of barium ions by strontium ions reduces

the lattice constant and moves the Curie point downwards, hence pressure may lower the Curie temperature. The results given in the present paper decide this question experimentally.

APPARATUS

The pressure apparatus* (Fig. 1) consists of a pressure generator and a crystal chamber interconnected by a steel capillary. Hydrostatic pressures up to 5000 atmos. were reached by inserting the generator in a standard hydraulic jack. The temperature in the crystal holder could be adjusted from that of liquid air through the Curie region up to *ca.* 150°C, made possible by using silicone oil as the hydrostatic pressure liquid. The behavior of the Curie point was determined by measuring the dielectric constant as a function of temperature and pressure at 10 kc. A thermocouple, inserted in a hole of the crystal holder casing about 2 mm from the crystal, served as the temperature control and allowed the measurement of relative temperature changes with a high degree of reproducibility (0.1°C).

Dependence of the Curie Temperature on Hydrostatic Pressure

In contrast to the behavior of rochelle salt, for which Bancroft⁸ found a shift of the Curie point to higher temperatures with increasing pressure, we found the opposite behavior for BaTiO₃ single crystals. Up to

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¹ A. von Hippel and co-workers, NDRC Contract OEMsr-191, Repts. VII (August, 1944) and XI (October, 1945); von Hippel, Breckenridge, Chesley, and Tisza, *J. Ind. Eng. Chem.* **38**, 1097 (1946).

² S. Roberts, *Phys. Rev.* **71**, 890 (1947).

³ B. T. Matthias and A. von Hippel, *Phys. Rev.* **73**, 1378 (1948).

⁴ R. D. Burbank and H. T. Evans, Jr., *Acta Cryst.* **1**, 330 (1948).

⁵ P. W. Forsbergh, Jr., *Phys. Rev.* **76**, 1187 (1949).

⁶ W. J. Merz, *Phys. Rev.* **75**, 687 (1949); **76**, 1221 (1949).

⁷ B. T. Matthias, *Phys. Rev.* **75**, 1771 (1949).

* This unit was built by P. W. Forsbergh, Jr. on the basis of information received from Professor P. W. Bridgman's laboratory at Harvard University.

⁸ D. Bancroft, *Phys. Rev.* **53**, 587 (1938).

about 2500 atmos. the Curie temperature θ falls linearly with increasing pressure with a slope dT/dp of -5.8×10^{-3} degree/atmos. (-5.74×10^{-9} degree cm^2/dyne) (Fig. 2). At higher values of the pressure the results become more involved because of a dependence on the prehistory, that is, on the temperature at which the pressure is applied and on the value from which the pressure is increased or decreased. This seems to be due to the existence of the domains and their response to the external pressure. The best results (straight line) at these higher pressures are therefore obtained by starting the compression above the Curie temperature when no domains exist.

The characteristic of the dielectric constant *vs.* temperature retains its well-known shape⁶ and only shifts to lower temperatures as the pressure is increased. However, there is a slight increase of the peak value of the dielectric constant at the Curie point at its position shifts downwards.

DISCUSSION

The transition at the Curie point is of the second order, hence we can use Ehrenfest's relation⁹ for the calculation of the change of the specific heat at the Curie point in contrast to the Clausius-Clapeyron equation which applies to a first order transition and gives the value of the latent heat. If Δc_p represents this change of the specific heat, ρ the density, θ the Curie temperature, and $\Delta\beta$ the change in the volume expansion

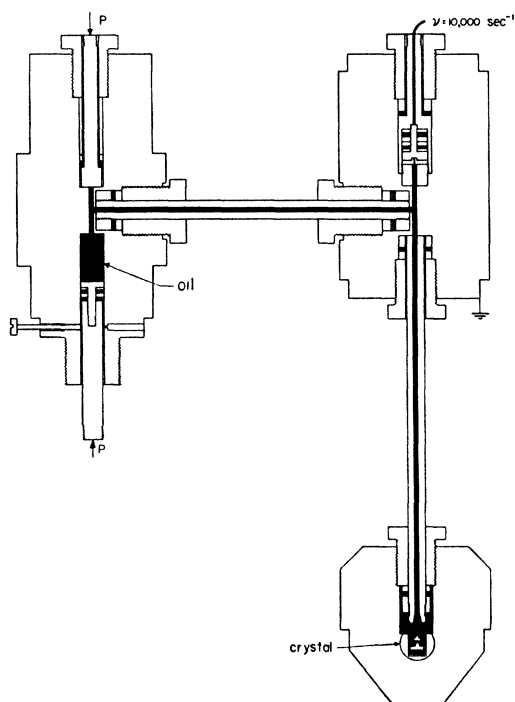


FIG. 1. Pressure apparatus.

⁹ P. Ehrenfest, Comm. Univ. Leiden, Suppl. 75b (1933).

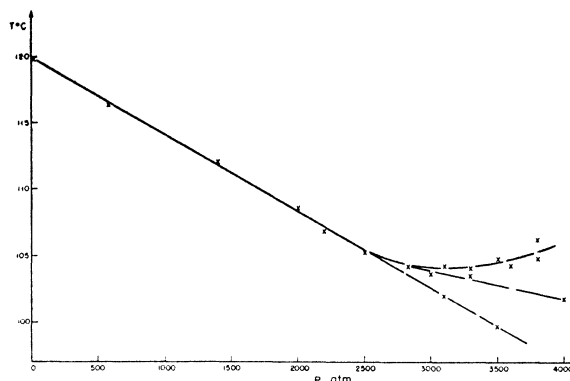


FIG. 2. Curie temperature *vs.* pressure. The divergence above 2500 atmos. because of prehistory is apparent.

coefficient at the Curie temperature, we have $dp/dT = \Delta c_p \cdot \rho / \theta \cdot \Delta\beta$. With $(dT/dp)_{p=0} = -5.74 \times 10^{-9}$ degree cm^2/dyne as given above, $\rho = 6.04$ g/cm^3 , $\theta = 393^\circ\text{K}$, and $\Delta\beta = 3\Delta\alpha = -18 \times 10^{-6}$ degree⁻¹ where $\Delta\alpha$ represents the change of the linear expansion coefficient obtained from the x-ray measurements of Megaw,¹⁰ we get for the change of the specific heat at the Curie point $\Delta c_p = 4.9 \times 10^{-3}$ cal./g degree. The value of Δc_p thus calculated is of the same order of magnitude as the measured values of Wul¹¹ (3×10^{-3}) and Harwood, Popper, and Rushman¹² (2.5×10^{-3}), but somewhat smaller than that of Blattner and Merz¹³ (20×10^{-3}). The small value agrees with the interpretation of the transition as a displacive one¹⁴ in contrast to the order-disorder transition for KH_2PO_4 , where a much larger value of Δc_p is observed. For the rochelle salt transitions, also classified as displacive, one gets, using the measurements of Bancroft for Δc_p , the values of 14×10^{-3} and 4.1×10^{-3} for the two Curie points⁵ in good agreement with the direct measurements of Wilson.¹⁵

Concerning dT/dp we have to expect for BaTiO_3 a negative value according to Ehrenfest's formula, since $\Delta c_p > 0$ and $\Delta\beta < 0$ as we traverse the Curie point from the ferroelectric tetragonal state to the cubic state. For rochelle salt we have dT/dp positive because both Δc_p and $\Delta\beta$ are positive at the upper Curie point and negative at the lower one.

Ehrenfest's formula for a transition of the second order can also be written as $dp/dT = \Delta\beta/\Delta k$ where $\Delta\beta$ is the change of the volume expansion coefficient at the Curie point as before and Δk is the change in the volume compressibility at the Curie point. With the known values of dp/dT and $\Delta\beta$ we obtain $+1.03 \times 10^{-13}$ cm^2/dyne for Δk , that is, the volume compressibility

¹⁰ H. D. Megaw, Proc. Roy. Soc. A189, 261 (1947).

¹¹ B. M. Wul, J. Phys. USSR 10, 95 (1946).

¹² Harwood, Popper, and Rushman, Nature 160, 58 (1947).

¹³ H. Blattner and W. J. Merz, Helv. Phys. Acta 21, 210 (1948).

¹⁴ L. Tisza, "On the General Theory of Phase Transitions," N.R.C. Symposium, Cornell University, August, 1948.

¹⁵ A. J. C. Wilson, Phys. Rev. 54, 1103 (1938).

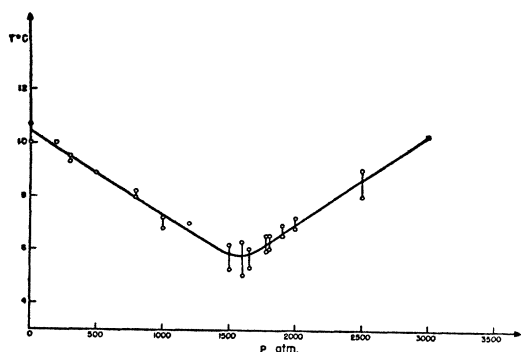


Fig. 3. λ -point vs. pressure.

is higher in the Curie region than above, quite analogous to rochelle salt at the upper Curie point.

The main interest of these measurements lies in the information they provide as to the dependence of the Curie point on the value of the lattice constant. The compressibility of BaTiO_3 can be calculated from Mason's values¹⁶ of the elastic constants of ceramics and used in the first approximation for our single crystals. Mason found at room temperature a Young's modulus $Y_0 = [\mu(3\lambda + 2\mu)/(\lambda + \mu)]$ of 11.3×10^{11} dyne/cm² and $\lambda + 2\mu = 14.2 \times 10^{11}$ dyne/cm² where λ and μ are the Lamé elastic constants. Thus $\lambda = 5.2 \times 10^{11}$ dyne/cm², $\mu = 4.5 \times 10^{11}$ dyne/cm² and the volume compressibility $k = 3/(3\lambda + 2\mu) = 12.2 \times 10^{-13}$ cm²/dyne. Hence the compressibility, as we traverse the Curie point with rising temperature, decreases as given above, by a value Δk corresponding to about 8.5 percent.

Now we can calculate the change of the lattice constant in the cubic region with applied pressure by assuming that the compressibility of the crystal is here $k - \Delta k$. Taking into account the thermal contraction of the crystal, we obtain finally for the ratio of the change of the Curie temperature to the change of the lattice

constant the value $\Delta\theta/\Delta x = +3.3 \times 10^3$ degree/angstrom.

Rushman and Strivens¹⁷ and other workers found a linear dependence of the Curie temperature and of the lattice constant on the amount of SrTiO_3 in BaTiO_3 crystals. For instance, a mixture of 64 percent BaTiO_3 and 36 percent SrTiO_3 gave a Curie temperature of 12°C with a lattice constant $a = b = c = 3.9620\text{Å}$. In comparing these values with those for BaTiO_3 , with $\theta = 120^\circ\text{C}$ and $a = b = c = 4.0011\text{Å}$, we derive $\Delta\theta/\Delta x = +2.8 \times 10^3$ degree/angstrom, a much better agreement with our value than one would expect since it can not be assumed that the change of the Curie temperature is due to the change of the lattice constant alone.

Effect of Hydrostatic Pressure on the First Order Transition Near 0°C

At this transition point we again find at first a decrease of the transition temperature with increasing pressure, but above *ca.* 1500 atmos. the situation is reversed (Fig. 3). Simultaneously a strong dependence on the prehistory is observed in this upper region. It may be that the change of the sign of dT/dp at 1500 atmos. is caused only by the domain pattern because at this transition point from the tetragonal to the orthorhombic state a considerable rearrangement of domains occurs.^{5,6}

The transition point at about -80°C has not yet been investigated as it appeared that not much information would be gained, as in the case of the 0° transition, due to rearrangement of domains.

The writer wishes to thank Professor A. von Hippel for many helpful discussions during the course of this work, and to acknowledge the valuable work done by P. W. Forsbergh, Jr. in developing the pressure apparatus. The transfer of Dr. Forsbergh to Europe prevented him from carrying through this investigation.

¹⁶ W. P. Mason, Phys. Rev. 74, 1134 (1948).

¹⁷ D. F. Rushman and M. A. Strivens, Trans. Far. Soc. 42A, 231 (1946).