

Dielectric Study of the Ferroelectric Phase Transition in DMAGaS Crystal

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Electric permittivity measurements as functions of temperature at constant dc electric field and as functions of the dc electric field at constant temperatures in the paraelectric phase have been performed for DMAGaS crystal. The changes of the permittivity maximum with the electric field intensity evidence the first-order character of the ferroelectric phase transition at T_{c1} . The field dependence of the permittivity $\epsilon(E)$ in the paraelectric phase is discussed, using the classical electric equation of state. A method for the determination of the corresponding coefficients is proposed. The obtained B and C coefficients, together with double hysteresis loop observed above T_{c1} prove the first-order character of the ferroelectric phase transition in DMAGaS crystal.

Key words: Ferroelectricity, Phase Transition, Dielectric Properties.

Introduction

Dimethylammonium gallium sulphate $(\text{CH}_3)_2\text{NH}_2\text{Ga}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (DMAGaS) crystal exhibits ferroelectric properties. It is isomorphous to $(\text{CH}_3)_3\text{NH}_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (DMAAS), an other ferroelectric material, known since 1988 [1–3]. At room temperature, both crystals belong to the nonpolar class $2/m$ and are in the ferroelastic state – the ferroelastic domain structure can be generated by external mechanical stress.

The first dielectric and pyroelectric studies of DMAGaS have shown that it undergoes two successive phase transitions at $T_{c1} = 136\text{ K}$ and $T_{c2} = 113\text{ K}$ [3]. The first phase transition is the ferroelectric one. The crystal changes its symmetry from $2/m$ to m . The direction of spontaneous polarization P_s , lying in the mirror plane, is taken as the x -axis of the system. The y -axis is parallel to the two-fold axis which is the crystallographic b -axis. At T_{c2} , the spontaneous polarization disappears abruptly [4–6]. From the way in which P_s vanishes and a large thermal hysteresis of transition at T_{c2} , the first-order phase transition can be concluded.

Both in DMAAS and DMAGaS the ferroelectric phase transition is of the order-disorder type, and the spontaneous polarization originates from dimethylammonium cation ordering [4]. The transition to the low-temperature phase at T_{c2} , is caused by a freezing of the reorientational motion of the cations [4]. The ferroelectric phase transition in DMAAS is continuous. The values of the

dielectric state equation coefficients indicate that the phase transition is close to a tricritical one [2].

The optical [7], ultrasonic [8], pyroelectric and dilatometric [6] studies of DMAGaS suggest the first-order character of the ferroelectric phase transition at T_{c1} . The results of the dielectric measurements are not so univocal. The crystal quality influences considerably such physical quantities as spontaneous polarization and dielectric constant $(\epsilon_r)_x$ measured in the ferroelectric direction. Sobiestianskas et al. [4], measuring P_s of DMAGaS, have noted that a tail of the spontaneous polarization appears already at 150 K. The effect is probably connected with the crystal quality, since the tail of polarization detected by pyroelectric measurements [6] was much smaller.

The maximum value of spontaneous polarization attained at T_{c2} is between $0.9\text{ }\mu\text{C}/\text{cm}^2$ [6] and $2\text{ }\mu\text{C}/\text{cm}^2$ [4, 5], depending on the crystal. The maximum of $(\epsilon_r)_x$ at T_{c1} lies between 1000 and 3000 for different crystals [4–6]. The discontinuity of the dielectric constant at T_{c1} , characteristic for first-order transitions, is difficult to detect. It is connected with the domain structure effect on the ϵ value. The Curie-Weiss law is well fulfilled in the paraelectric phase with a constant $C_{CW} = (2700 \div 3000)\text{ K}$ [4, 5]. That value is characteristic for order-disorder transitions. When the domain processes are suppressed by frequency, the Curie-Weiss constants ratio C^f/C^p of about 8 is characteristic for the first-order phase transition [4].

In this paper the results of a dielectric study of DMAGaS are presented. The aim of the study was a quantitative description of the crystal ferroelectric properties

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within the frame of the classical thermodynamic theory of phase transitions.

Experimental

DMAGaS crystal was grown by slow evaporation from a saturated water solution containing gallium sulfate and an excess of dimethylammonium sulfate (molar ratio dimethylammonium : Ga = 4:1). For the dielectric measurements an *x*-cut sample was prepared. Gold electrodes were evaporated on the *x*-faces. The sample was placed in the nitrogen gas exchange chamber of a cryostat. The temperature in the chamber was controlled with an accuracy not worse than 0.01 K. A precision LCR-meter HP 4284A was used for the dielectric measurements. The dielectric capacity of the sample was measured at 1 kHz, and the measuring field amplitude 1.5 V/cm. The temperature dependence of the electric permittivity was measured during a cooling run with a rate of 0.5 K/min under bias electric field up to 300 kV/m. The field dependence of the electric permittivity at constant temperature was obtained by applying an electric field of amplitude 350 kV/m and frequency 0.002 Hz. The hysteresis loops were observed at 0.01 Hz, using an electrometer.

Description of the Method

By measuring the electric permittivity as a function of temperature (at zero electric field) and the field dependence of the permittivity at constant temperature in the paraelectric phase, one can determine the coefficients A_0 , B and C of the dielectric state equation

$$E = A_0(T - T_0) \cdot D + B \cdot D^3 + C \cdot D^5. \quad (1)$$

At $E = 0$, the dielectric constant ϵ_r fulfills the Currie-Weiss law

$$\epsilon_r = \frac{C_{cw}}{(T - T_0)}, \quad (2)$$

and A_0 can be found from the relation

$$A_0 = \frac{1}{\epsilon_0 C_{cw}}, \quad (3)$$

where ϵ_0 is the electric permittivity of free space.

The coefficients B and C describe the non-linear properties of the ferroelectric crystal. In the paraelectric phase, those properties, manifest themselves by

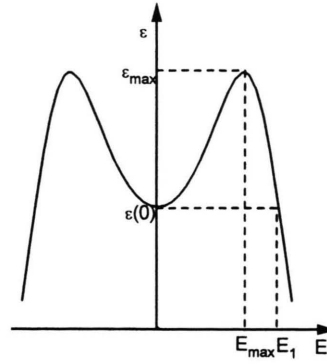


Fig. 1. Field dependence of the permittivity in paraelectric phase for first-order phase transitions.

a characteristic dependence of the electric permittivity on the electric field. For temperatures higher than $T^* = T_0 + \frac{B^2}{4A_0C}$, the field dependence of the electric permittivity is such as presented in Figure 1. The local minimum at $E = 0$ is very characteristic. In the beginning, the electric permittivity increases with the field, at E_m it reaches its maximum ϵ_m and then decreases monotonically. At E_1 , the electric permittivity has the same value $\epsilon(0)$ as at zero field.

The B coefficient can be found from a part of the $\epsilon(E)$ dependence corresponding to weak electric fields. When the electric field is sufficiently weak to assume a linear relation between D and E in first approximation one can write [9]

$$\epsilon(E) = \epsilon(0) - 3(\epsilon(0))^4 B E^2. \quad (4)$$

If the dielectric state equation can be limited to the first two terms (what is admissible for weak electric fields in the paraelectric phase) the electric permittivity fulfills the relation [10]

$$f(\epsilon) = \left(\frac{1}{\epsilon(E)} \right)^3 + 3 \frac{1}{\epsilon(0)} \left(\frac{1}{\epsilon(E)} \right)^2 - 4 \left(\frac{1}{\epsilon(0)} \right)^3 = 27 B E^2. \quad (5)$$

Drawing $\epsilon(E)$ or $f(\epsilon)$ versus E^2 , from the slope at $E = 0$ the coefficient B can be found. This method is very useful for second-order phase transitions, since (5) is satisfied for a large range of the electric field.

For first-order phase transitions, (4) and (5) are correct only for weak electric fields, when the CD^5 term can be neglected in the dielectric state equation. However, B

and C can be determined if $\varepsilon(0)$, ε_m and E_m (or E_1) are known from experiment. It can be shown that the following relations are fulfilled (see Appendix):

$$E_m = \frac{1}{\varepsilon(0)} \left[\frac{2}{3} \frac{\Delta(1/\varepsilon)}{B'} \right]^{1/2} - \frac{7}{10} B' \left[\frac{2}{3} \frac{\Delta(1/\varepsilon)}{B'} \right]^{3/2}, \quad (6)$$

$$E_1 = \frac{1}{\varepsilon(0)} \left[\frac{4}{3} \frac{\Delta(1/\varepsilon)}{B'} \right]^{1/2} - \frac{2}{5} B' \left[\frac{4}{3} \frac{\Delta(1/\varepsilon)}{B'} \right]^{3/2}, \quad (7)$$

$$C = \frac{9}{20} \frac{(B')^2}{\Delta(1/\varepsilon)}, \quad (8)$$

where $B' = -B$ and $\Delta(1/\varepsilon) \equiv \frac{1}{\varepsilon(0)} - \frac{1}{\varepsilon_m}$.

The Eqs. (6) and (7) can be solved numerically, giving B' ; next C can be found from (8).

Results and Discussion

The reciprocal dielectric constant of DMAGaS in the paraelectric phase is a linear function of temperature, as shown in Figure 2. The Curie-Weiss constant $C_{cw} = 2385$ K is lower than in the previous papers [4, 5], but the maximum of ε_r , equal of about 1600, is comparable with other results. Using (3), one obtains $A_0 = 4.74 \cdot 10^7 \frac{\text{Vm}}{\text{CK}}$.

At $T_c = (136.5 \pm 0.1 \text{ K})$, the step-like change of the dielectric constant takes place. The temperature can be considered as the phase transition temperature.

In the studied crystal, contrary to earlier results [4, 6], a tail of polarization in the paraelectric phase was not detected. At 0.1 K above T_c , the double hysteresis loop, characteristic for the first-order transition, was observed (Figure 3). It indicates the good quality of the crystal.

In Fig. 4, the temperature dependences of the dielectric constant, measured at different dc electric fields, are presented. Two characteristic features can be noted. The maximum of the dielectric constant increases initially with the field and subsequently decreases. The temperature T_{\max} at which the maximum of the dielectric constant occurs, increases linearly with the field with a slope $\frac{dT_{\max}}{dE} = 2.5 \cdot 10^{-6} \frac{\text{Km}}{\text{V}}$ (Figure 5). Both features are characteristic for first-order phase transitions, as in the

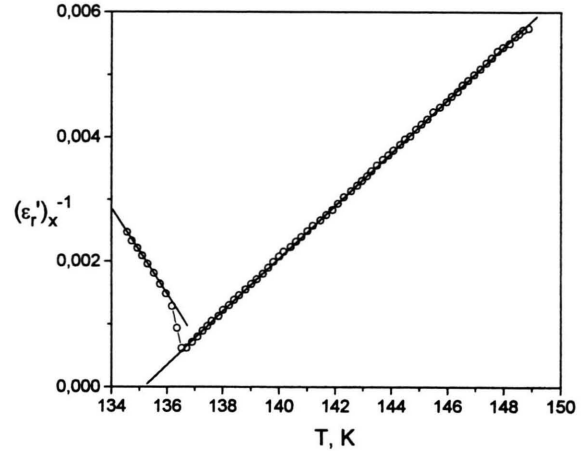


Fig. 2. The reciprocal dielectric constant of DMAGaS as a function of temperature.

case of second-order transitions ε_{\max} decreases monotonically with the field ($\varepsilon_{\max} \propto E^{-2/3}$), whereas T_{\max} increases proportionally to $E^{2/3}$.

To determine the coefficients B and C , the dielectric constant was measured as a function of the dc electric field at constant temperature in the paraelectric phase. The results are presented in Figure 6. The measured field dependences of the permittivity are similar to the curve presented in Figure 1. The local minimum $E = 0$ proves that B is negative. The B coefficients were found using (4) and (5) for experimental points close to $E = 0$. Next, the B values were calculated from (6). All results are shown in Figure 7. The scatter of the points gives an idea of the precision. The corresponding values of C , calculated using (8), are presented in Figure 8. The solid lines in Fig. 6 are generated from (1) and its derivative with the obtained A_0 , B and C values. The fitting quality proves the validity of the coefficients. The absolute values of B and C increase while approaching the phase transition temperature. A similar temperature dependence of B was found for BaTiO₃ crystal [9, 11].

The estimated B and C coefficients give new information about the phase transition and the ferroelectric properties of DMAGaS. The negative value of B shows clearly that the phase transition is of first-order. The spontaneous polarization at T_c , which is difficult to measure, can now be calculated as $P_s^c = \left(\frac{3B'}{4C} \right)^{1/2}$. Taking the B and C values obtained close to T_c , we obtain $P_s^c \approx 4 \cdot 10^{-3} \frac{\text{C}}{\text{m}^2}$. The value is reasonable if it is compared

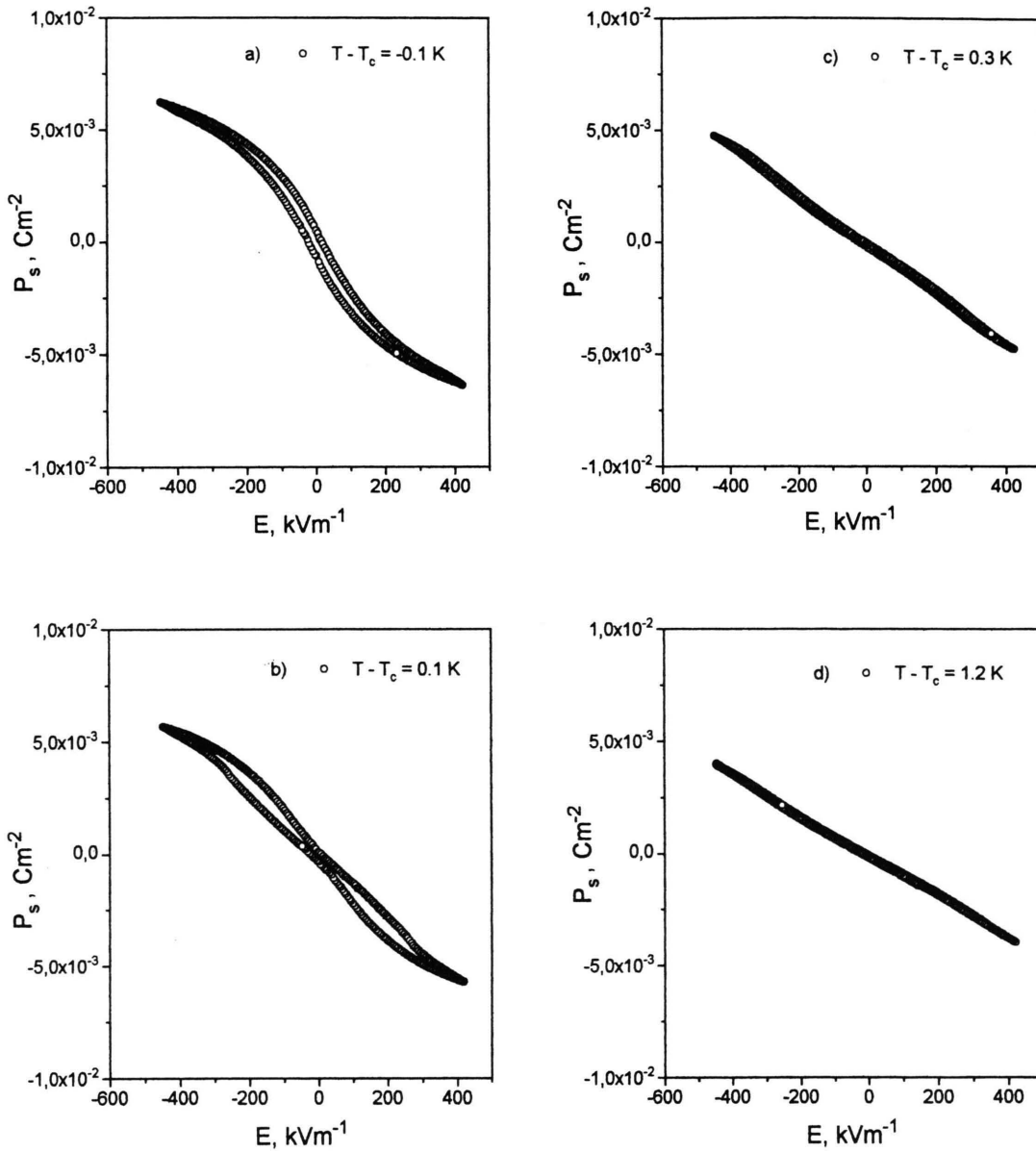


Fig. 3. The hysteresis loops of DMAGaS, observed near the phase transition temperature.

with experimental results [4–6]. One can estimate also the maximum value of the spontaneous polarization P_{\max} which is reached at T_{c2} . One obtains $P_{\max} = 1.14 \cdot 10^{-2} \frac{\text{C}}{\text{m}^2}$. The value is intermediate between the experimental results [4–6].

A maximum possible thermal hysteresis at phase transition, according to the presented results, should amount

to $\frac{B^2}{4A_0C} \cong 0.2 \text{ K}$. This means that the difference be-

tween the temperatures T_0 and T_c should be of the same order. It should be underlined that T_0 resulting from a comparison of experimental results with the simple Curie-Weiss law (2) is not the same as T_0 in the dielectric state equation (1). To have a correct temperature T_0 , the more realistic Curie-Weiss law should be applied to the

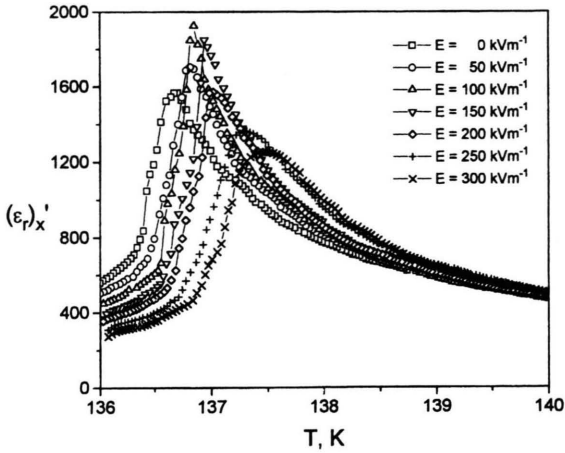


Fig. 4. Temperature dependence of the dielectric constant, measured at different dc electric fields.

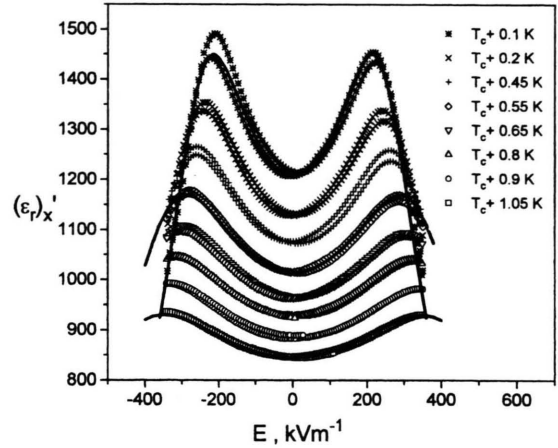


Fig. 6. Field dependences of the dielectric constant of DMA-GaS, measured in the paraelectric phase. Solid lines are generated from (1) and its derivative with determined values of the coefficients A_0 , B and C .

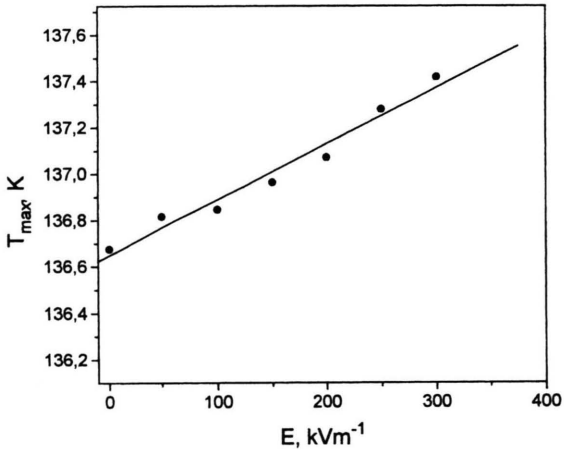


Fig. 5. Temperature at which the maximum of permittivity occurs as a function of the electric field strength.

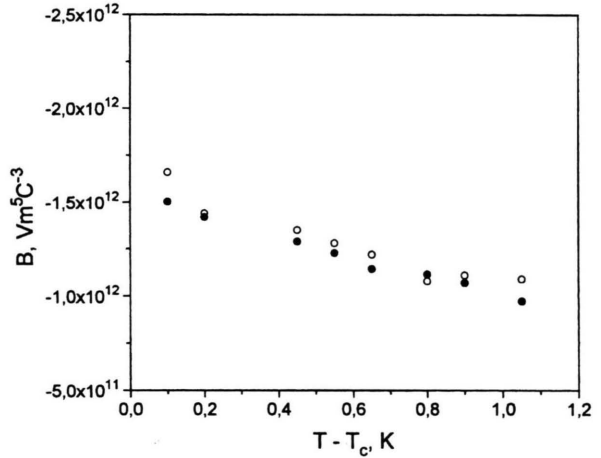


Fig. 7. The non-linearity coefficient B obtained by different methods: ● from (4) or (5), ○ from (6).

experimental results. This temperature dependence of dielectric constant can be written as

$$\frac{1}{\epsilon - \epsilon_\infty} = \frac{1}{\epsilon_s} + \frac{(T - T_0)}{C_{cw}}. \quad (9)$$

The first correction ϵ_∞ is the temperature-independent contribution to the dielectric constant. It takes usually values lower than 10, and if ϵ reaches very high values at the phase transition temperature this factor can be neglected. The second correction ϵ_s , which is usually supposed to be the contribution from the surface layer

[12–15], depends not only on the crystal but also on the electrode material. In the case of the second-order phase transition, ϵ_s is rather easy to find as the temperature T_0 , and T_c should be the same. If the transition is of first-order, the problem is more complicated.

On the ground of the presented investigation of DMA-GaS one can note:

- in the temperature range $T_{c1} \div T_{c1} + 0.1$ K, a double hysteresis loop is observed;
- T_{max} , at which the maximum electric permittivity occurs, increases linearly with dc electric field;

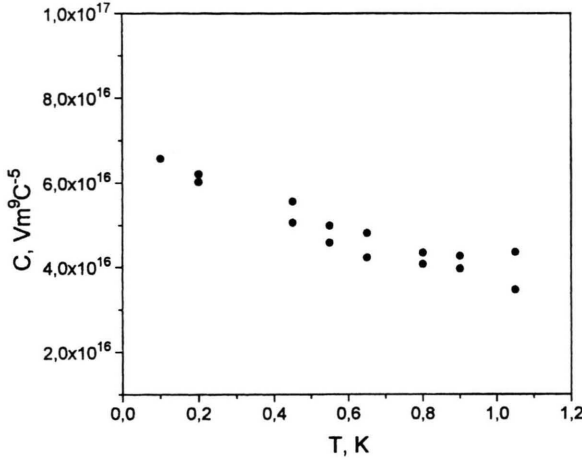


Fig. 8. C , obtained using (8) and B from Figure 7.

- the field dependence of electric permittivity is well described by the classical electric equation of state;
- the non-linearity coefficient B is negative;
- the absolute values of B and C increase in the paraelectric phase when the phase transition temperature is approached.

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Appendix

Starting from the elastic Gibbs function in the very simple polynomial form (D = electric displacement)

$$G_1(X, T, D) = G_1^0(X, T) + \frac{1}{2}AD^2 + \frac{1}{4}BD^4 + \frac{1}{6}CD^6, \quad (A.1)$$

by differentiation one obtains the electric equation of state

$$\frac{\partial G_1}{\partial D} = E = AD + BD^3 + CD^5. \quad (A.2)$$

The coefficients A , B , and C are in general temperature dependent. The conventional phenomenological theory assumes that the parameter A depends linearly on temperature

$$A = A_0(T - T_0), \quad (A.3)$$

where T_0 is the Curie-Weiss temperature. In the simplest model, B and C are constant. If the non-linearity coefficient B is negative, the above formulas describe a first-order phase transition. Differentiating (A.2), one obtains a formula for the reciprocal electric permittivity:

$$\begin{aligned} \frac{\partial^2 G_1}{\partial D^2} &= \frac{\partial E}{\partial D} = \frac{1}{\epsilon} \\ &= A_0(T - T_0) + 3B \cdot D^2 + 5C \cdot D^4, \end{aligned} \quad (A.4)$$

where $B' = -B$.

The coefficients B and C can be determined if $\epsilon(0)$, ϵ_m and E_m (or E_1) are known from experiment (see Figure 1). The condition for an extremum of the $\epsilon(D)$ function is

$$\frac{d\epsilon}{dD} = \frac{6B'D - 20CD^3}{(A - 3B'D^2 + 5CD^4)^2} = 0. \quad (A.5)$$

It is satisfied for $D = 0$ (minimum at $E = 0$) and for

$$D_m = \left(\frac{3B'}{10C} \right)^{1/2} \quad (A.6)$$

(maximum at E_m).

Putting D_m into (A.4), one obtains

$$\frac{1}{\epsilon_m} = \frac{1}{\epsilon(0)} - \frac{9}{20} \frac{(B')^2}{C} \quad (A.7)$$

and

$$\Delta(1/\epsilon) \equiv \frac{1}{\epsilon(0)} - \frac{1}{\epsilon_m} = \frac{9}{20} \frac{(B')^2}{C}. \quad (A.8)$$

From (A.2), the following expression results for E_m :

$$E_m = \frac{1}{\epsilon(0)} \left[\frac{3}{10} \frac{B'}{C} \right]^{1/2} - \frac{7}{10} B' \left[\frac{3}{10} \frac{B'}{C} \right]^{3/2}. \quad (A.9)$$

The equations (A.8) and (A.9) give possibility to find B' and C . Combining the last result with (A.8), we get

$$\begin{aligned} E_m &= \frac{1}{\epsilon(0)} \left[\frac{2}{3} \frac{\Delta(1/\epsilon)}{B'} \right]^{1/2} \\ &\quad - \frac{7}{10} B' \left[\frac{2}{3} \frac{\Delta(1/\epsilon)}{B'} \right]^{3/2}. \end{aligned} \quad (A.10)$$

As both E_m and $\Delta(1/\epsilon)$ are known from experiment, (A.10) can be solved numerically, giving the B' value.

Next, C can be easily found as

$$C = \frac{9}{20} \frac{(B')^2}{\Delta(1/\epsilon)}, \quad (\text{A.11})$$

B' and C can also be determined when the field E_1 (see Fig. 1) is known from experiment. The electric displacement D_1 , corresponding to E_1 satisfies the relation

$$\frac{1}{\epsilon(E_1)} = \frac{1}{\epsilon(0)} = \frac{1}{\epsilon(0)} + (5CD_1^2 - 3B')D_1^2, \quad (\text{A.12})$$

thus

$$D_1 = \left(\frac{3B'}{5C} \right)^{1/2}. \quad (\text{A.13})$$

Analogically, from (A.2) we get

$$E_1 = \frac{1}{\epsilon(0)} \left[\frac{2}{5} \frac{B'}{C} \right]^{1/2} - \frac{2}{5} B' \left[\frac{3}{5} \frac{B'}{C} \right]^{3/2}, \quad (\text{A.14})$$

and with (A.11)

$$E_1 = \frac{1}{\epsilon(0)} \left[\frac{4}{3} \frac{\Delta(1/\epsilon)}{B'} \right]^{1/2} - \frac{2}{5} B' \left[\frac{4}{3} \frac{\Delta(1/\epsilon)}{B'} \right]^{3/2}. \quad (\text{A.15})$$

The above equation, as (A.10), can be solved numerically with respect to B' .

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