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Dielectric and Thermal Study of Tri-Glycine Sulfate and Tri-Glycine Fluoberyllate*

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The dielectric constants ϵ_b of tri-glycine sulfate and tri-glycine fluoberyllate show a pronounced anomaly at the Curie temperature of 48°C and 70°C, respectively. The dielectric constants ϵ_a and ϵ_c are practically temperature-independent. In the vicinity of the Curie point, the square of the spontaneous polarization increases linearly with decreasing temperature. The transition of both salts is of the second order. Measurements of the specific heat as a function of temperature yield $\Delta S=0.48$ cal/mole degree for tri-glycine sulfate, and $\Delta S=1.17$ cal/mole degree for tri-glycine fluoberyllate. The results are discussed on the basis of Mueller's thermodynamic theory for ferroelectric transitions.

I. INTRODUCTION

FERROELECTRIC behavior has recently been discovered in a good number of sulfates, selenates, and fluoberyllates. The discovery of ferroelectricity in guanidinium aluminum sulfate hexahydrate, $C(NH_2)_3\cdot Al(SO_4)_2\cdot 6H_2O$, by Holden *et al.*,[1] the subsequent discovery of ferroelectric behavior in a good number of organic amine and ammonium alums, by Pepinsky *et al.*,[2,3] in ammonium sulfate, $(NH_4)_2SO_4$, by Matthias and Remeika[4] and in the isomorphous ammonium fluoberyllate, $(NH_4)_2BeF_4$, by Pepinsky and Jona,[5] and in di-ammonium di-cadmium sulfate, $(NH_4)_2Cd_2(SO_4)_3$, by Jona and Pepinsky,[6] emphasized the significance of the role played by $N-H\cdots O$ bonds and the sulfate or related ions in the occurrence of ferroelectricity in these types of compounds.

The most recent and, from the point of view of possible practical applications, the most important discovery is that of ferroelectricity in tri-glycine sulfate, $(CH_2NH_2COOH)_3\cdot H_2SO_4$, and tri-glycine selenate by Matthias *et al.*,[7] and in the isomorphous tri-glycine fluoberyllate, $(CH_2NH_2COOH)_3\cdot H_2BeF_4$, by Pepinsky *et al.*[8]

It is found that the substitition of $(BeF_4)^{-2}$ for $(SO_4)^{-2}$ in these tri-glycine salts raises the Curie point from 47°C in the sulfate (and 22°C in the selenate) to 70°C in the fluoberyllate. The values of the spontaneous polarization are of the same order of magnitude, since at room temperature the moment is 2.2×10^{-6} coulomb/cm^2 in the sulfate and 3.2×10^{-6} coulomb/cm^2 in the fluoberyllate. The reported values of the coercive field are about 2.5 times smaller for the sulfate (220 v/cm) than for the fluoberyllate (5 kv/cm). The latter comparison is actually unfair, since the values reported in the literature were measured for both salts at room temperature, which is only 24 degrees below the Curie point of the sulfate, but as much as 52 degrees below the Curie point of the fluoberyllate. It is interesting to note that in the case of the ammonium salts the replacement of the $(SO_4)^{-2}$ group by $(BeF_4)^{-2}$ has opposite consequences. The only conclusion possible at this stage for these experimental facts is that the transition mechanisms of the tri-glycine salts and the ammonium salts are not closely related.

Crystallographic and structural data are already available for all the ferroelectric tri-glycine salts.[8,9] The crystals are monoclinic both below and above the Curie temperature, with space groups $P2_1$ and $P2_1/m$, respectively.

The structure of the nonpolar phase has been recently elucidated by Okaya, Hoshino, and Pepinsky,[10] and reveals one glycine lying on the mirror plane, together with the inorganic anion, while the other two glycines are mirrored across the plane. The structure is maintained by hydrogen bonds. The mechanism of the onset of spontaneous polarization at the Curie point appears to be related to that hypothesized by Matthias *et al.*[7]: hydrogens of the glycine in the mirror plane twist out

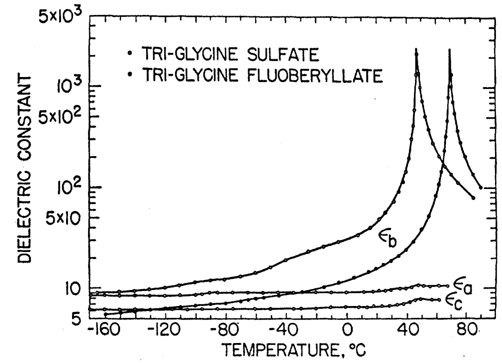

FIG. 1. Dielectric constants of tri-glycine sulfate and tri-glycine fluoberyllate, as functions of temperature.

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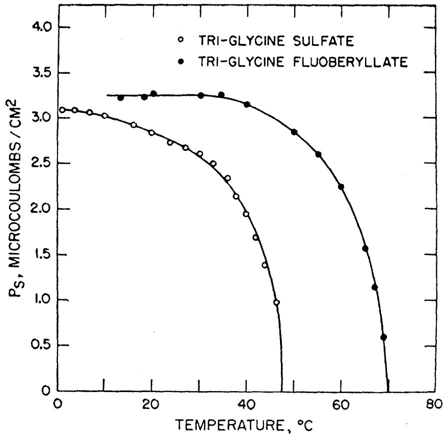

FIG. 2. Spontaneous polarization, P_S, of tri-glycine sulfate and tri-glycine fluoberyllate as a function of temperature.

of the plane, and this ion develops polarization along the monoclinic axis, therewith inducing a moment in the anion and the other glycines.

The case of the tri-glycine ferroelectrics seems to be the first, in the field of ferroelectricity, where a structural mechanism of the transition was given before phenomenological data were collected and a thermodynamical theory established. The purpose of the present investigation is the collection of dielectric and thermal data which allow the thermodynamical characterization of these ferroelectric transitions as phase changes of the second order, and the determination of the energy involved at the transition.

II. DIELECTRIC PROPERTIES: MEASUREMENTS AND DISCUSSION

The small-field dielectric constants, $\epsilon_b=\epsilon$, of a *b*-cut specimen of tri-glycine sulfate and tri-glycine fluoberyllate exhibit a pronounced anomaly at the Curie point of 48°C and 70°C, respectively. The temperature behavior of ϵ, measured with 1 v/cm at 10 kc/sec, is depicted in Fig. 1 for both tri-glycine salts.

Above the Curie point, ϵ satisfies the well-known Curie-Weiss law: $\epsilon=C/(T-T_c)$, where C is the Curie constant, T the temperature and T_c the extrapolated Curie temperature. C equals 3280° for tri-glycine sulfate and 2340° for tri-glycine fluoberyllate. Within the experimental error, T_c is only of the order of 0.5° smaller than the Curie temperature, for both salts.

Below the Curie point, the reciprocal of the dielectric constant is also a linear function of temperature within a range of about 20° for both tri-glycine sulfate and fluoberyllate.

The small-field dielectric constants measured along the crystallographic *a* and *c* axes, ϵ_a and ϵ_c, respectively, are an order of magnitude smaller than ϵ_b. Their temperature dependence is also included in Fig. 1 for tri-glycine sulfate, and is strictly similar to that of tri-glycine fluoberyllate. The small bumps in the curves of ϵ_a and ϵ_c *versus* temperature at the Curie point seem to be due to very small misorientation of the crystal plates measured.

Ferroelectric hysteresis loops are observed in *b*-cut specimens of both tri-glycine salts below their respective Curie points. The temperature dependence of the spontaneous polarization is represented in Fig. 2.

This graph shows that the spontaneous polarization is a continuous function of temperature. Just above the Curie point, the *P-E* curve, observed on an oscilloscope, appears to be curved downward, while at higher temperatures the *P-E* relationship is strictly linear. These observations, added to the fact that the peak value of ϵ at the Curie point is very large, indicate that the ferroelectric transition of the tri-glycine salts considered here is of the second order.

It has been shown by Mueller[11] that the characteristics of a second-order ferroelectric transition can be described with sufficient approximation upon assuming the following expression for the elastic Gibbs function G of the free crystal:

$$G=\tfrac{1}{2}\chi_0P^2+\tfrac{1}{4}\xi P^4, \tag{1}$$

where P is the polarization, which in our case is assumed to be directed along the crystallographic *b* axis, and χ_0 and ξ are characteristic constants of the crystal.

It is easily seen that χ_0 represents the reciprocal dielectric susceptibility of the *unpolarized* crystal.

Considering the well-known thermodynamic relations $E=\partial G/\partial P$ and $\chi=\partial^2G/\partial P^2$, we obtain from (1):

$$P_s^2=-\chi_0/\xi, \tag{2}$$

and

$$\chi=-2\chi_0, \tag{3}$$

where χ represents the reciprocal dielectric susceptibility of a single-domain crystal in the ferroelectric phase. If the dielectric constant of the free crystal is very large, as in the case of the tri-glycine salts considered here, we can assume $\epsilon\cong 4\pi/\chi$, and thus write Eq. (3) in the form

$$\epsilon=-\epsilon_0/2. \tag{4}$$

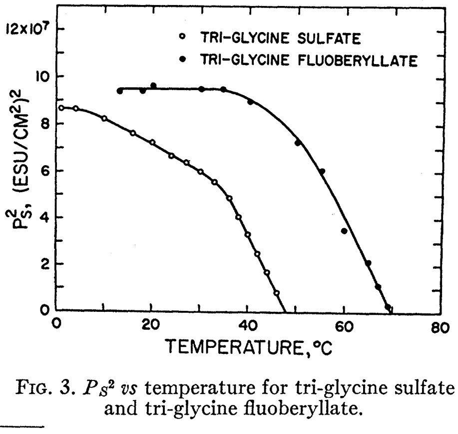

FIG. 3. P_S^2 *vs* temperature for tri-glycine sulfate and tri-glycine fluoberyllate.

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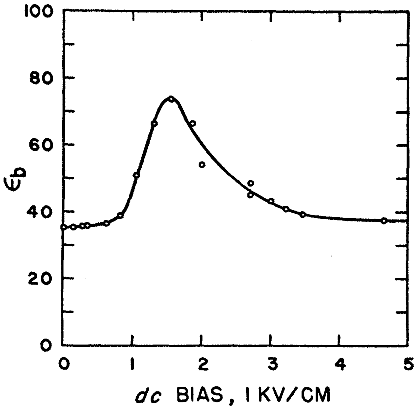

FIG. 4. Effect of dc bias on dielectric constant ϵ_b of tri-glycine sulfate at room temperature (ac field = 1 v/cm).

If we assume that χ_0 depends linearly on temperature also below the Curie point, Eq. (4) requires that $1/\epsilon$ is a linear function of T and that the downward slope is just twice as steep as the upward slope above the Curie point. Moreover, if we assume in addition that ξ is independent of temperature, Eq. (2) implies that P_s^2 is a linear function of temperature in the vicinity of the Curie point.

The latter linear dependence (of P_s^2) is found to be followed by the experimental data for both the tri-glycine salts considered here, as can be seen from Fig. 3. The former linear relation (for $1/\epsilon$), on the other hand, is found to be fulfilled satisfactorily only by tri-glycine fluoberyllate: the value of the Curie constant is 2340°, while the corresponding constant determined from the curve $1/\epsilon$ *versus* T, below the Curie point, is $-1110°$. The ratio between the slopes above and below the Curie temperature is therefore -2.11, which is in accordance, within the experimental accuracy, with the prediction of Eq. (4). The agreement is not so good in the case of tri-glycine sulfate: the following values of the Curie constant were determined from three different specimens, $C = 3270°$, 3150°, 3420°. Below the Curie point, the corresponding constant has, for the same three samples, the values $-830°$, $-1130°$, $-1260°$, respectively. The ratios between the three pairs of values are then -3.9, -2.8, and -2.7, respectively, which are definitely far from the expected value -2.

The explanation for this disagreement must be sought in the effect of domain clamping, as proved by Drougard and Young in the case of barium titanate.[12] The values of ϵ measured below the Curie temperature are domain-structure sensitive and turn out to be smaller than the dielectric constant of the free crystal.

The existence of a domain-clamping effect in these tri-glycine salts, similar to that observed in barium titanate crystals, can easily be proved by a study of the spontaneous strains which are associated with a spontaneous polarization P_s along the crystallographic b axis. Since the space group of the nonpolar phase of the tri-glycine salts is $P2_1/m$, it can be shown that these strains are, in the Voigt notation,[13] x_x, y_y, z_z, and x_z. They are proportional to the square of the spontaneous polarization, P_s^2. Hence the situation is practically the same as in barium titanate, and an effect due to domain clamping should be expected.

This expectation is confirmed by a study of the field dependence of ϵ, as represented in Fig. 4. The effect of a dc bias on the dielectric constant is found to be very similar to that found in barium titanate by Drougard and Young,[12] and seems to prove that the too-small values of ϵ measured in the ferroelectric phase of tri-glycine sulfate are to be ascribed to domain clamping effects.

Finally, Eq. (2) allows us to use the experimental results for the determination of the coefficient ξ of the expansion of the Gibbs function (1). The values obtained are $\xi = 0.93 \times 10^{-9}$ (esu/cm^2)$^{-2}$ for tri-glycine sulfate, and $\xi = 1.35 \times 10^{-9}$ (esu/cm^2)$^{-2}$ for tri-glycine fluoberyllate. The former is in excellent agreement with the value recently reported by Triebwasser.[14]

III. THERMAL PROPERTIES: MEASUREMENTS AND DISCUSSION

In order to study the thermal properties of tri-glycine sulfate and fluoberyllate through their transition points, a measurement of the specific heat of both compounds was undertaken in the temperature range from about 0°C to 80°C. The measurements were done with an adiabatic calorimeter of the modified Sykes type.[15] Larger crystals of both salts were ground to fine powder specimens of about 5 g and introduced into a thin paper vessel. The heat input to the specimen was about 0.002 cal/g sec, the heating rate approximately 0.5 degree/min.

Figure 5(a) and Fig. 6(a) show the results of the specific heat measurements on tri-glycine sulfate and tri-glycine fluoberyllate, respectively. The shape of the

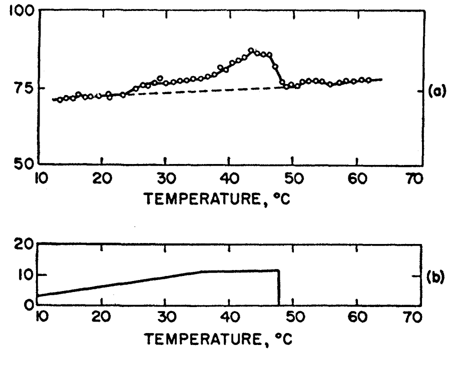

FIG. 5. Specific heat *vs* temperature curve of tri-glycine sulfate. (a) Experimental; (b) theoretical.

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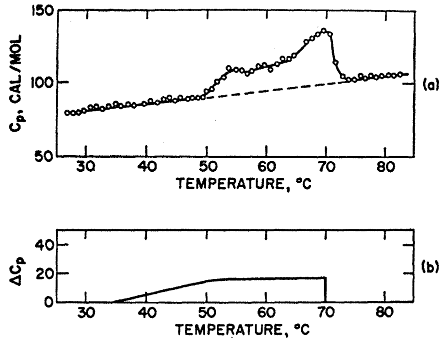

FIG. 6. Specific heat *vs* temperature curve of tri-glycine fluoberyllate. (a) Experimental; (b) theoretical.

experimental curves is the same for both salts and is typical for a transition of the second order. It should be noted that this is the first time, at least in the field of ferroelectrics, that the specific-heat anomaly of such a typical second-order transition is observed which is *not* of the usual λ type.

The integration of the experimental curves allows the determination of the heat of transition and the corresponding entropy change. The base lines were drawn as shown by the dotted lines in Figs. 5(a) and 6(a). In the case of tri-glycine sulfate the range of integration was taken from 20 to 50°C. For tri-glycine fluoberyllate the integration was performed within the temperature range from 40 to 75°C.

The corresponding values for the transition energy ΔQ and the entropy change ΔS are

tri-glycine sulfate:

$$\Delta Q = 0.15 \text{ kcal/mole},$$

$$\Delta S = 0.48 \text{ cal/mole degree}.$$

tri-glycine fluoberyllate:

$$\Delta Q = 0.40 \text{ kcal/mole},$$

$$\Delta S = 1.17 \text{ cal/mole degree}.$$

These experimental results can be compared with those expected theoretically on the basis of the free-energy expansion (1). Since the entropy S is equal to $-(\partial G/\partial T)_P$, if we assume again that the coefficient ξ of the expression (1) is independent of temperature, we obtain for the entropy change:

$$\Delta S = S_0 - S = \tfrac{1}{2}(\partial \chi_0/\partial T)P^2, \tag{5}$$

where S and S_0 represent the entropies of the polarized and unpolarized states, respectively, and P^2 the square of the spontaneous polarization.

The expression on the right-hand side of Eq. (5) contains quantities which are known from the study of the dielectric behavior of the crystal under consideration. Using the experimental data (see Sec. II), we obtain:

tri-glycine sulfate: $\Delta S = 0.64$ cal/mole degree,

tri-glycine fluoberyllate: $\Delta S = 1.11$ cal/mole degree.

The agreement with the experimental results of the thermal measurements is quite good for tri-glycine fluoberyllate, but only fair for tri-glycine sulfate. The reason for the latter is to be sought in the error involved in drawing the base line in Fig. 5(a) because of the fairly small transition energy of this crystal.

From Eq. (5) we can further compute the excess specific heat:

$$\Delta c_P = c_P - c_{P_0} = -\tfrac{1}{2}T\frac{\partial(P^2)}{\partial T}\frac{\partial \chi_0}{\partial T}, \tag{6}$$

where c_P and c_{P_0} represent the specific heats of the polarized and unpolarized states, respectively.

The quantities on the right-hand side of Eq. (6) are known from the dielectric study, so that the expected temperature dependence of Δc_p can be computed. The results of these calculations are represented graphically in Figs. 5(b) and 6(b) for tri-glycine sulfate and fluoberyllate, respectively.

The agreement between the experimental and theoretical curves is not as satisfactory as one would expect. This is rather surprising, because the evaluation of Δc_p from (6) was made on the same assumptions which were made for the explanation of the linear temperature dependence of P^2 from Eq. (2). These assumptions were that χ_0 is a linear function of T below the Curie point and that ξ is independent of T.

In this respect, it should be pointed out that a similar contradiction occurs, much more drastically, in the discussion of the lower Curie point of Rochelle salt. As was shown by Takahashi,[16] the theory of Mueller[11] predicts that the specific-heat anomaly be positive at the lower Curie temperature of Rochelle salt. The same anomaly, however, is expected to be negative on the basis of the Ehrenfest relation.[17]

It seems impossible to avoid these contradictions as long as we assume that the Gibbs function of the free crystal can be expressed in terms of polarization only, which can be looked upon as being a degree of long-range order. In order to obtain satisfactory results, short-range order effects should be taken into account, possibly along a path analogous to that followed by Bethe[18] for his theory of order-disorder transitions in alloys.

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