Ferroelectricity in Glycine Silver Nitrate*

R. Pepinsky, Y. Okaya, D. P. Eastman, and T. Mitsui

X-Ray and Crystal Analysis Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania

(Received June 6, 1957)

Glycine silver nitrate, $NH_2CH_2COOH \cdot AgNO_3$, is ferroelectric below $-55°C$. At $-195°C$ the spontaneous polarization is 0.55×10^{-6} coulomb/cm^2, and the coercive field is 740 v/cm. The transition appears to be of second order. A differential thermal analysis does not reveal a specific heat anomaly. No dielectric anomalies appear between $4°K$ and $-55°C$. The spontaneous polarization here, as in triglycine sulfate and isomorphs, is attributed to disturbance of the planarity of the glycine ion by the crystalline field.

MATTHIAS et al.[1] discovered ferroelectricity in triglycine sulfate, $(NH_2CH_2COOH)_3 \cdot H_2SO_4$, and the isomorphous selenate, and Pepinsky et al.[2] prepared the corresponding fluoberyllate and found it to be ferroelectric as well. The structure of triglycine fluoberyllate has subsequently been determined, and it is found that in the high-temperature phase (space group $P2_1/m$) the glycines are disposed so that in each asymmetric unit of the cell there is one glycine in a mirror
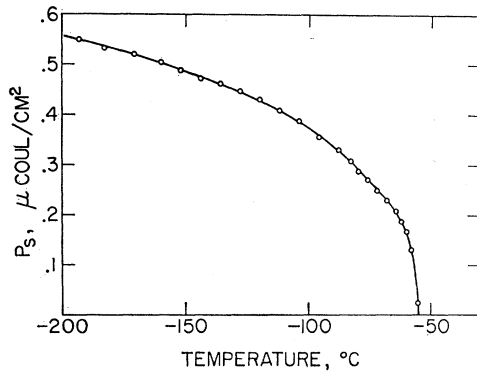

FIG. 1. Spontaneous polarization P_S of glycine silver nitrate, measured along b axis, as a function of temperature.

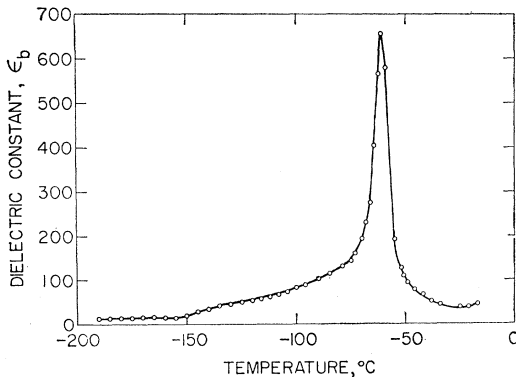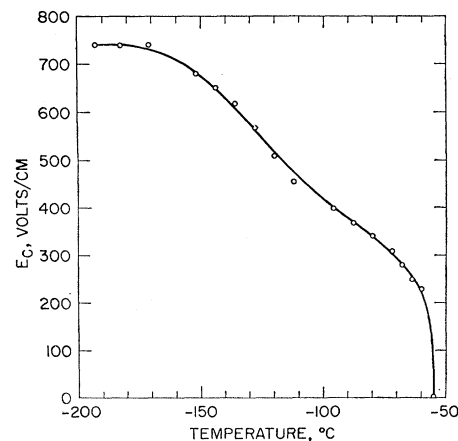FIG. 2. Dielectric constant ϵ_b of glycine silver nitrate, as a function of temperature.

[1] Matthias, Miller, and Remeika, Phys. Rev. **104**, 849 (1956).
[2] Pepinsky, Okaya, and Jona, Bull. Am. Phys. Soc. Ser. II, **2**, 220 (1957).

plane, two glycines mirrored across the plane, and an SO_4 group astride the mirror plane. The spontaneous polarization is a consequence of a slight departure from mirror symmetry, below the Curie point.

One would anticipate that a strictly coplanar arrangement of the C, N, and O atoms in glycine could readily be disturbed in a crystalline field, and as a consequence of the behavior of the triglycine sulfate series, it seemed worthwhile to prepare crystalline derivatives of various organic ions, the symmetries and dipolar characters of which might be altered by changes in crystalline fields, and to examine these dielectrically.

Glycine silver nitrate, $NH_2CH_2COOH \cdot AgNO_3$, crystallizes with monoclinic symmetry, space group $P2_1/a$, with cell constants $a=5.53$ A, $b=19.58$ A, $c=5.51$ A, $\beta=100°$. The density is 2.83 g/cm^3, and there are four molecules per cell. Cleavage is perfect perpendicular to the a axis, and good perpendicular to c. Large, water-clear plate-like crystals were obtained in the dark from a saturated aqueous solution of stoichiometric amounts of glycine and silver nitrate, by the slow introduction of ethyl alcohol vapor.

Dielectric examination of these crystals immediately revealed a ferroelectric transition at $-55°C$. The spontaneous polarization as a function of temperature, from room temperature to that of liquid nitrogen, is shown in

FIG. 3. Coercive field E_c of glycine silver nitrate along b axis, as a function of temperature.
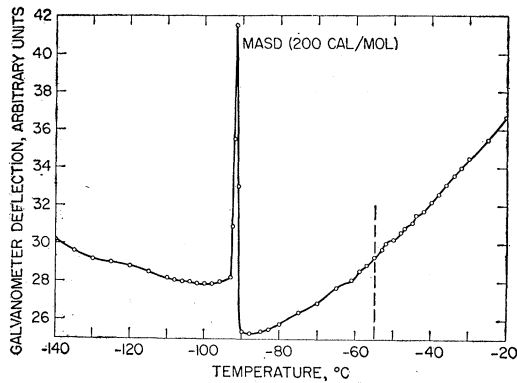
FIG. 4. Differential thermal analysis: glycine silver nitrate compared to methylammonium aluminum sulfate alum (MASD). Ordinate=galvanometer deflection, in arbitrary units. Vertical dashed line indicates temperature of dielectric anomaly of glycine silver nitrate.

field with temperature. The spontaneous polarization is 0.55×10^{-6} coulomb/cm^2 at 195°C. The behavior of the spontaneous polarization as a function of temperature suggests that the transition is of second order. The coercive field at -195°C is 740 v/cm, and this field drops as the Curie temperature is approached, in a manner suggestive of the behavior of triglycine sulfate.[3] No dielectric anomalies appear between -55°C and 4°K.

The result of a differential thermal analysis is shown in Fig. 4. Methylammonium aluminum sulfate alum is used as reference material. If a thermal anomaly exists in glycine silver nitrate, its magnitude is less than the experimental error.

An x-ray examination of the structure, both above and below the Curie point, is in progress.

Fig. 1; Fig. 2 shows the dielectric constant vs temperature curve; and Fig. 3 gives the variation of coercive

[3] Hoshino, Mitsui, Jona, and Pepinsky, Phys. Rev. (to be published).

Remarks on Zener's Classical Theory of the Temperature Dependence of Magnetic Anisotropy Energy

ROBERT BRENNER
Vacuumschmelze AG, Hanau, Germany
(Received May 24, 1957)

The temperature dependence of the first anisotropy constant for nickel is calculated by averaging the local anisotropy energy over a Langevin function. Reasonably good agreement with the experimental curve is obtained for $T/\theta>0.3$.

An estimate has been made of the variation of the local anisotropy constant with changes in volume.

ACCORDING to Zener's theory[1] the macroscopic anisotropy energy,

$$E_{\text{mag}}=K_1(\alpha_1{}^2\alpha_2{}^2+\alpha_2{}^2\alpha_3{}^2+\alpha_3{}^2\alpha_1{}^2)+\cdots,$$

of a cubic ferromagnetic crystal is the average of a local anisotropy,

$$e_{\text{mag}}=k_1(\alpha_1{}^2\alpha_2{}^2+\alpha_2{}^2\alpha_3{}^2+\alpha_3{}^2\alpha_1{}^2)+\cdots,$$

which for any particular magnetic spin moment results from the interaction with the orbital moments of its neighbors, the average taken over the whole distribution of spin orientations corresponding to a given temperature. Zener assumes k_1 to be constant $[k_1=K_1(0)]$ and uses for representation of spin deviations a random-walk function of the form

$$R(\theta)=\sum_{n=0}^{\infty} c_n\left(\frac{I_s(T)}{I_s(0)}\right)^{n(n+1)/2}P_n(\cos\theta),$$

[1] C. Zener, Phys. Rev. **96**, 1335 (1954).

which is a solution of the diffusion equation and is determined such as to give the correct average $\langle\cos\theta\rangle$ $=I_s(T)/I_s(0)$. Thus Zener obtains

$$K_1(T)=K_1(0)\{I_s(T)/I_s(0)\}^{10},$$

a result which fits excellently to the experimental curve for iron, but fails completely in the case of nickel where one finds approximately $K_1(T)=K_1(0)\{I_s(T)/I_s(0)\}^{21}$.
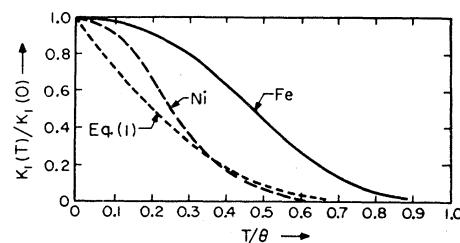

FIG. 1. Temperature dependence of anisotropy energy in Fe and Ni (experimental) and theoretical curve for Boltzmann-distributed spins [Eq. (1)].