Phenomenological Theory of the Ferroelectric Dispersion and Microwave Investigations of Colemanite

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The ferroelectric dispersion of the dielectric constant of colemanite is investigated by a coaxial equipment between −15 °C and +15 °C. In the entire temperature range the dispersion is of the mono-dispersive Debye type. In a first approximation both the relaxation time τ_ε and the static dielectric constant can be represented by a Curie-Weiß law. The relaxation time of the non-interaction dipole system shows a characteristic temperature dependence. The phenomenological theory assumes a non-linear coupling between certain quantities of state, and thus it constitutes a generalization of a known linear thermodynamic theory of relaxation phenomena. By this theory various material quantities which are temperature dependent are related to each other. The theory may be applied to all those ferroelectric crystals with a phase transition of the second order which are not piezoelectric in the paraelectric phase. The experimental results obtained for colemanite agree with the predictions of the theory.

I. Introduction

The ferroelectric property of the mineral colemanite, $CaB_3O_4(OH)_3 \cdot H_2O$, was first discovered by Goldsmith[1]. At room temperature colemanite is non polar with spacegroup 2/m but below approximately −3 °C it transforms to a phase that is piezo-, pyro-, and ferroelectric, with the monoclinic b-axis being the ferroelectric axis (space group 2). It could be shown by investigations of the structural basis of ferroelectricity in colemanite[2, 3] that one of the hydrogen atoms of the water molecule and the hydrogen of an adjacent hydroxyl group, which are in state of dynamic disorder in the nonpolar phase, settle into ordered noncentric positions in the ferroelectric phase. These results were confirmed by NMR experiments concerning the boron sites in colemanite[4].

According to these results one would expect that the ferroelectric dispersion of the complex dielectric constant is of the relaxation type[5]. Here the term "ferroelectric dispersion" refers to a dispersion of the dielectric constant which is caused by the characteristic motions of atoms or groups of atoms which are responsible for ferroelectricity. Several works deal with the dielectric behaviour of colemanite[1, 6]. But as far as we know there is only one recent note[7] dealing with the ferroelectric dispersion of the dielectric constant of colemanite. According to this work the ferroelectric dispersion can be described in good approximation by a mono-dispersive relaxation (Debye relaxation) above the Curie point.

But so far no detailed experimental results were published concerning the ferroelectric dispersion of colemanite. Therefore we measured the dependence on the frequency and on the temperature of the complex dielectric constant between $1.1 \cdot 10^8$ to $1 \cdot 10^9$ Hz in both, the paraelectric and ferroelectric phase. The results reported in Sect. II can be described by a single Debye relaxation formula relating the strongly temperature dependent static dielectric constant (Currie-Weiß law) and the strongly temperature dependent relaxation time (Currie-Weiß law, critical slowing down) to each other by a generalized Lyddane-Sachs-Teller relation[8, 9]. But it turns out that this rather simple theoretical picture is not sufficient for describing our experimental results in detail. Therefore in Sect. III a non-linear, phenomenological theory is developed, which may describe the effects reported in Sect. II and which may be applied to all those ferroelectric materials which are not piezo- and pyroelectric in the paraelectric phase. This condition holds in particular for colemanite and the crystals of the TGS group. It should be noted in this context that colemanite exhibits a phase transition of the second order. Thus, this material is very convenient for investigating the general properties of the ferroelectric relaxation.

II. Experimental Procedure and Results

Cylindrical samples with a diameter of 3,00 mm and a length of 0,50 mm were prepared by a lathe

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from natural single crystals found in death valley, California. In the frequency range between $1.1 \cdot 10^8$ and 10^9 Hz we used a coaxial reflectometer set up, which is described in detail elsewhere[10, 11]. The static dielectric constant was measured by a Wayne-Kerr bridge in the 100 kHz range.

In Figs. 1 and 2 some typical results of our experiments are reported. For all temperatures the locus of the dielectric constant $\varepsilon(\omega)$ in the complex plane is a semicircle with the centre located on the real axis. Furthermore, for all values $\varepsilon(\omega)$, measured at certain frequencies $\omega = 2\pi f$, a relaxation time $\tau_\varepsilon(\omega)$ was determined from the Debye formula (1). It turned out that, within the experimental errors, there was no dependence of τ_ε on the frequency ω. Thus, it can be stated that in the entire temperature region the dielectric constant of colemanite can be represented by a single relaxation

$$\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/(1 + i\,\omega\,\tau_\varepsilon)\,, \qquad (1)$$

where ε_∞, ε_s, τ_ε do not depend on the frequency but may depend on the temperature. Our experimental results are compatible with a nearly temperature independent ε_∞ in the range between 7 and 8.5. The static dielectric constant ε_s could be obtained either from a measurement with a Wayne-Kerr bridge at 100 kHz or from an extrapolation of a Debye semicircle to small frequencies. Both methods were applied yielding the same values within experimental errors. The relaxation time τ_ε was obtained as the weighted mean value of all $\tau_\varepsilon(\omega)$ measured at a fixed temperature T for various frequencies ω. According to Fig. 3, both, ε_s and τ_ε depend strongly on the temperature, in a first approximation according

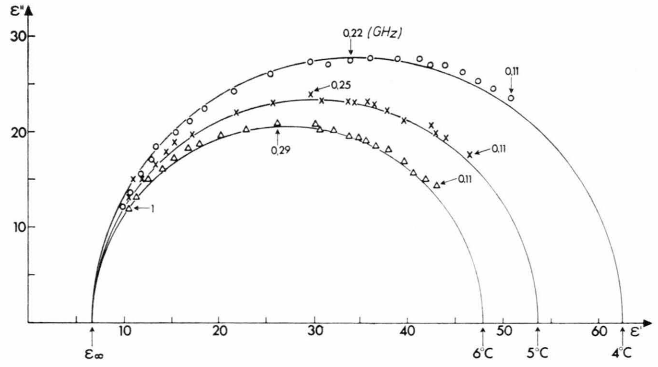

Fig. 1. Typical examples of the dependence of the complex dielectric constant $\varepsilon = \varepsilon' - i\,\varepsilon''$ on the frequency (in GHz) and the temperature (in °C) above T_c.

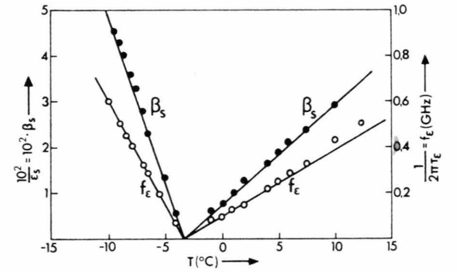

Fig. 3. Curie-Weiß laws of the static dielectric modulus β_s and of the relaxation frequency f_ε.

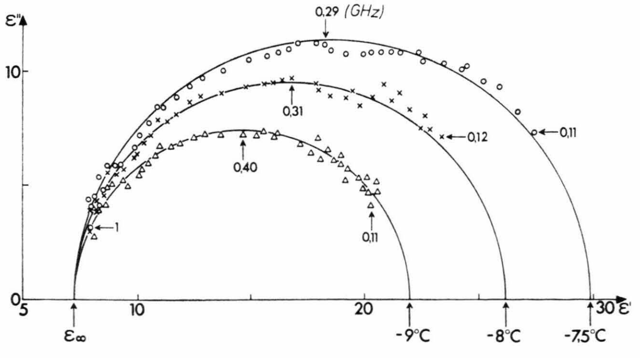

Fig. 2. Typical examples of the dependence of the complex dielectric constant $\varepsilon = \varepsilon' - i\,\varepsilon''$ on the frequency (in GHz) and the temperature (in °C) below T_c.

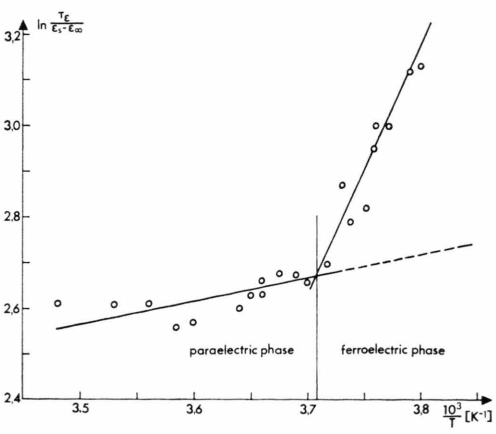

Fig. 4. Temperature dependence of the characteristic relaxation time $\tau_0 = \tau_\varepsilon / (\varepsilon_s - \varepsilon_\infty)$ (τ_0 is picoseconds).

to a Curie-Weiß law in both phases, i.e. the static dielectric modulus $\beta_s = \varepsilon_s^{-1}$ and the relaxation frequency $f_\varepsilon = (2\pi\tau_\varepsilon)^{-1}$ are both proportional to $|T - T_c|$. The ratios of the corresponding Curie constants in the paraelectric and ferroelectric phase are $C_p/C_f = 3.3 \pm 0.2$, with $C_p = 440$ K, and $C_p'/C_f' = 3.1 \pm 0.2$, respectively, which differ considerably from the classical value 2. Thus, these values are identical within the experimental errors, indicating that the quantity $\tau_\varepsilon/\varepsilon_s$ is temperature independent in a first approximation[8, 9]. However, above 8 °C systematic deviations from these results were observed: The values of the relaxation frequencies were greater than those expected from the Curie-Weiß law of Figure 3.

We now consider the relaxation time τ_0 which is defined by $\tau_0 = \tau_\varepsilon/(\varepsilon_s - \varepsilon_\infty)$. The temperature dependence of τ_0 is represented in Figure 4. According to Mason's theory of ferroelectricity[5, 8] the slope of the line in the paraelectric phase may be ascribed to a thermally activated process with an activation energy in the order of magnitude of $1.5\,kT$. Formally an "activation energy" of approximately $18\,kT$ may be attributed to the line in the ferroelectric phase, too. If one takes into consideration the fact, that the phase transition is of the second order, this jump of the "activation energy" is a rather strange result. In the following Sect. III a phenomenological theory is proposed which relates in a first approximation this temperature dependence of τ_0 and the deviation of the ratio of the Curie constants from the classical value 2 to an influence of the mechanical and thermal boundary conditions.

III. Phenomenological Theory

In the following a phenomenological theory will be proposed which is a generalization of a thermodynamic theory of relaxation phenomena developed in[8]. We consider the following system of equations between the thermodynamic variables of state which may be derived from an expansion of the appropriate thermodynamic potential

$$\boldsymbol{e} = \mathbf{K}_\infty \boldsymbol{\sigma} - \tfrac{1}{2} D^2 \boldsymbol{q}\,, \tag{2}$$

$$E = D\,\boldsymbol{q}^{\mathrm{T}} \boldsymbol{\sigma} + \beta_\infty D - \beta_\infty P\,, \tag{3}$$

$$-A = \quad -\beta_\infty D + R_{\mathrm{D}} P\,, \tag{4}$$

$$\dot{P} = L A\,. \tag{5}$$

The symbols have the following meaning: The thermodynamic conjugated variables of state D and E are the dielectric displacement, divided by the dielectric constant of the vacuum, and the electric field intensity in the ferroelectric direction. The internal variable of state P (order parameter) has the meaning of a polarization, devided by the dielectric constant of the vacuum, and its conjugated affinity A vanishes in equilibrium. Thus β_∞ and R_{D} are simply numbers. By the column vectors of conjugated variables $\boldsymbol{e}$ and $\boldsymbol{\sigma}$ all those non-critical variables are represented which influence the variables D and P via the non-linear terms in (2) and (3). So e.g. $\boldsymbol{e}$ may represent the elastic strains and $\boldsymbol{\sigma}$ may represent the elastic stresses. According to (3) β_∞ is the dielectric modulus for quick changes of state of a free crystal, i.e. $P = 0$ and $\boldsymbol{\sigma} = 0$. It can be shown[8] that the order parameter P may be defined always in that way that the coefficient between E and P or between A and D is $-\beta_\infty$. The positive coefficient L has the meaning of a reciprocal relaxation time and gives the relation between the rate of change of the internal variable P and the deviation from equilibrium A. It is important to note that according to (2) and (3) the coupling between the critical variables D and P and the non-critical variables $\boldsymbol{e}$ and $\boldsymbol{\sigma}$ is *assumed to be a quadratic one.* Consequently the theory can be applied only to those materials for which no linear coupling (e.g. piezoelectric effect) between the critical and non-critical variables exists in the paraelectric phase. This assumption holds for colemanite and crystals of the TGS-type. The constant column vector $\boldsymbol{q}$ represents the coupling constants between the critical and non-critical quantities (e.g. the electrostrictive constants). $\mathbf{K}_\infty$ denotes the symmetric matrix of the elastic constants for quick changes of state ($P = 0$).

Generally we are interested in relations between the thermodynamic variables of state which describe the behaviour of the material, both, above and below T_c. In this sense (2) to (4) are not appropriate relations because, according to thermodynamic stability[8], $\mathbf{K}_\infty$ is assumed to be positive definite in the entire temperature range and

$$\beta_\infty > 0, \quad R_{\mathrm{D}} > 0,$$
$$R_{\mathrm{E}} := R_{\mathrm{D}} - \beta_\infty = (T - T_c)/C_{\mathrm{p}} \tag{6}$$

holds at least for $T \geqq T_c$. C_{p} is the Curie-Weiß constant of the paraelectric phase. Thus, no coefficient of (2) to (4) exhibits an anomaleous temperature dependence near T_c and consequently in these relations no additional non-linear terms can be introduced giving rise to relations describing the behaviour below T_c, too. Relations of this type can be obtained by the following methods: If one solves (4) with respect to P and inserts the result into (3) instead of $\beta_\infty D$ in (3) $\beta_s D$ occurs, where we have defined the static dielectric modulus

$$\beta_s = \beta_\infty - \beta_\infty^2 / R_D \approx (T - T_c)/C_p \tag{7}$$

which vanishes at T_c. Consequently in this relation non-linear terms may be introduced describing the static behaviour of the material below T_c, too. Then it can be seen that in equilibrium ($A = 0$) the relations (2) to (5) reduce to two relations which are well known from conventional thermodynamic theories of ferroelectricity[12].

But we are interested in the dynamical behaviour and thus, this method cannot be applied. Rather we must solve (3) with respect to D and insert the result into all other relations. Then obviously problems arise from the non-linear coupling terms between the critical and non-critical variables in (2) and (3). For $T \geqq T_c$ the changes of state may be assumed to be so small that these non-linear terms can be neglected. Thus in this temperature range the thermal and mechanical boundary conditions do not influence the dielectric behaviour. But because of the influence of the spontaneous polarization below T_c the quadratic coupling terms generally must be taken into account except in the case $\sigma = 0$ (free and isothermal crystal). Introducing further non-linear dielectric terms we obtain on this condition from (3) and (4)

$$D = \varepsilon_\infty E + P, \tag{8}$$

$$-A = -E + R_E P + B P^3 + \dots \tag{9}$$

where B is a constant which is assumed to be positive in order to ensure a phase transition of the second order. By $\varepsilon_\infty = 1/\beta_\infty$ we denote the dielectric constant for quick changes of state. In accordance with the assumptions of Landau's theory of phase transitions[13] we assume that (8), (9) and (5) describe the static and dynamical behaviour above T_c, and, for a free crystal, below T_c. A detailed discussion of these relations was presented in[8]. Therefore we may restrict ourselves to some results which are important in this context. For $T < T_c$, $A = 0$ (equilibrium), and $E = 0$ (shorted crystal) a spontaneous polarization is obtained which is given by

$$D_s^2 = P_s^2 = -R_E/B, \tag{10}$$

where the relation given in (6) for R_E is assumed to be valid also for $T < T_c$. According to (2) this gives rise to a spontaneous value of $\boldsymbol{e}$

$$\boldsymbol{e}_s = -\tfrac{1}{2} D_s^2 \boldsymbol{q}. \tag{11}$$

In the following below T_c we are interested in the deviations from the spontaneous values, i.e. we write

$$D_t = D_s + D, \quad P_t = P_s + P, \quad \boldsymbol{e}_t = \boldsymbol{e}_s + \boldsymbol{e}, \tag{12}$$

where the suffix t refers to "total". The linear response is obtained by neglecting BP^3 for $T \geqq T_c$ and by replacing $(R_E P_t + B P_t^3)$ by the value $-2 R_E P$ for $T < T_c$. This yields

$$\varepsilon_s^f - \varepsilon_\infty = \left\{ \begin{array}{ll} R_E^{-1} & T \geqq T_c \\ -(2 R_E)^{-1} & T < T_c \end{array} \right\}, \tag{13}$$

$$(\tau_\varepsilon^f)^{-1} = \left\{ \begin{array}{ll} L R_E & T \geqq T_c \\ -2 L R_E & T < T_c \end{array} \right\}, \tag{14}$$

where τ_ε^f is the relaxation time of the internal variable P of a free crystal if E is the independent variable or, equivalently, of the free dielectric constant[8]. By ε_s^f we denote the static dielectric constant of a free crystal.

Thus, from (8), (9), (5), and (6) it can be concluded that, in accordance with our experimental results, the dielectric constant depends on the frequency according to a single Debye relaxation whose relaxation strength $\varepsilon_s^f - \varepsilon_\infty$ and relaxation time τ_ε^f obey Curie-Weiß laws in both phases. According to (13) and (14) the ratio of the Curie-Weiß constants in the both phases is given by the classical value $C_p/C_f = 2$, which is in contradiction to our experimental results. This is due to the fact, that we have assumed isothermal and free boundary conditions so far in the theoretical considerations, whereas in our experiments the crystal is thermally and mechanically clamped, i.e. the boundary condition is $\boldsymbol{e} = 0$ instead of $\sigma = 0$. Thus, in Figs. 3 and 4 the clamped dielectric constant and relaxation times are plotted, whereas in (13) and (14) the free values are given.

In order to take into account the external boundary conditions also for $T < T_c$ we derive from (2) and (4) and (12) the following linearized system of equations

$$\boldsymbol{e} = \mathbf{K}'_\infty \sigma - \varepsilon_\infty D_s \boldsymbol{q} E - D_s \boldsymbol{q} P, \tag{15}$$

$$D = -\varepsilon_\infty D_s \boldsymbol{q}^{\mathrm{T}} \sigma + \varepsilon_\infty E + P, \tag{16}$$

$$-A = D_s \boldsymbol{q}^{\mathrm{T}} \sigma - E + (-2 R_E) P, \tag{17}$$

where $\mathbf{K}'_\infty = \mathbf{K}_\infty + \varepsilon_\infty D_s^2 \boldsymbol{q} \boldsymbol{q}^T$. Since D_s depends on the temperature according to (6) and (10) the linear coupling terms between the critical and non-critical variables in (15) to (17) are strongly temperature dependent. They vanish for $T = T_c$. These relations and (5) determine the dynamical behaviour below T_c.

It should be noted that the methods introduced so far for describing relaxation processes are quite analogous to those well known in the theory of certain ferroelectric crystals with a soft mode of the optical lattice vibrations, e.g. $BaTiO_3$. Since $BaTiO_3$ is not piezoelectric in the paraelectric phase there is a strongly temperature dependent linear coupling below T_c between the soft optical phonon, which in the limit of long wave lengths corresponds to the internal variable P, and the acoustical phonons, the amplitudes of which correspond in the limit of long wave lengths to the variables of state $\boldsymbol{e}$ [14].

The results which are obtained for a free isothermal crystal have been discussed already. For a clamped adiabatic crystal, on the other hand, we have $\boldsymbol{e} = 0$ and consequently $\boldsymbol{\sigma}$ can be calculated from (15). If the result is inserted into (16) and (17) the following relations are obtained:

$$D = \varepsilon_\infty G(T) E + G(T) P, \tag{18}$$

$$-A = -G(T) E + R_E^c P, \tag{19}$$

where we have defined with the aid of (6) and (10)

$$R_E^c = (-2 R_E) + D_s^2 \boldsymbol{q}^T \mathbf{K}'^{-1}_\infty \boldsymbol{q} = (T_c - T)\left(\frac{2}{C_p} + \frac{1}{C}\right) = \frac{T_c - T}{C_f}. \tag{20}$$

As above we denote by C_f the Curie-Weiß constant of the ferroelectric phase and by C a constant which according to (10) and (20) depends on C_p, B, $\mathbf{K}'_\infty$, and the coupling constants $\boldsymbol{q}$. The function $G(T)$ which varies linearly with the temperature is defined by

$$G(T) = 1 - \varepsilon_\infty D_s^2 \boldsymbol{q}^T \mathbf{K}'_\infty \boldsymbol{q} = 1 - \varepsilon_\infty (T_c - T)/C \leqq 1. \tag{21}$$

The consequences of the foregoing relations may be summarized as follows.

For $T < T_c$ there is an influence of the external boundary conditions on the high frequency dielectric constant. According to (16) ε_∞ may be regarded as the free high frequency dielectric constant whereas according to (18) for the clamped high frequency dielectric constant

$$\varepsilon_\infty^c := \varepsilon_\infty G(T) \leqq \varepsilon_\infty \tag{22}$$

holds. For $T \geqq T_c$ there is no influence of clamping on ε_∞.

For the clamped static dielectric constant from (18) and (19) the following relation is obtained

$$\varepsilon_s^c - \varepsilon_\infty^c = G^2(T)/R_E^c \approx (R_E^c)^{-1} = C_f/(T_c - T). \tag{23}$$

Thus, we obtain a Curie-Weiß law with a Curie-Weiß constant C_f where according to (20) $C_p/C_f > 2$. For $T \geqq T_c$ there is no influence of clamping on ε_s.

We now look for the behaviour of the relaxation times. For the paraelectric phase and, in case of a free crystal, for the ferroelectric phase we consider the relaxation time

$$(2\pi f_0^f)^{-1} = \tau_0^f = \tau_\varepsilon^f/(\varepsilon_s^f - \varepsilon_\infty) = L^{-1}. \tag{24}$$

Below T_c for a clamped crystal according to (5) and (19) $\tau_\varepsilon^c = 1/L R_E^c$ and thus we obtain with the aid of (23)

$$(2\pi f_0^c)^{-1} = \tau_0^c = \tau_\varepsilon^c/(\varepsilon_s^c - \varepsilon_\infty^c) = 1/L G^2(T). \tag{25}$$

Thus, the free isothermal relaxation time τ_0^f generally differs from the clamped adiabatic relaxation time τ_0^c below T_c, whereas there is no influence of clamping above T_c. Since in our microwave measurements the crystal is clamped for $T < T_c$ all quantities reported in Sect. II for this temperature range refer to a clamped state. Thus, τ_0^f cannot be directly obtained from experimental data.

Discussing now the behaviour of the kinetic coefficient L we consider Mason's model of ferroelectricity which is equivalent to an Ising model in the mean field approximation [5, 8]. In this theory a symmetric double well potential for the motion of the electrical dipoles which are responsible for the polarization is assumed. The relaxation time of the non-interacting system depends on the temperature according to a thermally activated process. It can be shown [8] that in the paraelectric phase τ_0^f is proportional to the relaxation time of the non-interacting system with the constant of proportionality being nearly temperature independent. In the ferroelectric phase, however, another relaxation time occurs in the dynamical equations (even for a free crystal), because the double well potential becomes an assymmetric one below T_c [5]. Then from the correspondence which has been established between the kinetic coefficient L and the quantities of Mason's model[8] it can be concluded in a first approximation that for $T < T_c$

$$L_-^{-1}(T) = L_+^{-1}(T)\,[1 + \tfrac{3}{2}\,(T_c - T)/T_c]\,. \quad (26)$$

In this relation $L_-(T)$ denotes the kinetic coefficient L of a free ferroelectric crystal and $L_+(T)$ denotes the value of the kinetic coefficient which would be obtained if the crystal would be paraelectric at the temperature $T < T_c$ [note that the L's in (26) are related to the corresponding $\tau_0{}^{\mathrm{f}}$'s by (24)]. Combining (21), (24), (25), and (26) we finally obtain in a first approximation for $T < T_c$

$$\tau_0{}^{\mathrm{c}}(T) = \tau_{0+}^{\mathrm{f}}(T)\,[1 + (T_c - T)\,(3/2\,T_c + 2\,\varepsilon_\infty/C)]\,. \quad (27)$$

In this relation $\tau_0{}^{\mathrm{c}}(T)$ is the clamped relaxation time which can be measured by experiment [see (25) and Fig. 4], whereas $\tau_{0+}^{\mathrm{f}}(T)$ is the relaxation time, which would be obtained from an experiment if the crystal would be paraelectric at the temperature $T < T_c$. In the above experimental investigation (Fig. 4) $\tau_{0+}^{\mathrm{f}}(T)$ can be obtained by an extrapolation of the line obtained for $T \geqq T_c$ to temperatures below T_c. In a semilogarithmic plot one obtaines for $T < T_c$ in the above approximation

$$\ln \tau_0{}^{\mathrm{c}}(T) = \ln \tau_{0+}^{\mathrm{f}}(T) + \big((1/T - 1/T_c)\,T_c^2\,(3/2\,T_c + 2\,\varepsilon_\infty/C)\big)\,, \quad (28)$$

which agrees qualitatively with the behaviour reported in Figure 4.

In (27) and (28) it is clearly demonstrated that the different slopes of the lines obtained for the paraelectric and ferroelectric phase in Fig. 4 are mainly caused by an influence of the mechanical and thermal boundary conditions. It should be noted that according to (20) and (21) the various effects discussed so far are strongly correlated.

IV. Discussion

The theory developed in the preceding Sect. III may be partially verified by our experimental results obtained for colemanite. The value of C_{f} was reported in Sect. II and thus we may calculate C according to (20) with an error of approximately ±10%. The dielectric constant ε_∞ can be obtained also from Sect. II with an error of approximately ±15%. Thus, $2\,\varepsilon_\infty/C$ is known with an error of approximately ±25% and it turns out that this quantity is large if compared with $3/2\,T_c$. Consequently, according to (27) and (28), we may calculate the relaxation time $\tau_0{}^{\mathrm{c}}$ from the relaxation time τ_{0+}^{f} (dotted line in Figure 4). The result agrees very well within the error of ±25% with the experimental results in Figure 4. Thus it can be stated that the experimental results of Figs. 1 to 4 agree with the predictions of the phenomenological theory.

In our experiments the influence of the mechanical and thermal boundary conditions on ε_∞ predicted in (22) cannot be verified directly by experiment because in the ferroelectric phase only the clamped dielectric constant $\varepsilon_\infty^{\mathrm{c}}$ can be measured whereas a mechanically and thermally free crystal cannot be realized in the GHz-regime. Preliminary measurements at 8 GHz showed that the temperature variation of $\varepsilon_\infty^{\mathrm{c}}$ between −30 °C and +30 °C is smaller than 4%. According to (21) and (22) this implies that the free dielectric constant ε_∞ should increase with decreasing temperature below T_c.

In view of the error of ±25% obtained for $2\,\varepsilon_\infty/C$ in our investigations of colemanite one may look for investigations of the ferroelectric dispersion of other ferroelectric crystals being not piezoelectric in the paraelectric phase, which may yield further information on the validity of the thermodynamic theory. Recently in a detailed investigation of the behaviour of TGS and TGSe in the microwave region for τ_0 the same behaviour as reported for colemanite in Fig. 4 could be verified[10]. For these crystals the quantity $C_{\mathrm{p}}/C_{\mathrm{f}}$ is 4.75 ± 2% and 11.5 ± 10%, respectively, and consequently C is known with a much better accuracy than for colemanite. The error of ε_∞ may be in the same order of magnitude as for colemanite.

For TGS the difference between the two lines of the ferroelectric phase in Fig. 4 calculated according to (27) and (28) is about 50% of the measured one. This deviation may be caused by the following fact: In the relations (2) to (4) no quadratic coupling terms between the order parameter P and the other variables were taken into account. Thus, the most general ansatz is obtained, if the term $-\frac{1}{2}D^2\boldsymbol{q}$ in (2) is replaced by the quadratic from $-\frac{1}{2}(D^2\boldsymbol{q}_1 + P^2\boldsymbol{q}_2 + 2\,D\,P\,\boldsymbol{q}_3)$, if the term $D\,\boldsymbol{q}^{\mathrm{T}}\,\boldsymbol{\sigma}$ in (3) is replaced by $(D\,\boldsymbol{q}_1{}^{\mathrm{T}} + P\,\boldsymbol{q}_3{}^{\mathrm{T}})\,\boldsymbol{\sigma}$, and if an additional term $(P\,\boldsymbol{q}_2{}^{\mathrm{T}} + D\,\boldsymbol{q}_3{}^{\mathrm{T}})\,\boldsymbol{\sigma}$ is introduced in (4), where $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$ denote the vectors of the various coupling constants. Obviously these additional quadratic terms do not influence the behaviour for $T \geqq T_c$. For $T < T_c$, however, we may derive a linearized system of equations, which is analogous to (15) to (17), where $\boldsymbol{q}E$ and $\boldsymbol{q}P$ in (15) are replaced by $(\boldsymbol{q}_1+\boldsymbol{q}_3)E$ and $(\boldsymbol{q}_1+\boldsymbol{q}_2+2\,\boldsymbol{q}_3)P$, respectively. Furthermore instead of $\boldsymbol{q}^{\mathrm{T}}\boldsymbol{\sigma}$ in (16) and (17) the quantities $(\boldsymbol{q}_1+\boldsymbol{q}_3)^{\mathrm{T}}\boldsymbol{\sigma}$ and $(\boldsymbol{q}_1+\boldsymbol{q}_2+2\,\boldsymbol{q}_3)^{\mathrm{T}}\boldsymbol{\sigma}$ occur, respectively. Thus, there are two independent combinations of the coefficients in the new linear relations, i.e. $\boldsymbol{q}_1+\boldsymbol{q}_3$ and $\boldsymbol{q}_1+\boldsymbol{q}_2+2\,\boldsymbol{q}_3$. Then, of course, relations which are analogous to (18) and (19) may be derived. There are 3 different coefficients in these relations, i.e. two diagonal elements and one (antisymmetric) off-diagonal element. It can be concluded from these generalized equations that the consequences of (18) and (19) discussed in Sect. III are not principally altered, i.e. one obtaines a difference, depending on the temperature, between ε_∞ and $\varepsilon_\infty^{\mathrm{c}}$, analogous to (22), a Curie-Weiß law of the static dielectric constant analogous to (23), where $C_{\mathrm{p}}/C_{\mathrm{f}}>2$, and an influence of the boundary conditions on τ_0 analogous to (24) and (25). But in contrast of the results of Sect. III, it can be stated, that these effects are now generally independent of each other. The only general result is, that there is no influence of the boundary conditions on τ_0 if at least one of the quantities $R_{\mathrm{E}}{}^{\mathrm{c}}$ or $\varepsilon_\infty^{\mathrm{c}}$ is not influenced by the boundary conditions, i.e. if at least one of the vectors $\boldsymbol{q}_1+\boldsymbol{q}_3$ or $\boldsymbol{q}_1+\boldsymbol{q}_2+2\,\boldsymbol{q}_3$ vanishes.

Finally, it may be stated that for colemanite the main part and even for TGS a considerable part of the difference between $\tau_0{}^{\mathrm{c}}$ and τ_{0+}^{f} can be ascribed to an influence of the non-linear terms taken into account already in (2) to (4). These terms describe a property of the lattice which is not influenced by the dipoles. But, as has been pointed out already, there may be further non-linear terms which influence the behaviour of the material, too. It should be noted that it seems to be nearly hopeless to determine the material quantities describing the non-linear coupling according to (2) and (3) or according to the extended system with a sufficient accuracy by experiment.

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