

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 ($\text{NH}_2\text{CH}_2\text{COOH}\cdot\text{AgNO}_3$; 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 , $-17.1 \text{ deg kbar}^{-1}$, and $1.3 \text{ deg kbar}^{-2}$, respectively, for GSN; and -42.7°C , $-20.2 \text{ deg kbar}^{-1}$, and $1.7 \text{ deg kbar}^{-2}$, 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 $\text{NH}_2\text{CH}_2\text{COOH}\cdot\text{AgNO}_3$ (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 authors³⁾ 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, $[dT_c/dp]_{p=0} \sim -16 \text{ deg kbar}^{-1}$. Samara⁴⁾ 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 sulfate⁶⁾ 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 $\text{ND}_2\text{CH}_2\text{COOD}\cdot\text{AgNO}_3$.

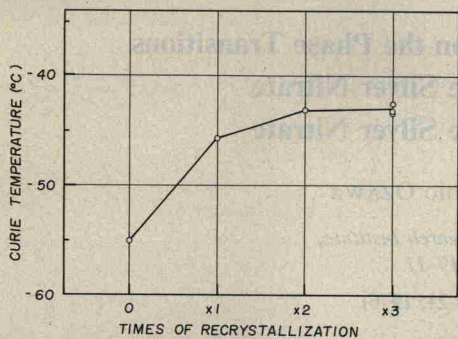


Fig. 1. Relation between the Curie temperature and the times of recrystallization from D_2O solution of glycine silver nitrate.

Silver paste was attached as electrodes on surfaces of (010) plates. The dimension of the specimens was $(0.6 \sim 1.1) \text{ mm} \times (0.03 \sim 0.1) \text{ cm}^2$. 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*-pentane. 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.

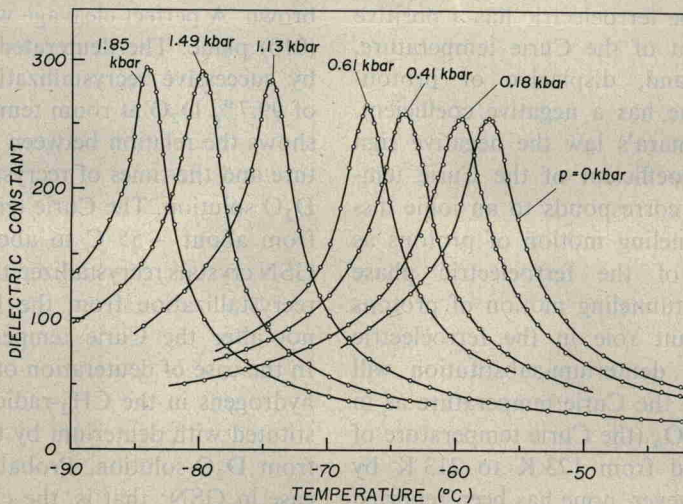


Fig. 2. Temperature dependence of the dielectric constant of GSN along the (010) direction at various pressures. Frequency: 1 kHz.

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 reproducibly 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

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

one may obtain the parameters as $T_c^0 = -57.1 \pm 0.2^\circ\text{C}$, $K = -17.1 \pm 0.5 \text{ deg kbar}^{-1}$, and $\gamma = 1.3 \pm 0.3 \text{ deg kbar}^{-2}$, 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

$$\epsilon = \epsilon_\infty + C/(T - T_0), \quad (2)$$

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 $860 \pm 40 \text{ K}$. The value is