

Low-frequency dielectric dispersion in ferroelectric crystals

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The dielectric permittivity function of the ferroelectric materials Rochelle salt, TGS, BaTiO₃, KDP, and LiTaO₃ was measured in the frequency range 1 mHz–1kHz. The measurements were done both above and below the ferroelectric transition, except for LiTaO₃, in which the highest measurement temperature was 146 °C. In the first four crystals, the dielectric function shows a central peak of width less than 1 Hz which disappears completely in the paraelectric phase. There are good indications that the central peak involves the diffusion of the heat generated by pyroelectric effect, but the pyroelectric coupling is not enough to account for the dispersion step. Switching of small polarization clusters with the exciting electric field is suggested to be a source of the enhanced central peak intensity. In LiTaO₃, a Debye relaxation of the polarization was observed, with relaxation time decreasing very quickly with increasing temperature. That relaxation is perhaps related to a central peak observed in light scattering in the 1970's. [S0163-1829(97)03921-0]

I. INTRODUCTION

Recently, the existence of low-frequency sample-size-dependent susceptibility dispersion in some systems has been demonstrated. That dispersion is related to a difference between the isothermal and adiabatic susceptibilities and to a crossover from adiabatic to isothermal behavior as the excitation frequency is decreased. That is the macroscopic analog of the heat diffusion central peak (CP) observed in light and neutron scattering in the 1970's. The low-frequency dispersion was observed in the dielectric permittivity¹ of KH₂PO₄ (KDP) and (NH₂CH₂COOH)₃H₂SO₄ (TGS) and subsequently in the elastic stiffness constant² in KSCN. In this paper we present improved data on the dielectric response of KDP and TGS and also original data on the dielectric response of NaKC₄H₄O₆·4H₂O (Rochelle salt), BaTiO₃, and LiTaO₃. By using a lock-in amplifier (PAR 5302) which is able to operate down to a few mHz, we could take more accurate data and also make a reliable separation of the real and imaginary parts of the dielectric function. The results show that the phenomenon is more complex than thought before. The intensity of the observed central peak is much higher than the value $K^T - K^S = Tp^2/\epsilon_0 C_p$ dictated by thermodynamics. In other words, the limit of the measured $K(f)$ as the frequency f goes to zero is much higher than K^T . That intensity depends on the electric-field bias used to polarize the samples, being smaller for larger fields.

In Rochelle salt, TGS, and BaTiO₃, the dispersion $K(f)$ can be satisfactorily fitted with the theoretical function arising from the heat diffusion process. However, the characteristic frequency f_{exp} of the dispersion is much smaller than that obtained from the relation $f_{\text{th}} = DL^2/\pi$ predicted by the

theory. Here, D is the thermal diffusivity and l is the thickness of the sample. In KDP the real part of $K(\omega)$ is well approximated by the expression $K'(\omega) = K'(\omega_0) - A \log_{10}(\omega/\omega_0)$ in the frequency range 2 mHz–100 Hz, with the constant A not depending on the temperature. In LiTaO₃ the dispersion $K(\omega)$ is described by a Debye relaxation.

We present the speculative explanation that the polarized samples are not in a truly single-domain state and that a fractional volume $\Delta V/V$ of the sample is composed by clusters that switch polarization under the action of the exciting external field. This extra compliance couples to the heat diffusion CP through the pyroelectric effect. The observed response is a coupled mode susceptibility. If the characteristic time of the domain switching is much smaller than the characteristic time of the thermal diffusion, the main result of the coupling is an enhancement of the thermal diffusion CP.

As for the results in LiTaO₃, it is not clear that the observed dispersion is related to the heat diffusion central peak. The experiments were done only up to 146 °C, much below the ferroelectric transition at 665 °C. The dispersion is Debye-like and the Debye relaxation time decreases very quickly with increasing temperature. We speculate that the dispersion reflects an internal disorder of the sample and that this is the same mechanism responsible for a low-frequency light scattering observed in LiTaO₃ two decades ago.³

II. THEORETICAL REVIEW

The theory presented to describe the central peak line shape was reviewed by Fally, Schranz, and Havlik,⁴ who presented an alternative theory for the effect. In fact the two

theories are equivalent and the equivalence of both differ only in the boundary conditions imposed to the sample. To show this we have first to describe in more detail the thermodynamics foundations of the theory in Ref. 1, in order to clarify points which were not clear to the authors of Ref. 4 and may be also confusing to other readers. By doing this we also demonstrate the complete generality of the theory, avoiding unnecessary approximations and suppositions, as for example, the supposition that the Landau theory of phase transitions is applicable.

The Gibbs free energy per unit volume of a dielectric material is given by

$$dG = -SdT - DdE, \quad (1)$$

where S is the entropy density, T is the temperature, D is the electric displacement, and E is the electric field. The pyroelectric coefficient is

$$p = -\left(\frac{\partial D}{\partial T}\right)E. \quad (2)$$

The Maxwell relation

$$\left(\frac{\partial S}{\partial E}\right)T = \left(\frac{\partial D}{\partial T}\right)E \quad (3)$$

allows us to write the entropy increment as

$$\Delta S = \frac{C^E}{T} \Delta T - p \Delta E, \quad (4)$$

which leads to

$$\frac{\partial S}{\partial t} = \frac{C^E}{T} \frac{\partial T}{\partial t} - p \frac{\partial E}{\partial t}. \quad (5)$$

Combining Eq. (5) with the diffusion equation

$$\frac{\partial S}{\partial T} = \mathbf{k} \frac{\nabla^2 T}{T}, \quad (6)$$

where k is the thermal conductivity, we obtain

$$\frac{\partial T}{\partial t} = D^E \nabla^2 T + \frac{pT}{C^E} \frac{\partial E}{\partial t}, \quad (7)$$

where $D^E = k/C^E$ is the thermal diffusivity. This is the same as Eq. (5) in Ref. 4.

In Ref. 1, Eq. (7) was solved for the case in which $\partial E/\partial t \approx \delta(t)$. This happens, for example, if a static external field E_0 is switched off at $t=0$. The microscopic modes, including the soft mode, are supposed to be much faster than the thermodynamics relaxation and consequently the system has a sudden uniform temperature increment ΔT_0 at $t=0$. The slow relaxation of the thermodynamics variables, as compared to the microscopic dynamics, is in fact the very foundation of thermodynamics. This is what allows us to integrate the energy related to the microscopic modes into the TS term of the free energy F and hence to consider F as the Lagrangean, as done, for example, in Ref. 4. The temperature increment inside the sample relaxes slowly as a function $\Delta T(\mathbf{r}, t)$ of position and time. This results in a re-

laxation of the polarization $\Delta P(\mathbf{r}, t) = -p \Delta T(\mathbf{r}, t)$. Standard linear-response theory says that

$$\chi(\omega) = -E_0^{-1} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \frac{d}{dt} \Delta \bar{P}(t), \quad (8)$$

where $\Delta \bar{P}(t)$ is the space average of the polarization and $\chi(\omega)$ is the contribution of the pyroelectric effect to the electric susceptibility. As done in Ref. 1, the scale factor in $\chi(\omega)$ can be adjusted at the end because the dispersion step $\chi(0) - \chi(\infty)$ in the susceptibility is $K^T - K^S$.

The function $\Delta P(\mathbf{r}, t)$, and hence also $\Delta \bar{P}(t)$ in Eq. (8), depends on the boundary conditions imposed to the sample. In Ref. 1 the thermal bath was considered as a thermal extension of the sample and hence the diffusivity D was the same inside and outside the sample. This condition is experimentally obtained if, for example, a capacitor is sandwiched between two thick plates of the same material that composes the capacitor. This is also what happens in a sample of disordered material consisting of clusters of ferroelectric domains immersed into paraelectric and/or antiferroelectric domains. This latter situation has been analyzed specifically in a recent work.⁵ For short times $\Delta \bar{P}(t)$ is not very sensitive to the boundary conditions and consequently for high frequencies $\chi(\omega)$ is a kind of universal function in which the real and imaginary parts are equal to each other and proportional to $\omega^{-1/2}$.

Fally, Schranz, and Havlik⁴ solved Eq. (7) for a thin plate of thickness L with both faces $x = \pm L/2$ held at the condition $\Delta T(\pm L/2, t) = 0$ and $E = E_0 L^{-i\omega t}$. This is experimentally attained if the capacitor plate is sandwiched between thick plates of infinite thermal diffusivity. For this boundary condition the solution presented in Ref. 1 is only an approximation and fails at low frequencies, as stated clearly there. As pointed out by Thomas,⁶ the steady-state solution of Eq. (7) in the case is

$$\Delta T(x, t) = \frac{pT}{C^0} \left[1 - \frac{\cosh(kx)}{\cosh(kL/2)} \right] E_0 e^{i\omega t}, \quad (9)$$

where $k = (1-i)(\omega/2D)^{1/2}$, and the susceptibility is

$$K(\omega) = K^S + (K^T - K^S) \frac{\tanh\{[(1-i)/2]\sqrt{\xi}\}}{[(1-i)/2]\sqrt{\xi}}, \quad (10)$$

where ξ is the dimensionless frequency $\xi = \omega L^2/2D$. The compact closed form of $K(\omega)$ given in Eq. (10) is equivalent to the series expansion expression given and checked out by Fally, Schranz, and Havlik.⁴ When the thermal environment of the capacitor has the same thermal diffusivity as its interior, the permittivity $K' + iK''$ is given by¹

$$K'(\omega) = K^S + \frac{K^T - K^S}{2\sqrt{\xi}} [1 - e^{-\sqrt{\xi}} (\cos \sqrt{\xi} - \sin \sqrt{\xi})], \quad (11a)$$

$$K''(\omega) = \frac{K^T - K^S}{2\sqrt{\xi}} [1 - e^{-\sqrt{\xi}} (\cos \sqrt{\xi} + \sin \sqrt{\xi})]. \quad (11b)$$

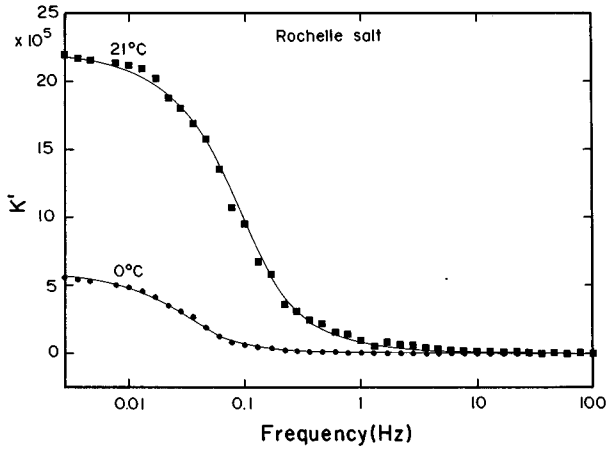


FIG. 1. Dispersion for two temperatures in the ferroelectric phase of a Rochelle salt.

The two forms of the permittivity function have the same behavior at high frequencies $\xi \gg 1$, i.e., the exact boundary conditions are not relevant in this limit.

The strict control of the thermal boundary conditions is a hard experimental problem, because there are not truly good thermal conductors or insulators. Theoretically, $K(\omega)$ in Eq. (10) holds when the capacitor is sandwiched between two thick plates of infinite thermal diffusivity and $K(\omega)$ in Eqs. (11) holds if the plates have the same thermal diffusivity as the capacitor. In both cases we are neglecting the interface (Kapitza) resistance between the capacitor and the plates. If the resistance is considerable, then another term in the form of a Debye relaxation must be added to $K(\omega)$ in Eqs. (10) and (11).

III. EXPERIMENTS AND RESULTS

The real and imaginary parts of the dielectric permittivity function were measured by the capacitive method. The sample was in a cryostat (furnace) sandwiched between plates of copper. The temperature stability was better than 0.1 K. The samples were made almost single domain by poling under electric-field bias above 100 V/mm and a cooling rate of about 2 K/min. All the crystals, except BaTiO₃ and LiTaO₃, were grown by water solution at room temperature or a little above. These two oxides were crystals of unknown provenance. All samples were colorless and transparent.

A. Rochelle salt

Figure 1 shows the dispersion curves of the Rochelle salt for two temperatures in the ferroelectric phase. The CP disappears completely in the paraelectric phase. Its intensity depends on the electric-field bias used for the poling: the higher the field, less intense is the CP. The intensity is always orders of magnitude higher than the theoretical values $K^T - K^S$ in Eqs. (10), (11). Figure 2 shows the dispersion for a completely polidomain sample p (zero-field bias) and for an almost monodomain sample (bias of 250 V/mm). It is seen that the intensity of the polidomain sample is more than one order of magnitude higher than for the monodomain sample. The decrease of the CP intensity for better poled

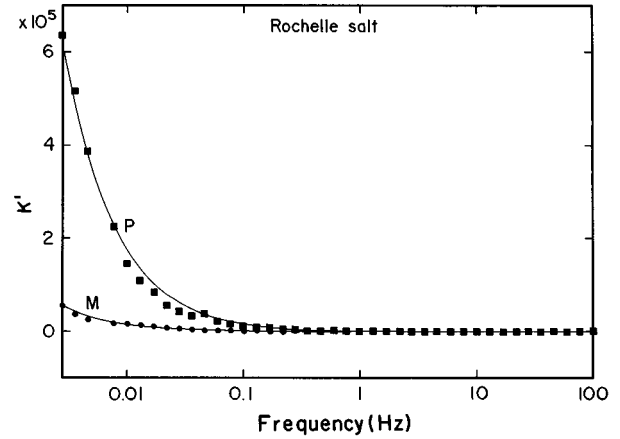


FIG. 2. Dispersion for a completely polidomain sample P (zero-field bias) and for an almost monodomain sample M (bias of 250 V/mm).

samples was also observed in TGS, KDP, and BaTiO₃, and no tests were made in LiTaO₃.

The solid lines in Figs. 1 and 2 are best fits with the formula in Eq. (11a). The fit with the real part in Eq. (10) was much less satisfactory at low frequencies. This is a somewhat intriguing result because the boundary conditions imposed on the sample are closer to the ideal conditions which result in Eq. (10). This result is specific for Rochelle salt. For TGS and BaTiO₃ the data could not discriminate between the real part in Eq. (10) and Eq. (11a), because the CP is too narrow and our measurements did not reach the low-frequency limit where the two formulas for $K(\omega)$ are really distinct. Using the values $C_p = 2.4 \times 10^6$ J/m³ K,⁷ $K = 0.53$ W/m K,⁸ we calculate $\pi/D = 14$ s/mm² and for $L = 1$ mm we have $\tau_{th} = \omega_{th}^{-1} = 14$ s at 21 °C. This is compared with the value in $\tau_{exp} = 27$ s obtained from the fitting of the data in Fig. 1. Hence, we have rather conflicting results: The dispersion can be satisfactorily fitted by the theoretical formula, the characteristic frequency is not out of order with the theoretical value, but the intensity is too high. In Sec. IV, where the results for all crystals are discussed, we present a possible explanation for the high intensity of the CP.

B. TGS

Figure 3 shows the dispersion for TGS at three temperatures in the ferroelectric phase. The solid line represents the best fitting with $K(\omega)$ given by the real part in Eq. (10). Equivalent fitting was also obtained with the use of Eq. (11a). Using the values $C_p = 2.7 \times 10^6$ J/m² K, (Ref. 9) and $K = 0.55$ W/m K,¹⁰ we calculate $\pi/D = 16$ s/mm² at 46 °C. For $l = 0.60$ mm, we have $\tau_{th} = 5.8$ s. This is to compare with the value $\tau_{th} = 2.9 \times 10^2$ s measured from the data in Fig. 3. These data were taken just after poling the sample under a bias of 100 V/mm. The intensity of the CP decreases with the time elapsed after poling. The effect is more pronounced if the sample is kept near the ferroelectric transition but is observed also at RT if longer waiting times are allowed. The time variation of the CP intensity in TGS is reported in detail in a separate publication.¹¹

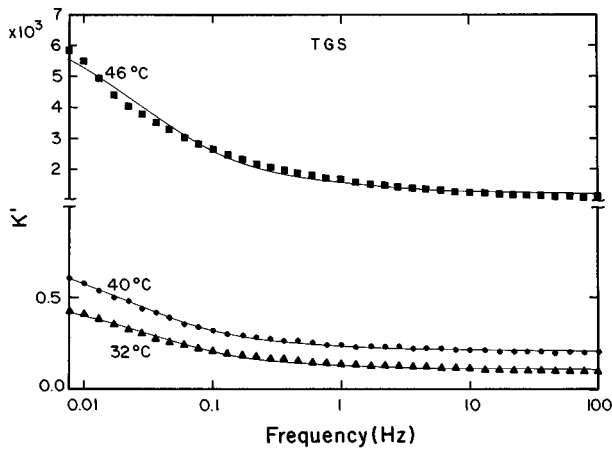


FIG. 3. Dispersion for TGS at three temperatures in the ferroelectric phase.

C. BaTiO₃

Figure 4 shows the dispersion for BaTiO₃ at three temperatures in the ferroelectric phase. The solid line represents the best fitting with $K(\omega)$ given by the real part in Eq. (10). Equivalent fitting was also obtained with the use of Eq. (11a). Using the values $C_p = 3.1 \times 10^6 \text{ J/m}^2 \text{ K}$,¹² $K = 8 \text{ W/m K}$,¹³ we calculate $\pi/D = 1.3 \text{ s/mm}^2$ at 120 °C. The theoretical characteristic times $\tau_{th} = \pi L^2/D$ are much smaller than the characteristic times obtained from the measured dispersion in three samples of different thickness. Also, we have observed that the measured characteristic times have small dependence on the sample thickness, in conflict with the theoretical prediction.

D. KDP

Figure 5 shows the dispersion for KDP at five temperatures in the ferroelectric phase. Distinctly from what has been found in the other materials, the dispersion does not have a characteristic frequency. In the frequency range 2 mHz–100 Hz, the data can be well approximated by $K'(\omega) - K'(\omega_0) = A \log_{10}(\omega/\omega_0)$. The constant A (the slope of the curves) is the same for all temperatures, within the experimental error.

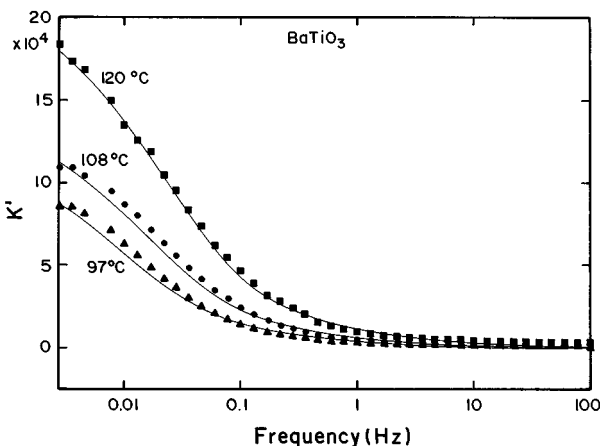


FIG. 4. Dispersion for BaTiO₃ at three temperatures in the ferroelectric phase.

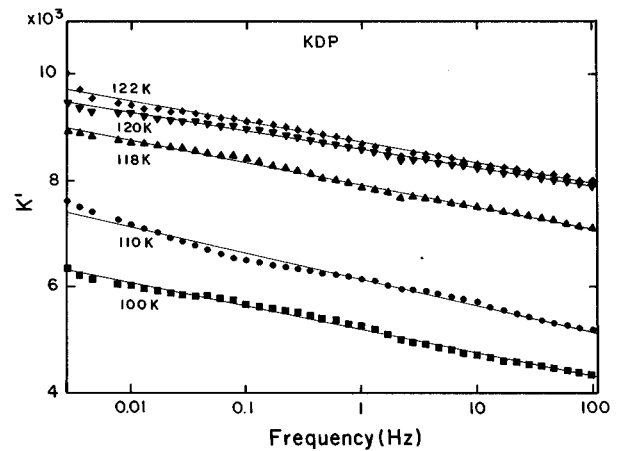


FIG. 5. Dispersion for KDP at five temperatures in the ferroelectric phase.

E. LiTaO₃

Figure 6 shows the dispersion for LiTaO₃ at temperatures much below the ferroelectric phase transition at 665 °C. The sample was a clear single-domain plate taken from a pyroelectric detector. The solid lines are fits with a Debye relaxation function $K(\omega) - K(\infty) = A/(1 + i2\pi f\tau_D)$. It is very questionable whether what is seen in the figure is related to the heat diffusion CP. Apparently we are too far from the phase transition to observe that effect. Attention is called to the fact that the characteristic time τ_D varies quickly with temperature. This is also in clear contrast with the observation in the other materials. Figure 7 shows a plot of $\log_{10} \tau_D$ as a function of $1/T$; it is seen that τ_D varies even faster than what is expected by the Arrhenius law. A Debye relaxation process had also been observed by Raman scattering in LiTaO₃ near the ferroelectric phase transition with

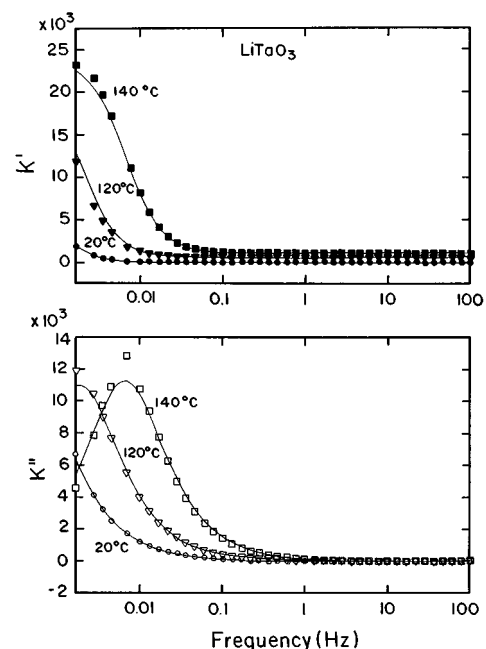


FIG. 6. Dispersion for LiTaO₃ at three temperatures much below ferroelectric phase transition at 665 °C.

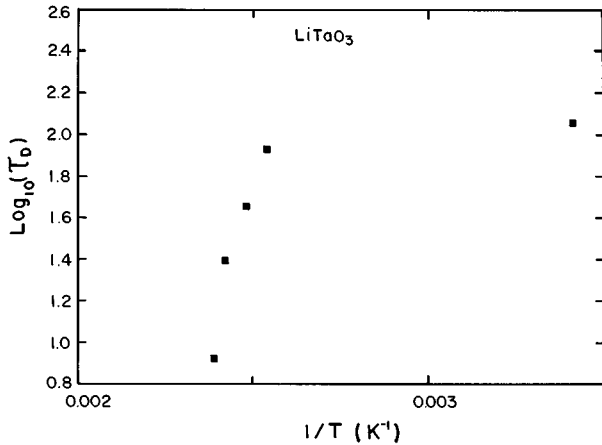


FIG. 7. Plot of $\log_{10} \tau_D$ as a function of $1/T$.

relaxation times on the order of 10^{-12} s.⁶ We advance the very speculative idea that the two processes are the same.

IV. DISCUSSION

It is clear that the thermal diffusion CP arising from the pyroelectric effect is not sufficient to account for the data in any of the materials covered by this report. In all, except LiTaO_3 , we have certified that the CP disappears completely above the ferroelectric transition. Thus, the crystal's spontaneous polarization is somehow involved in the CP observed in Rochelle salt, TGS, BaTiO_3 , and KDP. It is also important to notice that in all these crystals, except KDP, the dielectric dispersion follows the law theoretically defined for the heat diffusion CP, which strongly suggests that the thermal diffusion mechanism is also involved. Further attention is called to the fact that the intensity of the CP is smaller for samples with more perfect domain orientation.

These findings can be explained if one assumes that parts of the sample, with total volume ΔV , switch polarization following the external exciting field E even though $E \ll E_c$, where E_c is the coercive field. The value of ΔV depends on the intensity of the electric field used for the poling, the rate of cooling and perhaps also on defects which could pin the domains. In these circumstances, the effective polarization ΔP induced by the field is

$$\Delta P = \epsilon_0(K-1)E + P_s \frac{\Delta V}{V}, \quad (12)$$

where P_s is the spontaneous polarization.

Let us consider $E = 5 \times 10^2$ V/m as typically used in our measurements. For BaTiO_3 at 120°C , $K = 300$ (at 100 kHz), $P_s = 0.18$ C m⁻². This means that the second term in ΔP is larger than the first one for $\Delta V > 0.8 \times 10^{-5}$ V. In order to attain the value $K(0) = 1.8 \times 10^{-5}$ shown in Fig. 4, it is necessary to have $\Delta V/V = 5 \times 10^{-3}$. This would be the fraction of the crystal volume that switches with the field. The existence of a fraction of the sample volume that switches polarization is consistent with our observation that the intensity of the CP increases when more intense exciting fields are used. This compliance occurs only at very low frequencies and apparently has never been observed before.

A crucial point in this speculative proposal is to explain why the dispersion simulates the thermal diffusion central peak. This result will appear if the two responses are coupled—as they obviously must be—and if the domain switching is much faster than the thermal diffusion. This phenomenon can be illustrated by using a single model of two coupled Debye relaxation variables. The response of the system in this case is

$$R(\omega) = (a_1 a_2) \begin{pmatrix} 1 + i\omega\tau_1 & -\Delta \\ -\Delta & 1 + i\omega\tau_2 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}, \quad (13)$$

where a_1^2, a_2^2 are the oscillator strengths and Δ is the coupling between the two variables. We obtain immediately, for $\omega\tau_2 \ll 1$

$$R = \frac{a_1^2 + 2a_1 a_2 \Delta}{1 + i\omega\tau_1 - \Delta^2} + \frac{a_2^2(1 + i\omega\tau_1)}{1 + i\omega\tau_1 - \Delta^2}. \quad (14)$$

Equation (14) shows that the strength of the slow variable is enhanced. For $\Delta^2 \ll 1$ the response of the coupled system at low frequency is

$$R = (a_1^2 + a_2^2 + 2a_1 a_2 \Delta)(1 + i\omega\tau_1)^{-1}, \quad (15)$$

which corresponds to an enhanced simple Debye relaxation.

V. CONCLUSION

In Rochelle salt, TGS, BaTiO_3 , and KDP, the low-frequency dispersion of the dielectric permittivity is observed only in the ferroelectric phase and disappears completely above the ferroelectric phase transition. Hence, the spontaneous polarization of the crystal is essential to the phenomenon. The dispersion step, i.e., the intensity of the CP, is much larger than the difference between the isothermal and adiabatic permittivities. It is also larger for multidomain, as compared to almost single-domain samples. For all those crystals, except KDP, the dispersion can be well fitted with the theoretical formulas which result from the heat diffusion process, if we allow the width and intensity of the CP to behave as free fitting parameters. However, the observed CP is systematically narrower than predicted on the basis of the heat diffusivity and the thickness of the sample. In KDP, the permittivity has a very slow logarithmic dependence on the frequency and a characteristic frequency does not appear in the dispersion. This indicates that several scales in time (and probably also in length) are involved in the problem.

Hence, the simple theory, in which the heat diffusion is the only process involved and other “mechanical” phenomena are absent, is not sufficient to explain the observed data. We suggest that clusters of the polarized crystal switch polarization under the action of the exciting electric field and that this mechanical effect couples to the heat diffusion process. This idea cannot be exploited in any detail before a model for the mechanical process is available. The coupled system can have very varied and complex behavior. In the case in which the time involved in the polarization switching is small compared with the heat diffusion process, it is easy to see that the main effect of the coupling is to enhance the intensity of the CP. In summary, the low-frequency dispersion in the dielectric permittivity of ferroelectric systems is a complex phenomenon that is far from being understood.

In LiTaO_3 , much below the ferroelectric phase transition, we observed a Debye relaxation of the polarization which possibly originates from the same mechanism which generates a CP in Raman scattering near the ferroelectric transition.³

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