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Gap exponents determined from the pressure measurements of the nonlinear electric permittivity for triglycine sulfate in the paraelectric region

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From measurements of variations of the electric permittivity (ϵ) as a function of the electric field strength (E) at a constant temperature and various pressures near the critical point in the paraelectric region, values have been found for the power exponents $\gamma_0^* = \gamma^* = 1.0 \pm 0.05$, $\gamma_2^* = 4.1 \pm 0.2$, $\gamma_4^* = 7.2 \pm 0.4$, $\gamma_6^* = 10.3 \pm 0.6$ in the relations $\alpha_{2n} = A_{2n}^* [(p_c - p)/p_c]^{-\gamma_{2n}^*}$, where α_{2n} are the coefficients of the series $\epsilon \simeq \alpha_0 + \alpha_2 E^2 + \alpha_4 E^4 + \alpha_6 E^6 + \cdots$. The values of gap exponents $\Delta_4 = 1.55 \pm 0.05$, $\Delta_6 = 1.55 \pm 0.15$, $\Delta_8 = 1.5 \pm 0.2$ have been determined. It has also been confirmed that there is good agreement as to the order of the absolute values of the amplitude ratios $|A_2^* : A_0^*|$, $|A_4^* : A_2^*|$, and $|A_6^* : A_4^*|$.

The electric permittivity at a constant temperature is a function, among other things, of pressure, and of the strength of the electric field. For the paraelectric phase the relation between permittivity and the electric field may be expressed in the form of the following series:

$$\epsilon(p,E) = \alpha_0(p) + \alpha_2(p)E^2 + \alpha_4(p)E^4 + \alpha_6(p)E^6 + \cdots \quad . \qquad (1)$$

The coefficients α_{2n} are proportional to the corresponding derivatives of the Gibbs potential (for $\alpha_0 \gg 1$):

$$\alpha_{2n} \sim \left(\frac{\partial^{2n+2} G}{\partial E^{2n+2}} \right)_{E=0} . \qquad (2)$$

Taking into account the definition of gap exponents in the phase of higher symmetry (cf. Ref. 1), i.e.,

$$\left(\frac{\partial^{2l} G}{\partial E^{2l}} \right)_{E=0} \equiv G^{(2l)} \sim \tau^{-2\Delta_{2l}} G^{(2l-2)} , \qquad (3)$$

we find the relation between the coefficients α_{2n} and the gap exponents:

$$\alpha_{2n} \sim \tau^{-(\gamma + 2\sum_{i=1}^{n} \Delta_{2i+2})} = \tau^{-\gamma_{2n}} , \qquad (4)$$

where $\tau = (T - T_c)/T_c$. The exponents $\gamma_0 = \gamma$, γ_2, γ_4, Δ_4, and Δ_6 determined from temperature measurements are given in Refs. 2 and 3. Presented here are the results of measurements of the nonlinear properties of permittivity of a triglycine sulfate (TGS) crystal in the paraelectric phase as a function of pressure at a constant temperature. From these results it is possible to estimate the critical exponents analogous to those which are determined from temperature measurements. They may be defined as follows:

$$G^{(2l)} \equiv \left(\frac{\partial^{2l} G}{\partial E^{2l}} \right)_{E=0} \sim \pi^{-2\Delta_{2l}^*} G^{(2l-2)} , \qquad (5)$$

$$\alpha_{2n} \sim \pi^{-\gamma_{2n}^*} , \qquad (6)$$

$$\gamma_{2n}^* = \gamma^* + 2 \sum_{i=1}^{n} \Delta_{2i+2}^* , \qquad (7)$$

where $\pi = (p_c - p)/p_c$.

The method used here for measurement of nonlinearity of permittivity has been described in Ref. 3 (see also Ref. 4). In this method the capacitance C is measured for various values of constant voltage applied to the tested sample at determined values of temperature and pressure. Frequency of the measurement bridge was 1 kHz. The maximum voltage applied parallel to axis b of a sample of thickness about 1.3 mm cut from a TGS single crystal was 200 V. The hydrostatic pressure employed in the experiment varied from atmospheric pressure up to about 50×10^6 N/m^2. Temperature stability was of the order of 10^{-2} K, and accuracy of pressure measurement was $\pm 0.5 \times 10^6$ N/m^2. Immediately prior to measurements the sample was heated at a temperature of about 358 K for about 50 h.

Figure 1 shows the curves $C_{E=0}$, $-a$, b, $-c$ as functions of $(p_c - p)/p_c$ $(p_c = 48 \times 10^6$ N/m$^2)$ for $T \simeq T_c(p_{atm}) + 1.3$ K in a log-log scale, where $C_{E=0}$ is the capacitance of the capacitor with the sample in a zero electric field, and a, b, c are the coefficients in the expansion (for suitably weak voltages U):

$$C_{E \neq 0} = C_{E=0} + aU^2 + bU^4 + cU^6 . \qquad (8)$$

The value of p_c has been determined from the experimental dependence of T_c on pressure.[5]

From (1) and (8) we may calculate that $\alpha_0 = C_{E=0}/C_0$, $\alpha_2 = ak^2/C_0$, $\alpha_4 = bk^4/C_0$, and $\alpha_6 = ck^6/C_0$, where C_0 is the capacitor capacitance without the sample, and k is the characteristic constant of the capacitor ($U = kE$). The following values of exponents were found:

$$\gamma_0^* = \gamma^* = 1.0 \pm 0.05, \quad \gamma_2^* = 4.1 \pm 0.2 , \quad \gamma_4^* = 7.2 \pm 0.4, \quad \gamma_6^* = 10.3 \pm 0.6 . \qquad (9)$$

Values of the gap exponents determined from the experimental dependences $-a/C_{E=0}$ vs p, $b/-a$ vs p, $-c/b$ vs p are

$$\Delta_4^* = 1.55 \pm 0.05, \quad \Delta_6^* = 1.55 \pm 0.15, \quad \Delta_8^* = 1.5 \pm 0.2 . \qquad (10)$$

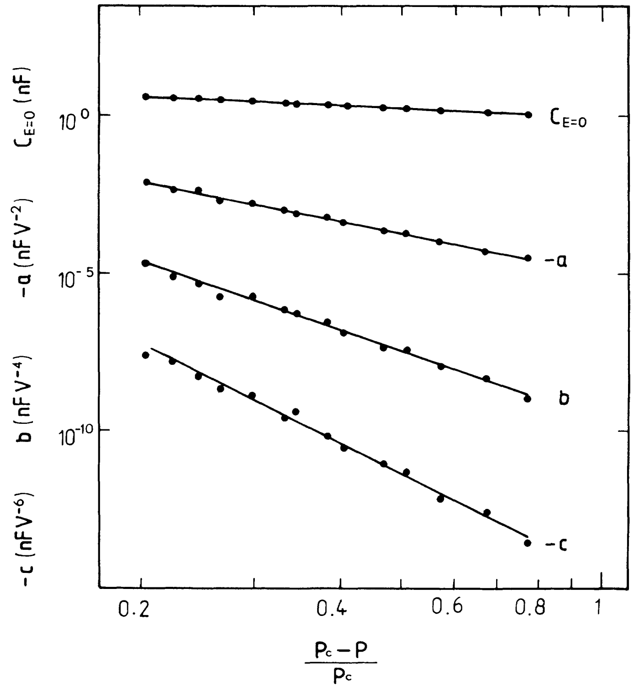

FIG. 1. Log-log plots of $C_{E=0}$, $-a$, b, and $-c$ vs $(p_c-p)/p_c$ in TGS.

Hence it may be seen that with an accuracy within the limits of error the results obtained are in good agreement with mean-field-theory predictions and also with results of measurements of $C_{E=0}$, $-a$, b as functions of temperature as given in Ref. 3.

The absolute values of the ratios of amplitudes A^*_{2n} in the relations

$$a_{2n}=A^*_{2n}\pi^{-\gamma^*_{2n}} \tag{11}$$

were also estimated (with an accuracy equal to constant k). The following values were obtained:

$$\left|\frac{A_2^*}{A_0^*}\right| \simeq k^2 10^{-4.9(\pm 0.1)} V^{-2},$$

$$\left|\frac{A_4^*}{A_2^*}\right| \simeq k^2 10^{-4.7(\pm 0.1)} V^{-2}, \tag{12}$$

$$\left|\frac{A_6^*}{A_4^*}\right| \simeq k^2 10^{-4.8(\pm 0.1)} V^{-2},$$

where $A_0^*>0$, $A_2^*<0$, $A_4^*>0$, $A_6^*<0$.

Thus a satisfactory agreement was achieved as to order between the absolute values of the consecutive ratios, similar to the results presented in Ref. 3.

Based on the results described here and those given in Ref. 3, a clear similarity may be stated between the behavior of the nonlinear electrical susceptibility as a function of temperature and of pressure. The occurrence of these analogies could be concluded from the results given in Ref. 6, where the linear form of the Curie temperature as a function of pressure for TGS was ascertained with a gradient coefficient of 2.6×10^{-3} deg/atm. From the equation $T_c=T_c^0+kp$, where T_c^0 is the critical temperature at atmospheric pressure, and from the relation $\epsilon \sim (T-T_c)^{-\gamma}$ may be deduced the proportionality $\epsilon \sim (p_c-p)^{-\gamma}$. In Ref. 7 a similar reasoning was used to explain the equivalence of the exponents $\gamma=\gamma^*$ for the temperature and pressure dependences of electric permittivity of other ferroelectrics. Moreover, our results are in agreement with the smoothness postulate (cf. Ref. 8).

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