

Curie constant were somewhat scattering. The Curie constant of DGSN decreases markedly with increasing pressure as in the case of GSN.

§4. Discussion and Conclusion

The effect of deuteration on the ferroelectric transition temperature of GSN is not so conspicuous as in KH_2PO_4 ; the fractional increase in the Curie temperature by deuteration of GSN is $(T_c^D - T_c^H)/T_c^H = 0.067$, and it is much smaller than 0.73 in KH_2PO_4 . This suggests that a tunneling motion of protons is not responsible for the ferroelectric process in GSN. Then, Samara's empirical law⁴⁾ suggests that GSN is a displacive type ferroelectric. The suggestion seems to be consistent with the very small entropy change of the transition.¹⁾ The effects of hydrostatic pressure on the ferroelectric transitions in GSN and DGSN are similar to each other; they are characterized by large negative values of initial pressure coefficients of the Curie temperatures, remarkable non-linearity of T_c vs p relations, and considerable pressure variation in the Curie constants. The initial pressure coefficients of the Curie temperatures are not very different in GSN and DGSN.

Mitani⁵⁾ estimated the electrostrictive coefficients of GSN from a dilatometric measurement by X-ray diffraction. By using Mitani's values of electrostrictive coefficients we got the volume electrostrictive coefficient as $Q_h = 2.8 \times 10^{-9}$ cgs esu.³⁾ Then, the thermodynamical relation

$$[dT_c/dp]_{p=0} \equiv K = -C_0 Q_h / (2\pi) \quad (3)$$

told us a very large value of $K = -196$ deg kbar^{-1} which is ten times larger than the observed one. The discrepancy between the measured and estimated pressure coefficients of the Curie temperature results from an over-estimation of Q_h . Inversely one can estimate the volume electrostrictive coefficient from the present result of $K = -17.1$ deg kbar^{-1} and $C_0 = 860$ K as $Q_h = 1.2 \times 10^{-10}$ cgs esu. The estimated value of Q_h is still two orders of magnitude as large as the one observed in typical order-disorder type ferroelectrics (e.g. $Q_h = -4 \times 10^{-12}$ cgs esu in triglycine sulfate,⁹⁾ -5.6×10^{-12} cgs esu in NaNO_2).¹⁰⁾ However, some of "improper" ferroelectrics¹¹⁾ show the same order of magnitude of the volume electro-

strictive coefficients as that of GSN (e.g. $Q_h = -7.8 \times 10^{-10}$ cgs esu in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$, -3.7×10^{-9} cgs esu in $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$).¹²⁾ Thus, so far as concerns the magnitude of the electrostrictive coefficients, GSN is classified into an "improper" ferroelectric unlike other glycine-containing ferroelectrics.

The change in the volume thermal expansion coefficient $\Delta\alpha$ at the Curie temperature can be estimated by the relation

$$\Delta\alpha = Q_h [dP_s^2/dT]_{T=T_c} \quad (4)$$

as $\Delta\alpha = 0.5 \times 10^{-5}$ deg⁻¹, where we used $[dP_s^2/dT]_{T=T_c} = -4.4 \times 10^4$ cgs esu given by Mitani.⁵⁾ Such an amount of $\Delta\alpha$ can hardly be recognized on the unit cell volume vs temperature curve given by Mitani⁵⁾ because of difficulty in determination of the base line which corresponds to the cell volume at $P_s = 0$.

An interesting point of the pressure effect on dielectric properties of GSN and DGSN is the marked pressure dependence of the Curie constants as shown in Figs. 4 and 8. Usually the pressure variation of the Curie constants of ferroelectrics is not very conspicuous; for example, $[d \ln C/dp]_{p=0} = 0.01 \sim 0.02$ kbar^{-1} in BaTiO_3 ¹³⁾ and PbTiO_3 .¹⁴⁾ The value of $[d \ln C/dp]_{p=0} = -0.17$ kbar^{-1} in GSN obtained in the present work is only comparable with -0.12 kbar^{-1} reported for the I-III transition of KNO_3 .¹⁵⁾ If one assumes that the volume electrostrictive coefficient Q_h is pressure independent and C is linearly dependent on p as $C = C_0(1 + \beta p)$, one can represent the pressure variation of T_c in a quadratic form of

$$T_c = T_c^0 + K \left(1 + \frac{\beta}{2} p \right) p \quad (5)$$

$$(K \equiv Q_h C_0 / (2\pi)).$$

Putting the observed values of $T_c^0 = -57.1^\circ\text{C}$, $K = -17.1$ deg kbar^{-1} , and $\beta = -0.17$ kbar^{-1} into eq. (5), one can obtain the pressure dependence of the Curie temperature as shown by the slashed curve in Fig. 3. The calculated curve well represents the experimental points below 2 kbar showing that the non-linearity in the T_c vs p relation and the pressure variation of the Curie constant is closely related to each other. It is interesting to check whether such a relation can be detected for other ferroelectrics, e.g. KNO_3 .

References

- 1) R. Pepinsky, Y. Okaya, D. P. Eastman and T. Mitsui: *Phys. Rev.* **107** (1957) 1538.
- 2) J. K. Mohana Rao and M. A. Viswamitra: *Acta cryst.* **B28** (1972) 1672.
- 3) K. Gesi and K. Ozawa: *Japan. J. appl. Phys.* **12** (1973) 1106.
- 4) G. A. Samara: *Advances in High Pressure Research*, ed. R. S. Bradley, Vol. 3 (Academic Press, London and New York, 1969) p. 155.
- 5) S. Mitani: *J. Phys. Soc. Japan* **19** (1964) 481.
- 6) Z. Málek, J. Štrajblová, J. Novotný and V. Mareček: *Czech. J. Phys.* **B18** (1968) 1224.
- 7) K. Gesi: *J. Phys. Soc. Japan* **26** (1969) 107.
- 8) E. Nakamura, T. Mitsui and J. Furuichi: *J. Phys. Soc. Japan* **18** (1963) 1477.
- 9) T. Ikeda, Y. Tanaka and H. Toyoda: *Japan. J. appl. Phys.* **2** (1963) 199.
- 10) K. Gesi: *Phys. Status solidi* (a) **15** (1973) 653.
- 11) J. Kobayashi, Y. Enomoto and Y. Sato: *Phys. Status solidi* (b) **50** (1972) 335.
- 12) K. Gesi and K. Ozawa: *J. Phys. Soc. Japan* **39** (1975) 1026.
- 13) G. A. Samara: *Phys. Rev.* **151** (1966) 378.
- 14) G. A. Samara: *Ferroelectrics* **2** (1971) 277.
- 15) M. Midorikawa, Y. Ishibashi and Y. Takagi: *J. Phys. Soc. Japan* **30** (1971) 449.