Effect of Hydrostatic Pressure on the Phase Transitions in Ferroelectric Glycine Silver Nitrate and Deuterated Glycine Silver Nitrate

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Effect of hydrostatic pressure on the ferroelectric phase transitions in glycine silver nitrate ($NH_2CH_2COOH \cdot AgNO_3$; GSN) and its deuterated analogue (DGSN) was studied by means of dielectric measurements. The Curie temperatures decrease with increasing pressure by a relation $T_c = T_c^0 + Kp + \gamma p^2$. Parameters T_c^0, K, and γ are determined as $-57.1 °C$, -17.1 deg kbar^{-1}, and 1.3 deg kbar^{-2}, respectively, for GSN; and $-42.7 °C$, -20.2 deg kbar^{-1}, and 1.7 deg kbar^{-2}, respectively, for DGSN. Considerable decrease in Curie constants was observed both in GSN and in DGSN as pressure increases.

§1. Introduction

Pepinsky *et al.*[1] first reported a ferroelectric activity in glycine silver nitrate $NH_2CH_2COOH \cdot AgNO_3$ (Abbreviated to GSN). The Curie temperature of GSN is about $-55 °C$, and the space group of the paraelectric phase is monoclinic $P2_1/a$.[1,2] The present authors[3] preliminarily studied the effect of hydrostatic pressure on the ferroelectric phase transition in GSN, and found a substantially large negative pressure coefficient of the Curie temperature, $[dT_c/dp]_{p=0} \sim -16$ deg kbar^{-1}. Samara[4] stated an empirical law of the relation between the type of a ferroelectric and the effect of hydrostatic pressure on the Curie temperature; an order-disorder type ferroelectric has a positive pressure coefficient of the Curie temperature, on the other hand, displacive or proton-tunneling type one has a negative coefficient. According to Samara's law the negative sign of the pressure coefficient of the Curie temperature in GSN corresponds to an ionic displacement or tunneling motion of protons as the mechanism of the ferroelectric phase transition. If the tunneling motion of protons plays an important role in the ferroelectric process in GSN, deuterium-substitution will drastically change the Curie temperature as in the case of KH_2PO_4 (the Curie temperature of KH_2PO_4 is raised from 123 K to 213 K by deuteration). However, none has been reported for the deuterium-substitution effect on the ferroelectric phase transition in GSN so far in the search of the present authors.

In the present work we grew single crystals of deuterated glycine silver nitrate (Abbreviated to DGSN), and measured the effects of deuteration and hydrostatic pressure on its ferroelectric phase transition. The results were discussed together with the hydrostatic pressure effect on GSN.

§2. Experimental

Single crystals of GSN were prepared by introducing ethyl-alcohol vapor into an aqueous solution containing equimolar amounts of glycine and $AgNO_3$ at around $30 °C$.[1,5] The as-grown crystals were colorless, transparent, and very soft. Light exposure makes the crystals brown. A perfect cleavage was found along the (010) plane. The deuterated salt was prepared by successive recrystallization from solutions of 99.7% D_2O at room temperatures. Figure 1 shows the relation between the Curie temperature and the times of recrystallization from the D_2O solution. The Curie temperature increases from about $-55 °C$ to about $-43 °C$ for the GSN crystals recrystallized three times. Further recrystallization from the D_2O solution does not alter the Curie temperature appreciably. In the case of deuteration of triglycine sulfate[6] hydrogens in the CH_2-radical can not be substituted with deuterium by the recrystallization from D_2O-solution. Probably the same is the case in GSN; that is, the chemical formula of deuterated glycine silver nitrate (DGSN) is $ND_2CH_2COOD \cdot AgNO_3$.
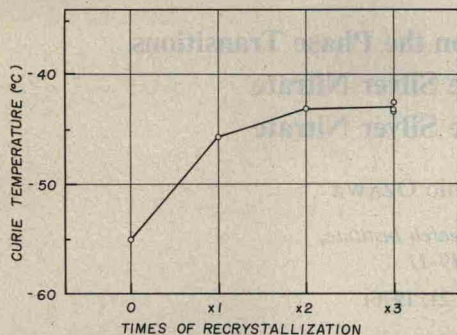
Fig. 1. Relation between the Curie temperature and the times of recrystallization from D_2O solution of glycine silver nitrate.

Silver paste was attached as electrodes on surfaces of (010) plates. The dimension of the specimens was $(0.6 \sim 1.1)$ mm $\times (0.03 \sim 0.1)$ cm^2. A Cu–Be pressure bomb was served for the high pressure measurements. The pressure-transmitting fluid used was 1:1 mixture of *iso*- and *n*-penthane. The pressure system used and experimental procedure were described elsewhere.[7] The dielectric constant of the specimen was measured with a three terminal capacitance bridge at 1 kHz. The measuring voltage amplitude was 3.5 V_{p-p}.

§3. Results

3.1 GSN

Figure 2 shows the temperature dependence of the dielectric constant of GSN along the (010) direction at different pressures. The Curie temperature decreases with increasing pressure.
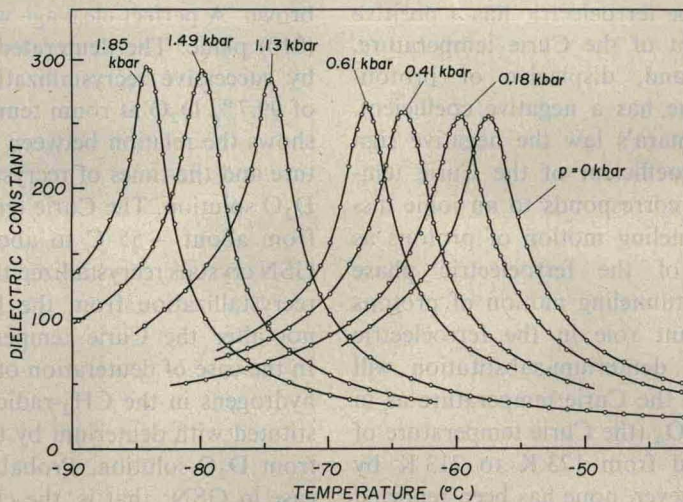
Although the crystal is soft and easily deformable with small shear stresses (it is easily bent even by fingers), hydrostatic pressure up to 7 kbar does not affect the appearance of the specimen after several high pressure-experiments at room temperature. Also the relation between the dielectric constant and temperature was reproduciblly obtained in the temperature range above about $-90°C$. The pressure dependence of the Curie temperature T_c is shown in Fig. 3. The relation between T_c and p is not linear in the pressure range studied. If one approximates the relation to be a quadratic equation of

$$T_c = T_c^0 + Kp + \gamma p^2, \qquad (1)$$

one may obtain the parameters as $T_c^0 = -57.1 \pm 0.2°C$, $K = -17.1 \pm 0.5$ deg kbar^{-1}, and $\gamma = 1.3 \pm 0.3$ deg kbar^{-2}, respectively. The calculated pressure dependence of T_c by eq. (1) with the above parameters is represented by the solid curve in Fig. 3. In a certain temperature range above the Curie temperature the dielectric constant ε at a constant pressure obeys a Curie-Weiss law of

$$\varepsilon = \varepsilon_\infty + C/(T - T_0), \qquad (2)$$

where T_0, C, and ε_∞ are the Curie-Weiss temperature, the Curie constant, and the electronic dielectric constant, respectively. In Fig. 4, the pressure dependence of the Curie constant is shown. The Curie constant at 1 atm is estimated to be 860 ± 40 K. The value is

Fig. 2. Temperature dependence of the dielectric constant of GSN along the (010) direction at various pressures. Frequency: 1 kHz.
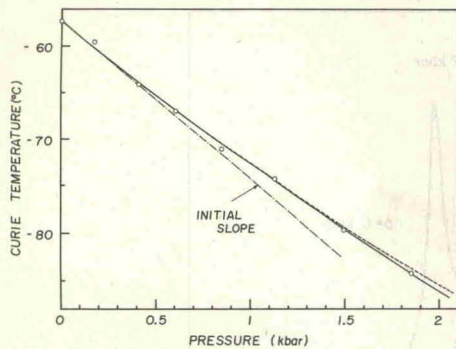
Fig. 3. Hydrostatic pressure dependence of the Curie temperature of GSN. The dott-and-slashed curve represents the initial slope. The slashed curve indicates the calculated curve from eq. (5).
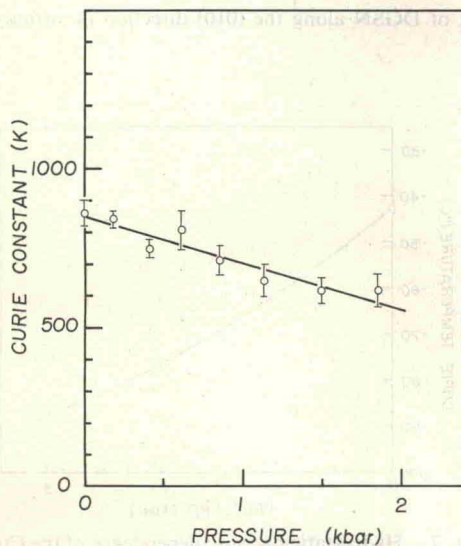

Fig. 4. Hydrostatic pressure dependence of the Curie constant of GSN.

considerably larger than $C=446$ K reported by Mitani,[5] but is comparable with $C=970$ K obtained by Nakamura et al.[8] from an analysis of the result by Pepinsky et al.[1] As seen in Fig. 4, the Curie constant is markedly pressure dependent. If one approximates the pressure variation of C by a linear function of $C=C_0(1+\beta p)$, one may get the parameter $\beta=-0.17\pm0.02$ kbar^{-1}. Here ambiguity in the determination of the Curie constant is brought about from several origins: First, in this work the pressure and temperature variation of the crystal dimension was not measured and then the correction of the dielectric constant from the elastic deformation and thermal expansion was not made. Second, the pressure was

slightly changed during temperature variation since the pressure system used was a constant-volume type ($\sim5\%$ of pressure change was typically seen during 50°C of temperature change). However, the correction for the Curie constant due to above origins is expected to be at most few per cent per 1 kbar, and it does not explain the large pressure variation of the Curie constant shown in Fig. 4.

In order to see whether or not there is an another phase of GSN under application of high pressure, we measured the pressure dependence of the dielectric constant at several temperatures above the Curie temperature. The result is shown in Fig. 5. The figure shows that there is no high pressure phase up to above 7 kbar and down to about −30°C. Also it is seen that there is a good reproducibility between the pressure-increasing and decreasing measurements. The pressure dependence of the dielectric constant at a constant temperature is not represented by a simple Curie-Weiss type
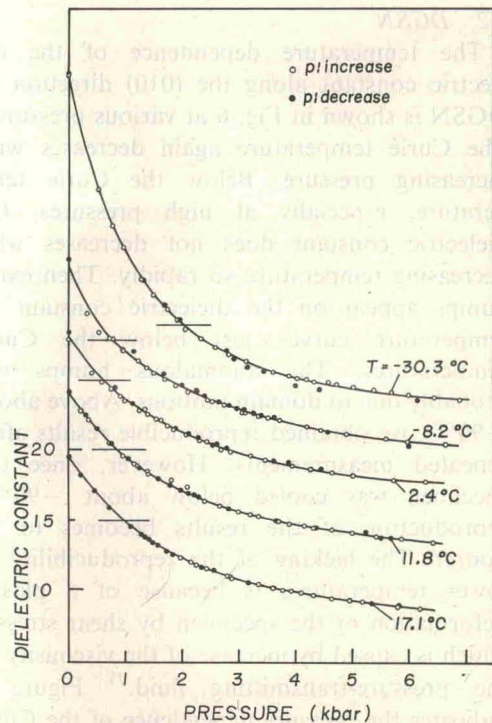

Fig. 5. Hydrostatic pressure dependence of the dielectric constant of GSN along the (010) direction at various temperatures in the paraelectric phase. Frequency: 1 kHz. The curves are shifted each other along the vertical direction in order to avoid confusion. The short horizontal bar attaching each curve shows the level of $\varepsilon=15$.
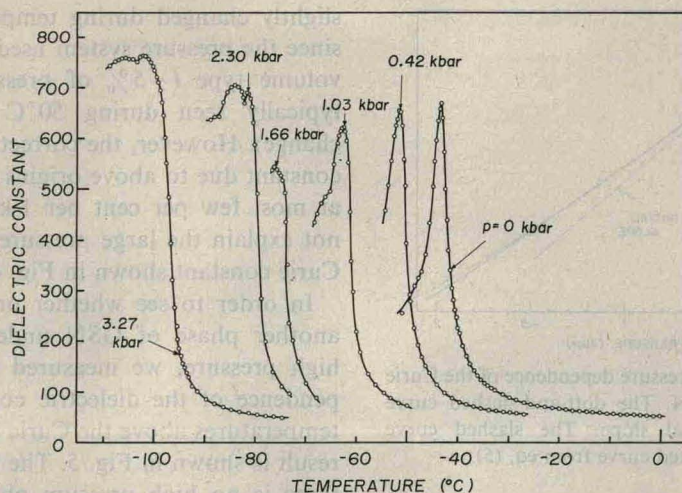
Fig. 6.   Temperature dependence of the dielectric constant of DGSN along the (010) direction at various pressures. Frequency: 1 kHz.

law of $\varepsilon = \varepsilon_\infty + C^*/(p-p_0)$ with a constant $C^{*4)}$ because of the pressure variation of the Curie constant C.

3.2   DGSN

The temperature dependence of the dielectric constant along the (010) direction of DGSN is shown in Fig. 6 at various pressures. The Curie temperature again decreases with increasing pressure. Below the Curie temperature, especially at high pressures, the dielectric constant does not decreases with decreasing temperature so rapidly. Then extra humps appear on the dielectric constant vs temperature curves just below the Curie temperatures. The anomalous humps are probably due to domain motions. Above about $-90\,°C$, we obtained reproducible results after repeated measurements. However, once the specimen was cooled below about $-90\,°C$, reproduction of the results becomes to be poorer. The lacking of the reproducibility at lower temperatures is because of a plastic deformation of the specimen by shear stresses which is caused by increase of the viscosity of the pressure-transmitting fluid.[7] Figure 7 indicates the pressure dependence of the Curie temperature of DGSN. The relation between the Curie temperature and pressure is against not linear, and it is approximated by eq. (1) with $T_c^0 = -42.7 \pm 0.5\,°C$, $K = -20.2 \pm 0.6$ deg kbar^{-1}, and $\gamma = 1.7 \pm 0.2$ deg kbar^{-2} as indicated by the bold curve in Fig. 7. The pressure dependence
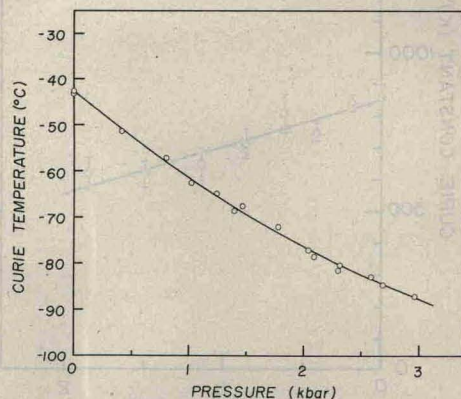

Fig. 7.   Hydrostatic pressure dependence of the Curie temperature of DGSN.
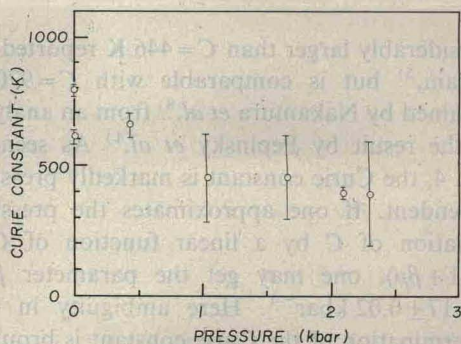

Fig. 8.   Hydrostatic pressure dependence of the Curie constant of DGSN.

of the Curie constant is shown in Fig. 8. The Curie constant of DGSN at 1 atm was about $C_0 = 700$ K although the measured values of the

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 law[4] 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.

Mitani[5] 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

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

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 overestimation 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" ferroelectrics[11] 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 Ca$_2$Sr(C$_2$H$_5$COO)$_6$, -3.7×10^{-9} cgs esu in Ca$_2$Pb(C$_2$H$_5$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

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

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 recognized on the unit cell volume vs temperature curve given by Mitani[5] 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

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

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

Putting the observed values of $T_c^0 = -57.1\,°$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.