

Ferroelectricity in Di-Glycine Nitrate $(\text{NH}_2\text{CH}_2\text{COOH})_2 \cdot \text{HNO}_3$

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$(\text{Glycine})_2 \cdot \text{HNO}_3$ is ferroelectric below -67°C . The room-temperature phase is monoclinic, space group $P2_1/a$, with $a=9.49_6$ Å, $b=5.10_7$ Å, $c=9.35_0$ Å, $\beta=98.8^\circ$, $\rho_{\text{obs}}=1.581_0$ g/cc, and $Z=2$. The nitrate groups must be disordered or rotating in this phase, since they are at centers of symmetry. The symmetry of the ferroelectric phase is Pa , as established from systematic absences and the fact that spontaneous polarization appears along the room-temperature $[101]$ direction below -67°C . The dielectric constant $\epsilon_{[101]}$, at 10 kc/sec and 5 v/cm, is 14 at room temperature, rises to a sharp peak of ~ 600 at -67°C , and falls to ~ 12 at -180°C . The transition appears to be of second order. At -77°C the spontaneous polarization is 0.60 $\mu\text{coul}/\text{cm}^2$, and the coercive field is 400 volts/cm. A specific heat anomaly similar to that in $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$ and $(\text{glycine})_3 \cdot \text{H}_2\text{BeF}_4$ is observed, with $\Delta E=0.15$ kcal/mole and $\Delta S=0.74$ cal/mole deg.

I. INTRODUCTION

FOLLOWING the discovery by Matthias, Miller, and Remeika¹ of ferroelectricity in $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$ and the corresponding selenate, and later observation that $(\text{glycine})_3 \cdot \text{H}_2\text{BeF}_4$ is ferroelectric,² Pepinsky and co-workers found ferroelectric behavior in $(\text{glycine}) \cdot \text{AgNO}_3$ and related mixed crystals³ and in $(\text{glycine})_2 \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$.⁴ We have recently observed that $(\text{glycine})_2 \cdot \text{HNO}_3$ becomes ferroelectric below -67°C . The present paper discusses some crystallographic and physical properties of the latter compound.

The fact that four crystallographically quite different glycine salts and intermolecular complexes show ferroelectric behavior confirms the importance for this phenomenon of the configuration of the glycine molecule, and the ease of disturbance of its conformation in a crystalline field.

II. CRYSTALLOGRAPHY OF $(\text{GLYCINE})_2 \cdot \text{HNO}_3$

$(\text{Glycine})_2 \cdot \text{HNO}_3$ crystallizes readily from stoichiometric quantities of the components in aqueous solu-

tion. The room-temperature density, measured by the flotation method, is 1.581_0 g/cc. X-ray measurements (Weissenberg camera, $\text{Cu } K\alpha$ radiation) show room-temperature cell constants $a=9.49_6$ Å, $b=5.10_7$ Å, $c=9.35_0$ Å, $\beta=98.8^\circ$, and space group $P2_1/a$. The molecular weight calculated from these constants is 213.6; this is to be compared to the weight computed from the formula, 213.2. There are two formula units in this centric monoclinic cell; and this requires that the N atoms of the nitrate groups are on centers of symmetry. This indicates statistical disorder of the NO_3 groups, or their rotation, at room temperature.

Ferroelectricity is observed below -67°C , with the monoclinic $[101]$ direction becoming the axis of spontaneous polarization. Therefore the twofold screw axis disappears below the Curie point, and the low-temperature symmetry must be either Pa or $P1$. X-ray observations at -170°C confirm the dielectric observation that the twofold axis disappears below the transition point, and unequivocally establish that the space group of the low-temperature phase is Pa . The type of symmetry change observed here is similar to that found in the ferroelectric transition in ammonium chloroacetate,⁵

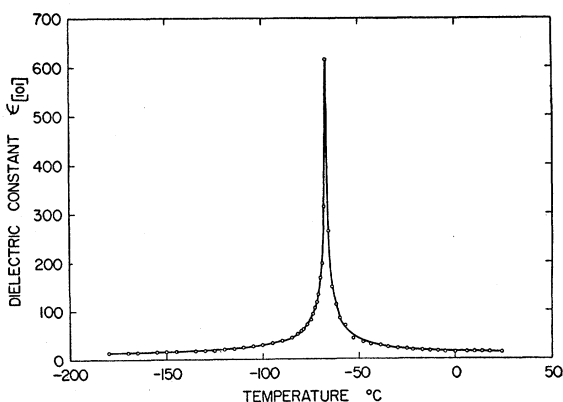


FIG. 1. $(\text{Glycine})_2 \cdot \text{HNO}_3$: dielectric constant measured along $[101]$, as a function of temperature.

¹ Matthias, Miller, and Remeika, Phys. Rev. **104**, 849 (1956).

² Pepinsky, Okaya, and Jona, Bull. Am. Phys. Soc. Ser. II, **2**, 220 (1957).

³ Pepinsky, Okaya, Eastman, and Mitsui, Phys. Rev. **107**, 1538 (1957).

⁴ Pepinsky, Vedam, and Okaya, Phys. Rev. **110**, 1309 (1958).

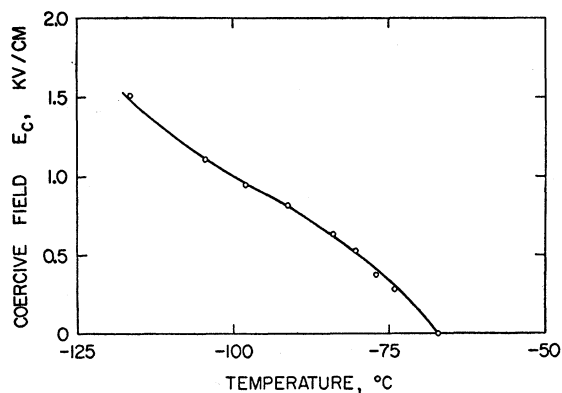


FIG. 2. $(\text{Glycine})_2 \cdot \text{HNO}_3$: coercive field E_c along $[101]$, as a function of temperature.

⁵ Pepinsky, Okaya, and Mitsui, Acta Cryst. **10**, 600 (1957).

where the direction of spontaneous polarization is along the paraelectric monoclinic [101] direction.⁴

III. DIELECTRIC BEHAVIOR

Although it was anticipated that spontaneous polarization, if it appeared at all, would occur along the paraelectric monoclinic axis, a dielectric anomaly was not observed in this direction. $\epsilon_{[010]}$ is about 9 at room temperature, and is fairly constant down to liquid nitrogen temperature. $\epsilon_{[101]}$ has a value of about 14 at room temperature, for a frequency of 10 kc/sec and a field of 5 v/cm; it climbs sharply to a peak value of about 600 at -67°C , as shown in Fig. 1, and then falls rapidly as the temperature is lowered, until it has a value of 12 at -180°C . $\epsilon_{[10\bar{1}]}$ has a value of 20 at room temperature, and decreases gradually to 16 at -180°C .

The value of the coercive field $E_c[101]$ shown in Fig. 2; and the spontaneous polarization $P_s[101]$ is

TABLE I. Values of T_c (in $^\circ\text{C}$), P_s (in $\mu\text{coul}/\text{cm}^2$) and E_c (in v/cm) for ferroelectrics of the monocarboxylic acid class. P_s and E_c values given for temperatures $\sim 10^\circ$ below Curie points, except as noted.

	T_c ($^\circ\text{C}$)	P_s	E_c
(Glycine) ₃ ·H ₂ SO ₄ ^a	47	2.2	220 ^b
(Glycine) ₃ ·H ₂ SeO ₄ ^a	22	3.2 ^a	780 ^a
(Glycine) ₃ ·H ₂ BeF ₄ ^b	79	2.2	5000 ^b
(Glycine)·AgNO ₃ ^c	-55	0.21	275
(Glycine)·(Ag _{0.82} , Tl _{0.18})NO ₃ ^c	-38	0.17	700
(Glycine)·(Ag _{0.82} , Li _{0.18})NO ₃ ^c	-38	0.20	1000
(Glycine) ₂ ·MnCl ₂ ·2H ₂ O ^d	...	1.3 ^b	5600 ^b
(Glycine) ₂ ·HNO ₃	-67	0.60	400
ClCH ₂ COONH ₄ ^e	-150	0.12	400
Ca ₂ Sr(C ₂ H ₃ COO) ₆ ^f	8	0.12	3200

- ^a See reference 1.
^b See reference 2.
^c See reference 3.
^d See reference 4.
^e See reference 5.
^f See reference 7.
^g Measured by the present authors.
^h At room temperature.

shown in Fig. 3. At -77°C these quantities are: $P_s = 0.60 \mu\text{coul}/\text{cm}^2$, $E_c = 400 \text{ v/cm}$.

The behavior of the P vs E curve just below the transition temperature suggests that the transition is of second order.

IV. THERMAL MEASUREMENTS

A specific heat measurement was carried out in our adiabatic calorimeter, in the temperature range between -92°C and -54°C . A powdered sample, 10 grams in weight, was enclosed in a vessel of thin paper. The heat input was $\sim 0.003 \text{ cal/g}$. The curve of C_p vs temperature is shown in Fig. 4. An anomaly appears in the range between -80°C and -65°C . The shape of the curve is quite similar to that of tri-glycine sulfate and tri-glycine fluoberyllate,⁶ and supports the di-

⁶ Hoshino, Mitsui, Jona, and Pepinsky, Phys. Rev. **107**, 1255 (1957).

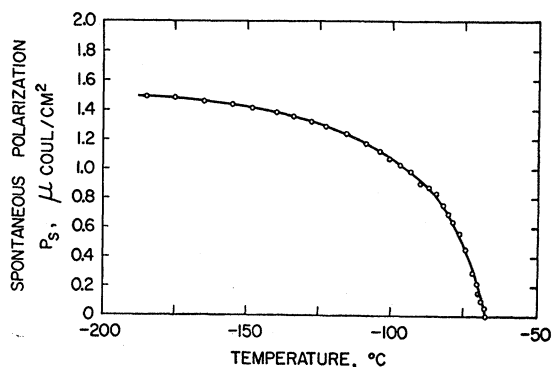


Fig. 3. (Glycine)₂·HNO₃: spontaneous polarization P_s measured along [101], as a function of temperature.

electric indication that the transition is of second order. The heat of transition ΔE is estimated to be 0.15 kcal/mole, and the entropy change ΔS is 0.74 cal/mole deg.

V. COMPARISON WITH OTHER FERROELECTRIC GLYCINE COMPOUNDS

It is evident that the conformation of the glycine molecule (or ion), and the possibility of its alteration in a crystalline field, is the prime element in the four crystallographically-dissimilar types of glycine compounds which show ferroelectric behavior.⁴ As pointed out earlier,⁴ glycine is itself a representative of the larger class of acetates or substituted acetates which are ferroelectric, the compounds ammonium chloroacetate⁵ and Ca₂Sr(propionate)₆,⁷ being additional members of the general family. It can be anticipated that many more ferroelectrics of the acetate (or substituted acetate) class will be found. These monocarboxylic acid derivatives should also be considered in connection with the ferroelectric tartrates, which are of course dihydroxy-substituted di-carboxylic (succinic) acid salts.⁸

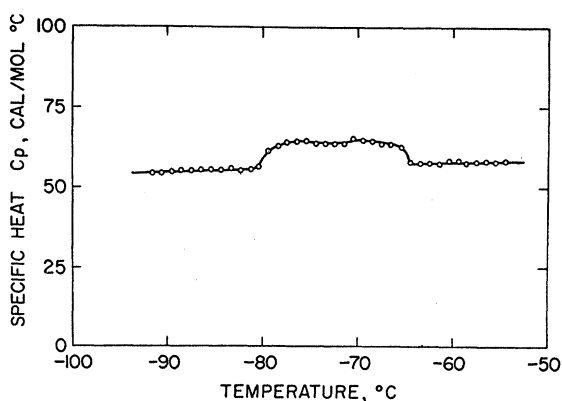


Fig. 4. (Glycine)₂·HNO₃: specific heat vs temperature.

⁷ B. T. Matthias and J. P. Remeika, Phys. Rev. **107**, 1727 (1957).

⁸ See Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. **43**, 1738 (1955).

Table I gives a comparison of the values of spontaneous polarization P_s and coercive field E_c of this family of ferroelectrics. Except for the case of (glycine)₂·MnCl₂·2H₂O, all of the values of P_s and E_c are taken at temperatures about 10° below the respective Curie points. No Curie temperature is observable for (glycine)₂·MnCl₂·2H₂O and the P_s and E_c values for it are those at room temperature.⁴

VI. ACKNOWLEDGMENTS

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Radiation Damage in Ge and Si Detected by Carrier Lifetime Changes: Damage Thresholds*

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Minority carrier lifetime, τ , in semiconductors is shown to be more sensitive, by a factor of 10⁴, to radiation-induced defects than the conductivity. Thus, in some cases, the introduction of as few as 10¹⁰ defects per cm³ can be detected by its effect on τ . Both direct measurements of τ , and measurements of dependent parameters (such as the photovoltaic effect and the particle voltaic effect) are described for Si and Ge. Using such parameters, and an electron accelerator, the minimum energy needed to produce a Frenkel defect was found to be 14.5±0.4 eV in Ge and 12.9±0.6 eV in Si. An analysis of the phenomenon shows how the location of the radiation-induced energy levels and the relative minority carrier capture cross sections can be determined experimentally. The shape of the curve of the displacement cross section *versus* the incident particle energy is compared to calculations from collision theory. Qualitative explanations for the observed "tail" on this curve are presented. Calculations based on these explanations fail to yield complete agreement with the experimental curves.

LIST OF IMPORTANT SYMBOLS

- σ ≡ conductivity of semiconductor.
 τ ≡ minority carrier bulk lifetime.
 N_r ≡ density of recombination centers.
 σ_c ≡ cross section for minority carrier capture.
 v ≡ thermal velocity of carriers.
 $\Delta(E_B)$ ≡ cross section for Frenkel defect formation.
 ρ ≡ resistivity of semiconductor.
 N_B ≡ number of bombarding particles per unit time.
 ϕ ≡ integrated bombarding flux.
 t ≡ time of bombardment.
 I_B ≡ current of bombarding particles.
 E_B ≡ energy of bombarding particle.
 E_{B0} ≡ minimum energy of impinging particles for producing defects.
 E_L ≡ energy imparted to a lattice atom in a collision.
 E_i ≡ energy level of recombination center.
 E_f ≡ energy of Fermi level.
 I_s ≡ photovoltaic short circuit current.
 e ≡ electron charge.
 L ≡ diffusion length of minority carriers.

- g ≡ electron-hole pair generation rate.
 D ≡ diffusion constant for minority carriers.
 Q ≡ fraction of generated carriers collected by a junction.
 α ≡ absorption constant for light.
 s ≡ surface recombination velocity.
 l ≡ semiconductor thickness.

I. INTRODUCTION

THE simplest consequence of a collision between a particle of high kinetic energy and an atom in a solid is the displacement of the struck atom to an interstitial position. By definition, the resulting vacancy-interstitial pair constitutes a Frenkel defect. Such defects can be introduced into the lattice only if the energy transferred to the crystal atom by the impinging particle is equal to, or exceeds, a threshold energy, which is identified with the energy that constrains the atom to remain in its equilibrium position. The magnitude of this threshold energy is of fundamental importance to an understanding of the mechanism of radiation damage and of crystal forces. Of the parameters available for measurement in previous experiments, the electrical conductivity, σ , seemed to be most sensitive to the presence of Frenkel defects. Consequently,

* Preliminary reports of this work have been given in earlier brief communications; *viz.*, P. Rappaport, Phys. Rev. **94**, 1409(A) (1954); J. J. Loferski and P. Rappaport, Phys. Rev. **98**, 1861 (1955); and P. Rappaport and J. J. Loferski, Phys. Rev. **100**, 1261(A) (1955).