

Effect of Hydrostatic Pressure on the Hysteresis Loop of Guanidine Aluminum Sulfate Hexahydrate

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The 60-cycle hysteresis loop of guanidine aluminum sulfate hexahydrate (G.A.S.H.) has been measured as a function of hydrostatic pressure. It was found that the spontaneous polarization P_s and the coercive field strength E_c increase with pressure. It could be shown that to a first approximation P_s and E_c are a function of the volume change alone, regardless of whether this volume change is obtained by hydrostatic pressure or by lowering the temperature. The measurements suggest that the shortening of the polar c axis causes an increase of the dipole moment along this axis.

I. INTRODUCTION

THE effect of hydrostatic pressure on the ferroelectric properties of Rochelle salt has been measured by Bancroft¹; the effect on BaTiO₃ by Merz² and by Forsbergh.³ It was found that in Rochelle salt the upper Curie point increases linearly with increasing hydrostatic pressure¹ whereas in BaTiO₃ the Curie point decreases linearly under the influence of a hydrostatic pressure² and increases under the influence of a two dimensional pressure.³ Since these two materials behave so differently it is of interest to find out how guanidine aluminum sulfate hexahydrate (G.A.S.H.), the newly discovered ferroelectric material,⁴ behaves under hydrostatic pressure. This is not only of general physical interest but the results might show whether G.A.S.H. can be grown in the nonferroelectric state in case the Curie point is lowered enough by pressure.

II. EXPERIMENTAL RESULTS

We measured the 60-cycle hysteresis loop of G.A.S.H. as a function of hydrostatic pressure up to about 5000 atmos. A series of hysteresis loops taken at room temperature is shown in Fig. 1. It can be seen that the higher the pressure, the larger the loop, that is, both the spontaneous polarization P_s and the coercive field strength E_c increase with pressure. Furthermore, the shape of the loop changes from reasonably square to very round ones.

By plotting P_s versus pressure p , we find that P_s increases linearly with pressure (Fig. 2). We thus can

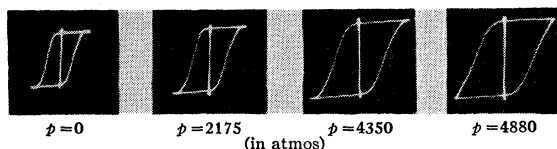


FIG. 1. 60-cycle hysteresis loops of G.A.S.H. under different hydrostatic pressures at room temperatures.

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¹ Dennison Bancroft, Phys. Rev. **53**, 587 (1938).

² Walter J. Merz, Phys. Rev. **78**, 52 (1950).

³ P. W. Forsbergh, Jr., Phys. Rev. **93**, 686 (1954).

⁴ Holden, Merz, Remeika, and Matthias, Phys. Rev. **101**, 962 (1956).

write

$$\Delta P_s / P_s = \chi' \Delta p, \quad (1)$$

where ΔP_s is the change in spontaneous polarization, Δp the applied hydrostatic pressure, and χ' is a constant which has the value $\chi' \cong 10 \times 10^{-5} \text{ atm}^{-1}$. From this linear shift in P_s , we might conclude that in G.A.S.H. the Curie point moves upwards linearly with pressure if we assume that the polarization versus temperature curve, $P_s(T)$, which has been published before,⁴ moves uniformly with pressure. It seems therefore very unlikely that G.A.S.H. can be grown in the nonferroelectric state by applying hydrostatic pressure.

If one looks at the sequence of hysteresis loops shown in Fig. 1, one is immediately reminded of the changes of the loops which take place when the temperature is

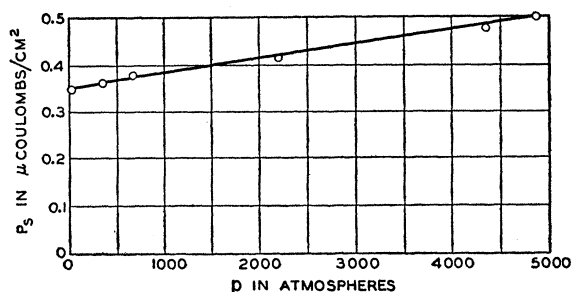


FIG. 2. Spontaneous polarization P_s of G.A.S.H. as a function of pressure.

lowered. In other words, it seems that P_s and E_c increase with hydrostatic pressure like they do by lowering the temperature. Also the shape of the loops changes the same way. The question thus arises whether the shape and size of the loops are a function of volume change alone, regardless of whether this volume change is obtained by hydrostatic pressure or by a temperature change.

We therefore write

$$\Delta P_s / P_s = -\alpha (\Delta V / V), \quad (2)$$

where ΔV is a volume change and α is a constant. We can determine α in two ways, first from compressibility data and second from thermal contraction data. Using

compressibility data, we can write for Eq. (2)

$$\Delta P_s/P_s = -\alpha(\Delta V/V) = +\alpha\chi\Delta p = +\chi'\Delta p, \quad (3)$$

where χ is the volume compressibility of G.A.S.H. and $\chi' = \alpha\chi$. Experimentally we found from Fig. 2 and Eq. (1) $\chi' \cong 10 \times 10^{-5} \text{ atm}^{-1}$. The compressibility χ of G.A.S.H. is not known. However, for order of magnitude comparison we can take the compressibility values of Rochelle salt, a material which is similar to G.A.S.H. in mechanical properties. Thus, with $\chi \cong 5 \times 10^{-6} \text{ atm}^{-1}$ (value for Rochelle salt), we obtain

$$\alpha = \chi'/\chi = 20. \quad (4)$$

On the other hand, using thermal contraction data, we can write Eq. (2) in the following way:

$$\Delta P_s/P_s = -\alpha(\Delta V/V) = -\alpha\gamma\Delta T = \gamma'\Delta T, \quad (5)$$

where ΔT is the temperature change, γ is the volume expansion coefficient, and $\gamma' = -\alpha\gamma$. Experimentally we find from the $P_s(T)$ curves which we published before⁴ that $\gamma' \cong -5 \times 10^{-3} \text{ degree}^{-1}$. This value is not very accurate because the $P_s(T)$ curve is not a straight line but shows some curvature. The thermal expansion coefficient γ of G.A.S.H. is not known. If we again take the value for Rochelle salt which is $\gamma \cong 2 \times 10^{-4} \text{ degree}^{-1}$, we obtain

$$\alpha = -\gamma'/\gamma = 25. \quad (6)$$

Expressions (4) and (6) thus show that we obtain about the same value for α both from the pressure and from the thermal experiment. The absolute values should of course not be taken too seriously since we had to assume values for χ and γ . However, since these two values do not vary much for similar crystals, it appears that the order of magnitude of $\alpha \cong 20-25$ is certainly right. Thus, the assumption that the change in P_s is proportional to the change of the volume seems to be reasonable.

A similar comparison can be made for the changes in coercive field E_c as a function of hydrostatic pressure or as a function of temperature. We obtain α values of the same order.

III. DISCUSSION

The most interesting result obtained from this pressure experiment is not the fact that the Curie temperature probably increases when pressure is applied, but the fact that the spontaneous polarization P_s increases appreciably. This result cannot be explained by the increase in density, that is by the increase of the number N of dipoles per unit volume because in that case the change of P_s would be

$$\Delta P_s/P_s = \Delta N/N = -\Delta V/V, \quad (7)$$

whereas we observe a change which is about 20-25 times larger. Thus by applying a hydrostatic pressure the dipole moments themselves become larger. This is an unusual behavior both for ferroelectric and nonferroelectric crystals. In nonferroelectric materials the polarizability of the ions usually drops when pressure is applied and thus the dielectric constant usually drops except in some cases where the increase in density overcompensates the drop in polarizability. In ferroelectric materials the situation is complicated by the fact that additional changes in P_s can be caused by the high piezoelectric coupling. Rochelle salt does not show any measurable changes in P_s when hydrostatic pressure is applied,⁵ in contrast to the case of a two-dimensional pressure in the y - z plane. In that case P_s drops very fast⁵ because of the extremely strong piezoelectric coupling between P_s in the x direction and the shear stress in the y - z plane. BaTiO₃ behaves very similarly in that under hydrostatic pressure, P_s drops only a little since the Curie temperature drops by a few degrees.² Under two-dimensional pressure, P_s increases in BaTiO₃ owing to the high piezoelectric coupling between P_s in the z direction and the normal stresses along the x and y directions.

In G.A.S.H. the piezoeffect is small, and G.A.S.H. seems to be an exceptional material in that the dipole moment increases appreciably when hydrostatic pressure is applied. Since it shows a very pronounced cleavage plane perpendicular to the ferroelectric c -axis we can assume that the compressibility is largest along this axis. Thus it appears that the increase of the dipole moment along the c axis is caused by a shortening of the unit cell along this axis. An explanation for this very unusual result cannot be given before the details of the structure of G.A.S.H. are known. We can assume, however, that the components of the hydrogen bonds along the c axis are responsible for this behavior. This indicates that in G.A.S.H. the components of the hydrogen bonds along the ferroelectric axis have to be large and that they are directly responsible for the dipole moment. This would be in contrast to KH₂PO₄ where the hydrogen bonds are perpendicular to the polar axis and only act as a trigger for the motions of the K and P ions⁶ along the c axis which in turn determine the dipole moment.

IV. ACKNOWLEDGMENTS

I would like to thank D. W. McCall for the use of his high-pressure equipment and for his help and advice, and J. B. Darby for technical assistance.

⁵ R. David, *Helv. Phys. Acta* 8, 431 (1935).

⁶ B. C. Frazer and R. Pepinsky, *Acta Cryst.* 6, 273 (1953).

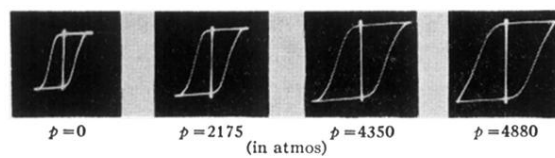


FIG. 1. 60-cycle hysteresis loops of G.A.S.H. under different hydrostatic pressures at room temperatures.