Defect-mediated relaxation and non-linear susceptibilities of Rochelle salt

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Abstract
The deformable pseudospin Mitsui model is modified in order to take into account interactions of the ordering dipoles of Rochelle salt with dipoles, associated with switchable crystal defects. Using the Glauber-type kinetics of the ordering and defect pseudospins, we calculate the linear, second, and third order dynamic susceptibilities and piezoelectric coefficients of the system. The defect-assisted dispersion of the dynamic characteristics below 1 kHz is described. Behavior of the linear and non-linear susceptibilities close to $T_{C1,2}$ is also satisfactorily described by the presented model.

Keywords: Rochelle salt, non-linear susceptibility, relaxing defects, rigid defects, Mitsui model, internal bias field

1. Introduction
Rochelle salt is a curious system, where the ferroelectric phase exists only in a temperature interval between two second order phase transitions at 255 and 297 K. Its behavior is usually described within a two-sublattice Ising model with an asymmetric double-well potential (Mitsui model [1, 2]) or its deformable versions [3, 4, 5, 6] that take into account the piezoelectric coupling with the shear strain $\varepsilon_4$ and diagonal extensional strains $\varepsilon_1, \varepsilon_2, \varepsilon_3$. Rochelle salt thus serves as a convenient toy model for a theoretical exploration of various physical effects in ferroelectrics with the help of a simple mathematical language, since already the mean field approximation appears to be satisfactory here.

Dynamic dielectric response of Rochelle salt exhibits several dispersions. Those are: related to domain walls motion [7] or central thermal peak [8] (below 1 kHz), piezoelectric resonance [9, 10] (between 10 kHz and 10 MHz), microwave relaxation [11], and the submillimeter (100-700 GHz) resonances [12]. Unruh, Möser, and others also observed a Debye-like relaxation of the dynamic permittivity [13, 14] and piezoelectric coefficient $d_{14}$ [15] of Rochelle salt below 1 kHz both in the paraelectric and ferroelectric phases, which could not be related to the domain-wall motion. It was found to be strongly dependent on the humidity of the atmosphere in which the sample were stored and, therefore, attributed to the influence of lattice defects produced by intake or loss of crystallization water molecules.

Miga et al. [16] recently measured the second and third order dielectric susceptibilities of Rochelle salt. The static values of these characteristics, calculated within the Mitsui model, albeit qualitatively correct, are in a severe quantitative disagreement with the experiment near
the Curie temperatures (we discuss this in detail later). The theoretical curves diverge at $T_{C1,2}$, whereas in experiment the anomalies of the susceptibilities are lowered down and smeared out. It is generally known that the behavior of the physical characteristics of ferroelectrics in the transition regions is strongly affected by the presence of defects in the crystals. Hence, the above-mentioned relaxation below 1 kHz and the observed smearing of the susceptibilities anomalies can be of the same origin and attributed to the defect-induced fields and defect-assisted relaxation in the system.

In the present paper we develop a model that describes both the low-frequency relaxation and the behavior of the linear and non-linear susceptibilities in Rochelle salt. The paper is organized as follows. In Section 2 a short review of the literature on the notion of the defect-induced intrinsic field in ferroelectrics is given. In Section 3 the model is formulated, and its static thermodynamic properties are calculated. In Section 4 we consider dynamics of the system and obtain expressions for the linear and non-linear dynamic susceptibilities and piezoelectric coefficients of Rochelle salt. Numerical calculations are performed in Section 5, and concluding remarks are presented in Section 6.

2. Defect-associated fields. Switchable defects

Ferroelectric crystals may have various defects. We shall deal here mostly with the dipole or polarized defects that cannot migrate over a crystal, but can be reoriented (switched) by external electric field or relax thermally. The notion of the defect-induced internal bias field relies on the assumption that switchable or relaxing defects give rise to a bias field $E_e$, which direction always coincide with the direction of polarization (crystal polarization in the case of a single domain crystal or with domain polarization in the multi-domain case) and which magnitude is proportional to the value of polarization [13]

$$\varepsilon_0 E_e = \varepsilon_0 P.$$  \hspace{1cm} (1)

The linear correlation between the internal bias field $E_e$ of switchable defects and spontaneous polarization has been experimentally confirmed, for instance, for Rochelle salt [13], γ-irradiated TGS [17], and lossy KH$_2$PO$_4$ [18]. Temperature variation of the parameter $A$ in Rochelle salt and its dependence on the value of atmosphere humidity, in which the samples were stored for sufficiently long periods of time, has been explored in [14]. Arlt et al. [19] found the parameter $A$ to be inversely proportional to the dielectric constant of the host ferroelectric material, but their calculations did not take into account the converse effect: a strong dependence of the dielectric constant of the ferroelectrics on the electric field at temperatures close to the Curie point.

Dynamics of the bias field $E_e$ is relaxational, most easily described by the equation [13]

$$-\tau \frac{dE_e}{dt} = E_e - E_{e0}, \hspace{0.5cm} E_{e0} = \frac{A}{\varepsilon_0} P.$$  \hspace{1cm} (2)

The quantity $E_{e0}$, towards which the field $E_e$ is relaxing, is proportional to the momentary value of polarization $P$. Matsubara et al. [20] considered, instead of $E_e$, motion of defects in a two-well potential. For the difference between populations of the two wells they obtained an equation similar to Eq. (2), and the analog of $A$ was found to be inversely proportional to temperature. Existence of relaxing internal bias fields directed along the domain polarization explains, for instance, an anomalous temperature behavior of the coercive field in lossy KH$_2$PO$_4$ [18, 20], as well as the transient double hysteresis loops in various defective ferroelectrics.
The relaxation time $\tau$ has been found \cite{13, 14} to have an Arrhenius behavior $\tau = \tau_0 \exp(\frac{W}{k_B T})$. The activation energy $W$ in Rochelle salt varied between 0.4 and 0.8 eV.

3. The model

The system we consider consists of i) ordering dipoles; ii) switchable defect dipoles, iii) rigid defects, and iv) host lattice.

The ordering dipoles are those responsible for the phase transitions and formation of spontaneous polarization in the crystal. They are described by the deformable Mitsui model \cite{3, 6}, which considers motion of pseudospins $\sigma_{qf} = \pm 1$ in two interpenetrating sublattices $f = 1, 2$ with asymmetric double well potentials and their interactions to the lattice strains and electric fields; $q$ is the unit cell index.

The switchable defect dipoles are believed to be trapped on specific sites within a given unit cell. The switching is a jump-like process between two potential wells. Thus, the orientation of a dipole sitting on the site $i$ in the $q$-th unit cell can be described by the pseudospin operator $S_{qi} = \pm 1$. In the case of Rochelle salt the switchable defects are, most likely, the dipoles formed by water vacancies or interstitials, for samples stored in highly dry or wet atmosphere, respectively.

Rigid dipole defects that cannot be reoriented (or if their reorientation is so slow that it can be ignored on the time scales of the motions of switchable dipoles and of ordering dipoles) are assumed to create a constant bias field $E_b$, directed along the axis of spontaneous polarization (100) and proportional to the concentration of these defects. The transverse components of this field are ignored, and it is taken to be temperature independent. The rigid dipoles can be formed, for instance, by impurity-vacancy complexes, like those observed in doped Rochelle salt \cite{22} and having the relaxation times of the order of 10 min at $T_{C2}$ and $10^3$ min at $T_{C1}$. Another option is that screw dislocations are the source of the constant bias, creating around them a shear stress $\sigma_{4b}$. This stress, just like the longitudinal electric field $E_1$, induces polarization $P_1$ and shear strain $\varepsilon_4$. Since the action of $E_1$ and $\sigma_4$ is equivalent, we can describe the influence of rigid dipoles either via $E_b$ or via $\sigma_{4b}$.

Strictly speaking, if the external bias field conjugate to the order parameter is applied, the second order phase transitions in the system are smeared out. Physical characteristics of the system, such as the dielectric susceptibility or piezoelectric coefficient associated with the order parameter, then have only rounded maxima at temperatures close to the Curie temperatures of a crystal, not placed in a bias field. Nevertheless, we shall call the temperatures of these maxima the Curie temperatures $T_{C1}$ and $T_{C2}$, remembering that those are not truly second order phase transitions.

The total Hamiltonian of the system will be written in the following form

$$H = H_\sigma + H_S + H_{int} + NU_{\text{seed}},$$

(3)

where $H_\sigma$ is the Hamiltonian of the modified Mitsui model \cite{3, 6}.

$$H_\sigma = \frac{1}{2} \sum_{qq'} \sum_{ff'} R_{qq'}^{ff'} \frac{\sigma_{qf} \sigma_{q'f'}}{2} - \Delta \sum_q \left( \frac{\sigma_{q1} + \sigma_{q2}}{2} \right) - \left[ \mu_1 (E_1 + E_b) - 2\psi_4 \varepsilon_4 \right] \sum_q \sum_{f=1}^2 \frac{\sigma_{qf}}{2}. \quad (4)$$

Here the parameter $\Delta$ describes the asymmetry of the double well potential; $\mu_1$ is the effective dipole moment of the ordering pseudospins. The model parameter $\psi_4$ describes the internal field created by the piezoelectric coupling with the shear strain $\varepsilon_4$; $E_1$ is an external longitudinal
electric field. $R_{qq}^{11} = R_{qq}^{22} = J_{qq}$ and $R_{qq}^{12} = R_{qq}^{21} = K_{qq}$ are the potentials of interaction between
the ordering pseudospins, belonging to the same and to different sublattices, respectively.

The second and third terms in Eq. (3) describe interactions of the defect dipoles with the
external and constant bias electric fields, their coupling to the shear strain $\varepsilon_{44}$

$$H_S = - \sum_{qq'} \left[ m_1 (E_1 + E_0) - 2\Psi_4 \xi_4 \right] \frac{S_{qq} X_{qq}}{2},$$

and to the ordering pseudospins $\sigma_{qq'}$

$$H_{\text{int}} = - \sum_{qq'} \sum_{j=1}^2 \sum_{i} \lambda_{ij} S_{ij} \frac{\sigma_{ij} S_{ij}(X_{ij})}{2}.$$

Here summation over $i$ is carried out over the sites that can be occupied by defects in a given
cell; $m_1$ is the dipole moment of a defect dipole; $X_{qq} = 1$ if the defect dipole site is occupied, and
$X_{qq} = 0$ otherwise. $\sum_i (X_{ij}) = c$ is the concentration of the defect dipoles: the average number
of defects per unit cell (two formula units of Rochelle salt). It is assumed to be small, so the
interactions between the defect dipoles, which would be proportional to $c^2$, are not considered.

Finally, the phenomenological part of the Hamiltonian $NU_{\text{seed}}$ is a “seed” energy of the host
lattice of heavy ions which forms the asymmetric potentials for the ordering pseudospins

$$U_{\text{seed}} = \psi_4 \left( E_1 + E_0 \right) - \frac{E_0}{2} \sum_{ij} \epsilon_{ij} e_{ij}^4 (E_1 + E_0)^2 + \frac{v}{2} \sum_{ij} \epsilon_{ij}^2 e_{ij}^2 - v \sum_{ij} \epsilon_{ij}^4 (E_1 + E_0) (T - T_0) e_j.$$

Here $N$ is the number of the unit cells; $E_0$ is the vacuum permittivity; $v$ is the unit cell volume
of the model; $\epsilon_{ij}^4, \epsilon_{ij}^2, \epsilon_{ij}^1, \epsilon_{ij}^0$ are the “seed” constants describing the phenomenological
contributions of the crystal lattice into the corresponding observed quantities.

Using the mean field approximation, we obtain the following expression for the thermodynamic
potential of the system (per one unit cell)

$$g_{2E}(\gamma, \xi) = -4 \sum_{i} \sigma_i \xi_i + U_{\text{seed}} - \frac{2 \ln 2}{\beta} + \frac{J}{4} \gamma + \frac{K}{4} \xi + c \lambda S \xi$$

$$- \frac{1}{\beta} \ln \cosh \frac{\gamma + \beta \xi S + \delta}{2} \cosh \frac{\gamma + \beta \xi S - \delta}{2} - c \ln \cosh \frac{2 \lambda \xi - 2 \Psi_4 \xi_4 + m_1 (E_1 + E_0)}{2},$$

where $\beta = 1/k_B T$, $k_B$ is the Boltzmann constant, $\sigma_i$ are the components of the elastic stress
tensor, and

$$\gamma = \beta \left[ J + K \xi + 2 \psi_4 \xi_4 + \mu_1 (E_1 + E_0) \right], \quad \delta = \beta \left( J - K \xi \sigma + \Delta \right).$$

Here $J$, $K$, $\lambda$ are the Fourier-transforms (at $\mathbf{k} = 0$) of the constants of interaction between the
ordering and defect pseudospins. $J$ and $K$, along with the asymmetry parameter $\Delta$, are taken to be linear functions of the diagonal strains $\xi_i$

$$J \pm K = J_0 \pm K_0 + 2 \sum_{i=1}^3 \psi_i^\pm \xi_i, \quad \Delta = \Delta_0 + 3 \sum_{i=1}^3 \psi_3 \xi_i.$$
For \( J \) and \( K \) such an expansion is equivalent to taking into account the electrostrictive coupling with the diagonal strains. The system behavior is described in terms of the mean pseudospin values

\[
\xi = \frac{\langle \sigma_{q1} \rangle + \langle \sigma_{q2} \rangle}{2}, \quad \sigma = \frac{\langle \sigma_{q1} \rangle - \langle \sigma_{q2} \rangle}{2}, \quad S = \langle S_{qi} \rangle
\]  

(9)

\( \xi \) is the parameter of ferroelectric ordering in the system. They are determined from the saddle point of the thermodynamic potential (6): a minimum of \( g_{2E}^2 \) with respect to \( \xi \) and \( S \) and a maximum with respect to \( \sigma \) are realized at equilibrium. The corresponding equations can be written as

\[
\xi = \frac{1}{2} \left[ \tanh \frac{\gamma + \beta \lambda c S + \delta}{2} + \tanh \frac{\gamma + \beta \lambda c S - \delta}{2} \right],
\]

\[
\sigma = \frac{1}{2} \left[ \tanh \frac{\gamma + \beta \lambda c S + \delta}{2} - \tanh \frac{\gamma + \beta \lambda c S - \delta}{2} \right],
\]

\[
S = \tanh \beta \frac{2 \lambda \xi - 2 \Psi_4 \epsilon_4 + m_1 (E_1 + E_b)}{2}.
\]  

(10)

Note that in the thermodynamic potential (6) and in Eq. (9) \( \xi, \sigma, S, \) and \( c \) are taken to be independent of the unit cell index \( q \), i.e. the spatial fluctuations of the defect concentration and of the pseudospin mean values are ignored.

The stress-strain relations and polarization are derived from the thermodynamic potential

\[
\sigma_i = \frac{1}{v} \left( \frac{\partial g_{2E}}{\partial E_i} \right)_{E_1, \sigma},
\]

\[
\sigma_4 = \xi_0 \epsilon_4 - \psi_4^* \psi_3 + \epsilon_1 \xi + c \Psi_4 \xi,
\]

\[
P_1 = -\frac{1}{v} \left( \frac{\partial g_{2E}}{\partial E_1} \right) = \xi_0 \epsilon_4 + \chi_{11} \xi_0 (E_1 + E_b) + \frac{\mu_1}{v} \xi + c \frac{m_1}{2v} S.
\]  

(11)

Linearizing the last of Eq. (10) and substituting the result into the two first equations, one can see that coupling to the defect dipoles is equivalent to appearance of an additional field \( E_e \), acting on the ordering dipoles

\[
E_e = \frac{\beta \lambda c^2 \xi}{\mu_1}.
\]  

(12)

It is inversely proportional to temperature and proportional to the order parameter \( \xi \) and, if we neglect all the contributions into polarization Eq. (11) other than due to \( \xi \), also to the polarization \( P_1 \). In this case we can relate parameters of our model to the constant \( A \) of Eq. (1), introduced by Unruh et al [13], as

\[
A = \frac{v \epsilon_0 \beta c \lambda^2}{\mu_1^2}.
\]  

(13)

4. Dynamic linear and non-linear susceptibilities of Rochelle salt

We consider a dielectric and piezoelectric response of a thin rectangular \( l_x \times l_z \) plate of a Rochelle salt crystal cut in the (100) plane (0° X-cut, the sample edges parallel to [010] and
[001]), induced by a time-dependent harmonic electric field $E_1 \exp(i\omega t)$. This field gives rise to the shear strain $\varepsilon_4$ at all temperatures, as well as to the diagonal strains $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$ in the ferroelectric phase. Influence of the in-plane extensional vibrational modes associated with $\varepsilon_2$ and $\varepsilon_3$ on the dynamic permittivity of Rochelle salt X-cuts has been explored in detail in [23]. In particular, it was shown that the extensional modes are excited only in the ferroelectric phase (as follows from the system symmetry), and that the lowest piezoelectric resonance frequency is always associated with the shear mode. For the sake of simplicity, in the present consideration the dynamics of the diagonal strains will be ignored.

Dynamics of the strain $\varepsilon_4$ will be described, using classical (Newtonian) equations of motion [24] of an elementary volume

$$\rho \frac{\partial^2 \eta_i}{\partial t^2} = \sum_k \frac{\partial \sigma_{ik}}{\partial x_k},$$

(14)

where $\rho = 1767 \text{ kg/m}^3$ is the crystal density; $\eta_i$ are displacements of an elementary volume along the axis $x_i$; $\sigma_{ik}$ are components of the stress tensor. From here one easily derives that

$$\rho \frac{\partial^2 \varepsilon_4}{\partial t^2} = \frac{\partial^2 \sigma_4}{\partial y^2} + \frac{\partial^2 \sigma_4}{\partial z^2}.$$  

(15)

Dynamics of the ordering and defect pseudospins will be described within the Glauber approach [25]. The kinetic equations for the time-dependent variables $\xi$ and $\sigma$, associated with the ordering pseudospins, read [3]

$$-\alpha \frac{d}{dt} \xi = \xi - \frac{1}{2} \left[ \tanh \frac{1}{2} \left( \gamma + \beta \lambda cS + \delta \right) + \tanh \frac{1}{2} \left( \gamma + \beta \lambda cS - \delta \right) \right],$$

$$-\alpha \frac{d}{dt} \sigma = \sigma - \frac{1}{2} \left[ \tanh \frac{1}{2} \left( \gamma + \beta \lambda cS + \delta \right) - \tanh \frac{1}{2} \left( \gamma + \beta \lambda cS - \delta \right) \right].$$

(16)

Here $\alpha$ is the parameter setting the time scale of this dynamics; its value is usually found by fitting theoretical curves of the permittivity in the microwave frequency range to experiment [3, 4, 26].

For dynamics of the defect pseudospins a similar equation is obtained

$$-\tau \frac{d}{dt} S = S - \tanh \beta \frac{2\lambda \xi - 2\Psi_1 E_4 + m_1 (E_1 + E_b)}{2},$$

(17)

however, with a different time scale parameter $\tau$.

These equations, in fact, describe three different dynamic phenomena: the intrinsic dynamics of the pseudospin subsystem, expected to occur at microwave frequencies, the strain dynamics, yielding the piezoelectric resonances, and the defect-mediated relaxation, expected to occur below 10 kHz. We shall show that all three processes take place in well separated frequency ranges, in particular, that the piezoelectric resonances do not overlap with the defect-mediated relaxation.

We present the dynamic variables $\xi$, $\sigma$, $\varepsilon_4$, $S$, and their linear functions $\gamma$ and $\delta$, Eq. (7) as sums of the equilibrium values and of the fluctuational deviations, while the deviations are taken to be in the form of harmonic waves, e.g.

$$\xi = \xi^{(0)} + \sum_n \xi^{(n)}(y,z) \exp(i\omega t), \quad \xi^{(n)}(y,z) \sim E_{1n}^z,$$

etc. Fluctuations of the diagonal strains $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$ are neglected.
Equations (11), (15)–(17) are expanded in these deviations up to the cubic in $E_{1l}$ terms. Then in these equations the terms proportional to the same power of $E_{1l}$ are collected. For the equilibrium quantities we obtain equations (10) and (11) with $\xi, \sigma, \varepsilon, S$ replaced with their equilibrium values $\xi^{(0)}, \sigma, \varepsilon, S$.

As the constitutive equations are linear, their fluctuation parts of the order of $E_{1l}^n$ for each $n \geq 1$ can be written as

$$
o_{1(l)}^{(n)}(y, z) = \frac{\varphi_{14}}{v} \varepsilon_{14}^{(n)}(y, z) - \frac{\psi_{14}}{v} S^{(n)}(y, z),$$

$$p_{14}^{(n)}(y, z) = \frac{\psi_{14}}{v} \varepsilon_{14}^{(n)}(y, z) + \frac{\mu_1}{v} S^{(n)}(y, z) + \frac{m_1}{2v} S^{(n)}(y, z).$$  \hspace{1cm} (18)

$\delta_{n,1}$ is the Kronecker symbol.

Equations for the strain (15) are linear too, yielding

$$-\rho(n\omega)^2 \varepsilon_{14}^{(n)} = \frac{\psi_{14}}{v} \left( \frac{\partial^2 \varepsilon_{14}^{(n)}}{\partial z^2} + \frac{\partial^2 \varepsilon_{14}^{(n)}}{\partial y^2} \right) + \frac{2\psi_4}{v} \left( \frac{\partial^2 \varepsilon_{14}^{(n)}}{\partial z^2} + \frac{\partial^2 \varepsilon_{14}^{(n)}}{\partial y^2} \right) + \frac{\psi_{14}}{v} \left( \frac{\partial^2 S^{(n)}}{\partial z^2} + \frac{\partial^2 S^{(n)}}{\partial y^2} \right).$$  \hspace{1cm} (19)

We shall also linearize Eq. (17), thus

$$S^{(n)} = \frac{\beta}{2} \frac{2\lambda \varepsilon^{(n)} - 2\Psi_0 \varepsilon_4^{(n)} + m_1 E_{1l} \delta_{n,1}}{1 + i\omega \tau}. \hspace{1cm} (20)$$

Kinetic equations (16) are non-linear and remain so, hence their form is different for different $n$.

### 4.1. Linear characteristics

Linear in $E_{1l}$ part of Eqs. (16) reads

$$-\xi^{(1)}(1 + i\omega) + c_2 \left( \gamma^{(1)} + \beta \lambda \varepsilon^{(1)} + \delta^{(1)} \right) + c_2 \left( \gamma^{(1)} + \beta \lambda \varepsilon^{(1)} - \delta^{(1)} \right) = 0,$$

$$-\sigma^{(1)}(1 + i\omega) + c_2 \left( \gamma^{(1)} + \beta \lambda \varepsilon^{(1)} + \delta^{(1)} \right) - c_2 \left( \gamma^{(1)} + \beta \lambda \varepsilon^{(1)} - \delta^{(1)} \right) = 0,$$  \hspace{1cm} (21)

where

$$c_2 = \frac{1}{4} \left[ 1 - \tanh^2 \frac{\gamma^{(0)} + \beta \lambda \varepsilon^{(0)} \pm \delta^{(0)}}{2} \right].$$  \hspace{1cm} (22)

We shall be mostly interested here in the system behavior in the frequency range below 10 kHz. At these frequencies and with the value of $\alpha \sim 10^{-13} \, \text{c}^{-1}$ chosen to describe the microwave relaxation in Rochelle salt, the terms proportional to $i\omega$ are negligibly small and shall be omitted. The intrinsic dynamics of the ordering pseudospin subsystem becomes irrelevant. The value of $\tau$, on the other hand, will be chosen to describe the possible dispersion of the permittivity below 10 kHz, caused by dynamics of the defect dipoles (Eq. (17)).

From Eqs. (18), (20) and (21) at $n = 1$ we find

$$\xi^{(1)}(y, z) = \frac{\beta [\mu_1 + \Delta_\phi(\omega)]}{2} F_1(\omega) E_{1l} - \beta [\psi_4 + \Delta_\phi(\omega)] F_1(\omega) \varepsilon_{14}^{(1)}(y, z),$$

$$\sigma^{(1)}(y, z) = \frac{\beta [\mu_1 + \Delta_\phi(\omega)]}{2} F_1^*(\omega) E_{1l} - \beta [\psi_4 + \Delta_\phi(\omega)] F_1^*(\omega) \varepsilon_{14}^{(1)}(y, z).$$  \hspace{1cm} (23)
Here

\[
F_1(n\omega) = \frac{\varphi_2 - \Lambda_v(n\omega)\varphi_3}{\varphi_2 - \Lambda_v(n\omega)\varphi_3},
\]

\[
\Lambda_v(n\omega) = \frac{1}{2} \frac{\beta\varepsilon_0}{1 + in\omega\tau}.
\]

Substituting Eq. (23) into Eq. (19), we obtain an equation for the strain \(\varepsilon^{(1)}_4(y, z)\)

\[
-\rho \omega^2 \varepsilon^{(1)}_4 = \frac{\partial^2 \varepsilon^{(1)}_4}{\partial y^2} + \frac{\partial^2 \varepsilon^{(1)}_4}{\partial z^2}.
\]

The boundary condition follows from the assumption that the crystal is traction free at its edges (at \(y = 0, y = l_y, z = 0, z = l_z\), to be denoted as \(\Sigma\)): \(\sigma_{4z}\big|_{\Sigma} = 0\). Using the constitutive equations we get

\[
\varepsilon^{(1)}_4 \big|_{\Sigma} = d^{(1)}_{44}(\omega)E_{1t},
\]

with linear dynamic piezoelectric coefficients and elastic constant given by

\[
d^{(1)}_{44}(\omega) = \frac{e_{14}(\omega)}{c^{(1)}_{44}(\omega)},
\]

\[
e_{14}(\omega) = \varepsilon_0 + \Delta_C(\omega) - \beta [\mu_1 + \Delta_v(\omega)] \frac{\psi_4 + \Delta_\phi(\omega)}{v} F_1(\omega),
\]

\[
c^{(1)}_{44}(\omega) = \varepsilon_0 + \Delta_C(\omega) - \beta [\psi_4 + \Delta_\phi(\omega)]^2 F_1(\omega).
\]

Here

\[
\Lambda_v(n\omega) = \frac{1}{2} \frac{m_1\beta\varepsilon_0}{1 + in\omega\tau}, \quad \Delta_C(n\omega) = -\frac{1}{v} \frac{\beta\varepsilon_0^2}{1 + in\omega\tau}
\]

A solution of Eq. (25) with the boundary condition (26) can be written as

\[
\varepsilon^{(1)}_4 = d^{(1)}_{44}(\omega)E_{1t} \left[ 1 + \sum_{\alpha \beta} \frac{1}{\pi^2(2k + 1)(2l + 1)\omega^2} \frac{\omega^2}{l_t} \sin \frac{\pi(2k + 1)y}{l_y} \sin \frac{\pi(2l + 1)z}{l_z} \right],
\]

where \(\omega_{\alpha \beta}\) are given by equation

\[
\omega_{\alpha \beta} = \sqrt{\frac{c^{(1)}_{44}(\omega_1)\pi^2}{\rho} \left[ \frac{(2k + 1)^2}{l_t^2} + \frac{(2l + 1)^2}{l_z^2} \right]}.
\]

The observable linear dynamic dielectric susceptibility is expressed via the derivative from the polarization averaged over the sample volume

\[
X^{(1)}_{11}(\omega) = \frac{1}{l_y l_z \varepsilon_0} \frac{1}{\varepsilon_0} \frac{\partial}{\partial E_{1t}} \int_0^{l_y} dy \int_0^{l_z} dz F^{(1)}_{11}(y, z) = X_{11}^{(0)} + \frac{\beta\mu_1^2}{2\varepsilon_0} F_1(\omega) + e_{14}(\omega)d^{(1)}_{44}(\omega)R_3(\omega),
\]
with
\[ R_4(\omega) = 1 + \sum_{kl} \frac{64}{\pi^2(2k+1)(2l+1)} \frac{\omega^2}{\omega_{kl}^2 - \omega^2}. \]
It has a resonance dispersion with peaks at frequencies where \( \text{Re}[R_4(\omega)] \to \infty. \)

Figure 1: Temperature dependences of the lowest resonance frequency of the Rochelle salt X-cut with \( l_y = 1.60 \text{ cm}, \ l_z = 2.45 \text{ cm} \). Solid line: the present theory with the defect-mediated relaxation, \( A_0 = 1.1 \cdot 10^{-4}, E_b = 4.5 \cdot 10^3 \text{ V/m}, \tau_0 = 5.95 \cdot 10^{-16} \text{ s}, W = 0.5 \text{ eV}, \) dashed line: the earlier theory [23]. Symbols: experimental points of [9]. The choice of the values of \( A_0 \) and other model parameters is discussed in Section 5.

Figure 1 shows the lowest resonant frequency \( \nu_{00} = \omega_{00} / 2\pi \) of a rectangular Rochelle salt X-cut, calculated within the model without the defect-mediated relaxation [23] and within the present model. Both theories yield identical results for all temperatures except for the very narrow regions around the Curie temperatures. At the transition points the resonant frequency goes to zero in an ideal crystal, whereas in a crystal with defects they do not drop below 10 kHz even for a relatively large sample with \( l_y = 1.60 \text{ cm}, l_z = 2.45 \text{ cm}. \)

Hence, in the frequency range of interest (\( \nu \lesssim 1 \text{ kHz} \)) we have \( \omega_{kl}^2 \gg \omega^2, \) and \( R_4(\omega) \approx 1. \) Therefore, we can ignore the spatial variation of the dynamical variables \( \xi, \sigma, \varepsilon_4. \) In this case \( e_4^{(1)} = d_{14}^{(1)}(\omega)E_{14}; \) the linear dynamic piezoelectric coefficient \( d_{14}^{(1)}(\omega) \) is given by
\[ d_{14}^{(1)}(\omega) = \frac{e_0^{(0)} + \Delta_4(\omega)}{c_{44}^{(0)} + \Delta_4(\omega)} - \frac{\beta \mu'_1(\omega)}{\nu[c_{44}^{(0)} + \Delta_4(\omega)]} [\psi_4 + \Delta_4(\omega)] N(\omega) \varphi_3, \] (31)
whereas the linear susceptibility reads
\[ \chi_{11}^{(1)}(\omega) = \chi_{11}^{(0)}(\omega) + \frac{\beta [\mu'_1(\omega)]^2}{2\nu e_0} N(\omega) \varphi_3, \] (32)
where
\[ N(\omega) = \frac{1}{\varphi_2 - \Lambda_4(\omega) \varphi_3 - \Lambda(\omega) \varphi_3}, \]
\[ \mu'_1(\omega) = \mu_1 + \Delta_4(\omega) - 2 \frac{e_0^{(0)} + \Delta_4(\omega)}{c_{44}^{(0)} + \Delta_4(\omega)} [\psi_4 + \Delta_4(\omega)]], \]
\[ \Lambda(\omega) = \frac{2\beta [\psi_4 + \Delta_4(\omega)]^2}{\nu[c_{44}^{(0)} + \Delta_4(\omega)]}, \]
\[ \chi_{11}^{(0)}(\omega) = \chi_{11}^{(0)} c \frac{\beta \mu'_1(\omega)^2}{4\nu e_0} + \frac{[e_0^{(0)} + \Delta_4(\omega)]^2}{c_{44}^{(0)} + \Delta_4(\omega)}. \] (33)
As one can see, taking into account the influence of switchable defect dipoles led to a frequency-dependent renormalization of almost all constants of the Mitsui model (see Eqs. (13), (33)). However, the role of this renormalization in the system dynamics is minor. The defect-mediated relaxational dispersion of the linear susceptibility $\chi^{(1)}_1(\omega)$ and piezoelectric coefficient $d^{(1)}_{11}(\omega)$ is mostly caused by the term $\Lambda_\delta(\omega)\varphi_3$ in the denominator of $N(\omega)$. The susceptibility dispersion width is roughly given by the expression

$$\Delta \chi^{(1)}_{11} = \frac{\nu \varepsilon_0}{\mu_1} \beta c \Lambda^{2} [\chi^{(1)}_{11}(\infty)]^2 = A[\chi^{(1)}_{11}(\infty)]^2,$$

(34)

where $A$ is given by Eq. (13), and $\chi^{(1)}_{11}(\infty)$ is the susceptibility at frequencies above the defect-mediated dispersion but below the piezoelectric resonances. The dispersion width strongly increases as temperature approaches the transition points. No dispersion is present if $A = 0$, i.e., without interactions between ordering and switchable defect dipoles.

4.2. Non-linear susceptibilities

Quadratic in $E^{(2)}_{li}$ part of the kinetic equations (16) reads

$$\begin{align*}
-\xi^{(2)} + c_3^+ (\gamma^{(2)} + \beta c \Lambda (2) + \sigma^{(2)}) + c_3^- (\gamma^{(2)} + \beta c \Lambda (2) - \sigma^{(2)}) \\
+ c_3^+ (\gamma^{(1)} + \beta c \Lambda (1) + \sigma^{(1)})^2 + c_3^- (\gamma^{(1)} + \beta c \Lambda (1) - \sigma^{(1)})^2 = 0, \\
-\sigma^{(2)} + c_3^+ (\gamma^{(2)} + \beta c \Lambda (2) + \sigma^{(2)}) - c_3^- (\gamma^{(2)} + \beta c \Lambda (2) - \sigma^{(2)}) \\
+ c_3^+ (\gamma^{(1)} + \beta c \Lambda (1) + \sigma^{(1)})^2 - c_3^- (\gamma^{(1)} + \beta c \Lambda (1) - \sigma^{(1)})^2 = 0,
\end{align*}$$

(35)

where

$$c_3^\pm = \frac{1}{8} \left[ \tanh \frac{\gamma^{(0)} + \beta c \Lambda (0) + \sigma^{(0)}}{2} - \tanh \frac{\gamma^{(0)} + \beta c \Lambda (0) - \sigma^{(0)}}{2} \right].$$

The spatial variation of the strain $e_4^{(2)}$ is neglected, and the strain is found from the constitutive equations (18) at $\sigma_4^{(0)} = 0$, instead of Eq. (19).

Using the obtained in the previous subsection $\xi^{(1)}$, $\sigma^{(1)}$, $e_4^{(1)}$, and $S^{(1)}$ to find $\gamma^{(1)}$ and $\sigma^{(1)}$ (see Appendix), we solve the system of equations (18)-(20) and (35) with respect to the second order quantities $\xi^{(2)}$, $e_4^{(2)}$, etc., and from whence obtain the second order dynamic dielectric susceptibility

$$\chi^{(2)}_{111}(\omega) = \frac{1}{2 \varepsilon_0} \left[ \frac{\partial^2 \rho^{(2)}_{li}}{\partial E^{(2)}_{li}} \right] = -\frac{\beta^2 [\mu_1'(\omega)]^2 \mu_1'(2\omega)}{4 \nu \varepsilon_0} N^2(\omega) N(2\omega) K^{(2)}$$

(36)

and piezoelectric coefficient

$$d^{(2)}_{114}(\omega) = \frac{1}{2} \left[ \frac{\partial^2 e^{(2)}_4}{\partial E^{(2)}_{li}} \right] = \frac{\beta^2 [\mu_1'(\omega)]^2}{2 \nu} \left[ \frac{\psi_4 + \Delta_\omega(2\omega)}{\epsilon_3^{(0)} + \Delta c(2\omega)} N^2(\omega) N(2\omega) K^{(2)} \right],$$

(37)

where

$$K^{(2)} = \left[ (1 - \beta \frac{J - K}{4} \lambda_1)^2 + \beta^2 \frac{J - K}{4} \lambda_2^2 \right] (\xi^{(0)} \varphi_3 - \sigma^{(0)} \varphi_3)$$

$$+ 2 \beta \frac{J - K}{4} \lambda_2 \left[ 1 - \beta \frac{J - K}{4} \lambda_1 \right] (\xi^{(0)} \lambda_2 - \sigma^{(0)} \varphi_3).$$
As one can easily verify, $\chi_{111}^{(2)}(\omega)$ and $\sigma_{114}^{(2)}(\omega)$ are different from zero only at $\varepsilon^{(0)} \neq 0$ (non-zero polarization), i.e. in the ferroelectric phase or in presence of an external bias field.

In the similar way we find the third-order susceptibility. Cubic in $E_{11}$ kinetic equations for the spin variables read

\[
\begin{align*}
-\xi^{(3)} + c^{+}_1 (\gamma^{(3)} + \beta \alpha c S^{(3)} + \delta^{(3)}) + c^{-}_2 (\gamma^{(3)} + \beta \alpha c S^{(3)} - \delta^{(3)}) \\
+ 2c^{+}_1 (\gamma^{(1)} + \beta \alpha c S^{(1)} + \delta^{(1)}) (\gamma^{(2)} + \beta \alpha c S^{(2)} + \delta^{(2)}) + 2c^{-}_2 (\gamma^{(1)} + \beta \alpha c S^{(1)} - \delta^{(1)}) (\gamma^{(2)} + \beta \alpha c S^{(2)} - \delta^{(2)}) \\
+ c^{+}_1 (\gamma^{(1)} + \beta \alpha c S^{(1)} + \delta^{(1)})^3 + c^{-}_2 (\gamma^{(1)} + \beta \alpha c S^{(1)} - \delta^{(1)})^3 = 0, \\
-\sigma^{(3)} + c^{+}_1 (\gamma^{(3)} + \beta \alpha c S^{(3)} + \delta^{(3)}) - c^{+}_2 (\gamma^{(3)} + \beta \alpha c S^{(3)} - \delta^{(3)}) \\
+ 2c^{+}_1 (\gamma^{(1)} + \beta \alpha c S^{(1)} + \delta^{(1)}) (\gamma^{(2)} + \beta \alpha c S^{(2)} + \delta^{(2)}) - 2c^{+}_2 (\gamma^{(1)} + \beta \alpha c S^{(1)} + \delta^{(1)}) (\gamma^{(2)} + \beta \alpha c S^{(2)} - \delta^{(2)}) \\
+ c^{+}_1 (\gamma^{(1)} + \beta \alpha c S^{(1)} + \delta^{(1)})^3 - c^{+}_2 (\gamma^{(1)} + \beta \alpha c S^{(1)}) - \delta^{(1)})^3 = 0,
\end{align*}
\]

with

\[
c^{+}_4 = \frac{1}{48} \left[ -2 + \cosh \frac{\gamma^{(0)} + \beta \alpha c S^{(0)} + \delta^{(0)}}{2} \right] \frac{1}{\cosh^2 \frac{\gamma^{(0)} + \beta \alpha c S^{(0)} + \delta^{(0)}}{2}}.
\]

Following the same procedure, we obtain the third order dynamic susceptibility

\[
\chi_{111}^{(3)}(\omega) = \frac{1}{6\varepsilon_0} \frac{\partial^3 \mu_1^0}{\partial E_{11}^3} = -\left[ \frac{\mu'_1(\omega)N(\omega)}{v\varepsilon_0} \right] ^2 \left[ N(\omega)K_1^3(\omega) + K_2^3 \right],
\]

Notations introduced here are given in Appendix.

5. Numerical analysis

The found above dynamic characteristics of Rochelle salt are expressed via the equilibrium values of the order parameters $\varepsilon^{(i)}$, $\sigma^{(i)}$, $S^{(i)}$ and the strains $\varepsilon^{(i)}_E$ ($i = 1 - 4$). Those quantities are calculated by finding extrema of the thermodynamic potential $\mathcal{U}$ and using Eqs. (11). The values of the parameters of the modified Mitsui model $J_0$, $K_0$, $\Delta_0$, $\psi_4$, $\psi_4$, $c_{44}^{(0)}$ and others were chosen in [6,26] by fitting the theoretical pressure dependences of the transition temperatures, as well as the temperature dependences of several dielectric, piezoelectric, and elastic characteristics to experimental data. In particular, the major criterion of the fitting was to get $T_C2 = 297$ K and $T_C1 = 255$ K at ambient pressure. The values of all these parameters except for $\psi_4$ and $c_{44}^{(0)}$ remain unchanged and can be found in [6,26].

Inclusion of the interactions with the defect dipoles into the model alters the transition temperatures in the system, increasing $T_{C2}$, decreasing $T_{C1}$, and widening the ferroelectric phase, which is in agreement with experiment [14] (see fig. 2 and the discussion thereof). Both the constant bias field $E_b$ of the rigid dipoles and the switchable field of the relaxing dipoles act in this way. Since the experimentally observed values of $T_{C2}$ and $T_{C1}$ correspond to real crystals, in which defects are unavoidable, we have to tweak slightly some parameters of the model in such a way that the theory would yield $T_{C2} < 297$ K and $T_{C1} > 255$ K for a perfect crystal and $T_{C2} \approx 297$ K and $T_{C1} \approx 255$ K for crystals with defects. We take $\psi_4 = -748.5$ K and $c_{44}^{(0)} = 1.182 \times 10^{10}$ N/m$^2$ (c.f. $\psi_4 = -750$ K, and $c_{44}^{(0)} = 1.180 \times 10^{10}$ N/m$^2$ for the model without defects [6]).

Also we need to determine the following parameters of the defect-mediated relaxation: $E_b$, $\lambda$, $\Psi_4$, $m_1$, $c$, $r_0$, and $W$. As it has been shown in the previous section, the piezoelectric resonances
do not overlap with the dispersion region of the defect-assisted relaxation. Therefore, the sample dimensions are irrelevant.

If \( m_1 \) and \( \mu_1 \) are the dipole moment of the defect dipoles and host molecules, respectively, then for the dipole-dipole interaction constants we have \( J_0 + K_0 \sim \mu_1^2 \), \( \lambda \sim m_1 \mu_1 \), and for the constants of the piezoelectric coupling of the dipoles to the shear strain \( \varepsilon_4 \) we have \( \psi_4 \sim m_1 \), \( \Psi_4 \sim \mu_1 \). Then we can write that

\[
\frac{\lambda}{J_0 + K_0} \approx \frac{\Psi_4}{\psi_4} \approx \frac{m_1}{\mu_1}.
\]

After such a substitution, the final expressions for the susceptibilities and piezoelectric coefficients contain only a single combination \( \frac{c}{\lambda} \), instead of the four parameters \( \lambda, \Psi_4, m_1, c \). It is, however, more convenient to use the parameter \( A \) instead of \( c \). We need to set its value at the upper transition point (to be denoted as \( A_0 \)). It should also be mentioned that the values of the susceptibilities are not very sensitive to the exact values of \( \Psi_4 \) and \( m_1 \).

The coefficient \( A_0 \) and the constant bias field \( E_b \) are determined by concentrations of switchable and rigid defects, respectively and are, therefore, strongly dependent on the sample prehistory, its quality, etc. So are the relaxation time constant \( \tau_0 \) and the activation energy \( W \). These parameters are to be specified for each sample.

The activation energy \( W \) has been experimentally found \([14]\) to vary between 0.4 and 0.8 eV, depending on the sample. To ascertain its value in each particular case, we would need data on the susceptibility dispersion at two different temperatures for each sample, preferably near the lower and upper transition points, unfortunately not always available. We take \( W = 0.5 \) eV in all cases. At this value of \( W \) the relaxation time \( \tau \) increases by two orders of magnitude on cooling from the upper to the lower Curie temperature, in agreement with experiment \([13]\).

The parameters \( A_0 \), \( E_b \), and \( \tau_0 \) are found by fitting to the frequency dependence of the linear susceptibility, or to the Cole-Cole curves of susceptibility and linear piezoelectric coefficient, or to the temperature curves of the linear and non-linear susceptibilities. Note that at frequencies below and above the defect-mediated dispersion, the susceptibilities do not depend on \( \tau_0 \) or \( W \).

Figure 2 compares the calculated dependences of the transition temperatures on the parameter \( A_0 \sim c \) in absence of rigid defects \( (E_b = 0) \) with the experimental dependences of \( T_{C1,2} \) on the humidity of the storage atmosphere. Overall, a good quantitative agreement is obtained, although the experimental \( T_{C1,2} \) vs humidity dependences are non-linear. This discrepancy stems from the assumed here linear dependences of \( A_0 \) and the switchable defect concentration \( c \) on the changes in the humidity, while the experimental results \([14]\) indicate some non-linearity.

The frequency variation of the linear permittivity and loss angle of Rochelle salt just above the upper Curie temperature is shown in fig. 3. The Cole-Cole diagrams of the linear permittivity and piezoelectric coefficients are given in fig. 4. As one can see, behavior of the dielectric and piezoelectric characteristics, driven by the dynamics of switchable defects, has a typical relaxational character and is well described by the present theory. The dispersion width and the imaginary part of \( d_{14}^{(1)}(\omega) \) are, however, slightly smaller than experimentally observed. Because of the Arrhenius behavior of the relaxation time \( \tau \), the dispersion region is shifted to lower frequencies, as temperature decreases.

In figures 5-7 we plot the temperature dependences of the linear, second, and third order dynamic susceptibilities of Rochelle salt at different frequencies. The theory is compared to the experimental data of \([16]\), which have been obtained simultaneously for all three susceptibilities and have, therefore, be described consistently, using a single set of \( A_0, E_b, \tau_0, W \). We do not
Figure 2: Dependence of the transition temperatures on the concentration of switchable defects \((c \sim A_0)\) and on the storage atmosphere humidity. Lines: the present theory; \(E_0 = 0\). Symbols: experimental points of \[14\].

Figure 3: Frequency dependences of the real part of permittivity and loss angle of Rochelle salt at 297.25 K (1) and 254.3 K (2). Lines: the present theory; \(A_0 = 8 \cdot 10^{-5}, E_b = 6.2 \cdot 10^3\) V/m, \(\tau = 4 \cdot 10^{-4}\) s at 297.25 K and \(4.4 \cdot 10^{-2}\) s at 254.3 K \((\tau_0 = 5.95 \cdot 10^{-16}\) s, \(W = 0.5\) eV). Symbols: experimental points of \[21\].

expect to obtain any quantitative description of experiment in the ferroelectric phase, where the domain contributions, not included into our model, are predominant.

The dashed lines correspond to static susceptibilities of a perfect crystal without defects \((A_0 = 0, E_b = 0)\). Their behavior is typical for ferroelectrics with the second-order phase transitions and agrees with the predictions of the Landau theory \[27\], where all three susceptibilities actually diverge at the Curie temperature. A quantitative agreement with experimental data in the transition regions, however, is poor.

On the other hand, the dynamic susceptibilities, calculated for a crystal with defects \((A_0 \neq 0, E_b \neq 0, \text{solid lines})\), are in a much better agreement with experiment. For \(\chi_{11}^{(1)}\) and \(\chi_{1111}^{(3)}\) a very good fit is obtained, especially near \(T_{C2}\), whereas for \(\chi_{11}^{(2)}\) the agreement is still not satisfactory. The non-zero values of the second order susceptibility \(\chi_{1111}^{(3)}\) in the paraelectric phases are caused by the bias field of the rigid defects \(E_b\). The observed smearing of the anomalies is caused both by the bias field \(E_b\) and by the relaxational dispersion owing to the switchable defects. At temperatures far from the transition points the dispersion width is small (see Eq. \(34\)), and the influence of the constant bias field is minor; hence, the susceptibilities of crystals with and
Figure 4: Cole-Cole diagrams of the linear permittivity $\chi_{11}^{(1)}$ at 298.14 K (left) and piezoelectric coefficient $d_{31}^{(1)}$ at 298.15 K (right). Lines: the present theory; $A_0 = 4.7 \cdot 10^{-5}$, $E_b = 2.8 \cdot 10^3$ V/m, $\tau = 6.75 \cdot 10^{-4}$ s ($\tau_0 = 9.95 \cdot 10^{-16}$ s, $W = 0.5$ eV). Symbols: experimental points of [15] for 298.15 K.

without defects are practically the same.

Figure 5: Temperature dependence of the real part of the linear permittivity $\chi_{11}^{(1)}$ of Rochelle salt at 1 kHz. Insert: $\chi_{11}^{(1)}$ vs $T$ in the vicinity of the upper transition point at 0 Hz, 0 Hz, 100 Hz, 200 Hz, and 1 kHz (frequency increases along the arrow). Lines: the present theory; solid lines: $A_0 = 1.1 \cdot 10^{-4}$, $E_b = 4.5 \cdot 10^3$ V/m, $\tau_0 = 5.95 \cdot 10^{-16}$ s, $W = 0.5$ eV; dashed lines: $A = 0$, $E_b = 0$ (an ideal crystal). Symbols: experimental points of [16] for 1 kHz.

The best agreement with experimental data for different samples, as illustrated in figs. [17] is obtained when the bias field $E_b$ is in the range $10^3 \div 10^4$ V/m, which seem to be reasonable values, and when $A_0$ is in the range $4 \cdot 10^{-5} \div 3 \cdot 10^{-4}$, which accords well with the results of [13, 14].

6. Concluding remarks

We propose a model that considers interactions of the ordering dipoles of a ferroelectric with dipoles, associated with crystal defects that can be switched by the external electric field. As an example of the ferroelectric, the Rochelle salt is taken, for which the deformable pseudospin Mitsui model is used. The calculated shifts of the transition temperatures with increasing defect concentration are in a good agreement with experimental observations. Assuming the Glauber-type kinetics of both ordering and defect pseudospins, we calculate the linear, second, and third order dynamic susceptibilities and piezoelectric coefficients of the system.
The presented general scheme of taking into account the defect-mediated relaxation can be easily generalized to other order-disorder ferroelectrics, described by pseudospin models (e.g. of the K\textsubscript{H}\textsubscript{2}PO\textsubscript{4} family).

Dispersion of the dynamic characteristics below 1 kHz, caused by dynamics of the relaxing defects, is described; a satisfactory agreement with experiment is obtained. The influence of the defect-mediated dynamics on the physical characteristics of Rochelle salt is essential in the vicinities of the transition points, whereas far from these temperatures the role of this dynamics is minor. Behavior of the linear and non-linear susceptibilities close to $T_{C1,2}$ cannot be satisfactorily described without taking into account of this dynamics and of the constant bias field of the rigid defects.

Note that the calculations were performed within the mean field approximation; in particular, spatial fluctuations of defect concentration were neglected. For instance, it might be expected that the concentration of water vacancies/interstitials is larger in the near-surface regions of crystal samples. Possibly this is one of reasons for the remaining discrepancies between theory and
experiment for the second-order dielectric susceptibility $\chi^{(2)}_{111}$.

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Appendix

Notations introduced in Eq. (23) are

$$F_{\sigma}^\sigma(\omega) = -\frac{\lambda_2}{\varphi_2 - \Lambda_\varphi(\omega)\varphi_3},$$

$$\varphi_2 = 1 - \frac{\beta J}{2} \lambda_1 + \frac{\beta^2}{16} J^2 - K^2 \left(\lambda_1^2 - \lambda_2^2\right), \quad \varphi_3 = \lambda_1 - \frac{\beta(J - K)}{4} \left(\lambda_1^2 - \lambda_2^2\right),$$

$$\lambda_1 = 1 - (\varepsilon^{(0)})^2 - (\sigma^{(0)})^2, \quad \lambda_2 = 2\varepsilon^{(0)}\sigma^{(0)}.$$
The intermediate results for the order parameters, strains, and their linear combinations are

\[ \xi^{(1)} = \beta \mu_1'(\omega)N(\omega) \frac{\partial^3}{2} E_{1r}, \]

\[ \gamma^{(1)} + \beta \lambda c S^{(1)} = \beta \mu_1'(\omega)N(\omega) \left[ 1 - \frac{\beta(J - K)}{4} \lambda_1 \right] E_{1r}, \]

\[ \alpha^{(1)} = -\beta \mu_1'(\omega)N(\omega) \frac{\lambda_2}{4} E_{1r}, \]

\[ \delta^{(1)} = -\beta \mu_1'(\omega)N(\omega) \frac{\beta(J - K)}{4} \lambda_2 E_{1r}, \]

\[ \xi^{(2)} = -\frac{\beta^2}{4} \left[ \mu_1'(\omega) \right]^2 N^2(\omega)N(2\omega)K^{(2)} E_{1r}, \]

\[ \xi_r^{(2)} = \frac{\beta^2}{2} \left[ \mu_1'(\omega) \right]^2 N^2(\omega)N(2\omega)K_r^{(2)} E_{1r}, \]

\[ \gamma^{(2)} + \beta \lambda c S^{(2)} = -\frac{\beta^2}{2} \left[ \mu_1'(\omega) \right]^2 N^2(\omega)N(2\omega)Z(2\omega)K^{(2)} E_{1r}, \]

\[ \alpha^{(2)} = \frac{\beta^2}{4} \left[ \mu_1'(\omega) \right]^2 N^2(\omega)N(2\omega)K_r^{(2)} E_{1r}, \]

\[ \delta^{(2)} = \frac{\beta^2}{2} \frac{J - K}{2} \left[ \mu_1'(\omega) \right]^2 N^2(\omega)N(2\omega)K_r^{(2)} E_{1r}, \]

Notations used in the expression for the third order susceptibility are

\[ K_1^{(2)}(2\omega) = \frac{1}{8} (\xi^{(0)} + \sigma^{(0)})(\lambda_1 - \lambda_2) \left[ 1 - \frac{\beta(J - K)}{4} \lambda_1 \right] \]

\[ \times \left[ Z(2\omega) K^{(2)} - \beta \frac{J - K}{4} K_r^{(2)} \right] - \frac{1}{8} (\xi^{(0)} - \sigma^{(0)})(\lambda_1 + \lambda_2) \left[ 1 - \frac{\beta(J - K)}{4} \lambda_2 \right] \]

\[ \times \left[ Z(2\omega) K^{(2)} + \beta \frac{J - K}{4} K_r^{(2)} \right] \]

\[ K_2^{(2)} = -\frac{1}{48} [2 - 3(\lambda_1 + \lambda_2)](\lambda_1 + \lambda_2) \left[ 1 - \frac{\beta(J - K)}{4} \lambda_1 \right]^4 \]

\[ -\frac{1}{48} [2 - 3(\lambda_1 + \lambda_2)](\lambda_1 + \lambda_2) \left[ 1 - \frac{\beta(J - K)}{4} \lambda_2 \right]^4, \]

where

\[ K_r^{(2)} = \left[ (1 - \beta \frac{J - K}{4} \lambda_1)^2 + \beta^2 \left( \frac{J - K}{4} \lambda_1 \right)^2 \lambda_2^2 \right] (\xi^{(0)} \lambda_2 - \sigma^{(0)} \lambda_1 + \sigma^{(0)} Z(2\omega) (\lambda_1^2 - \lambda_2^2)) \]

\[ -2\beta \frac{J - K}{4} \lambda_1 \left[ 1 - \frac{\beta(J - K)}{4} \lambda_1 \right] \sigma^{(0)} \lambda_2 - \xi^{(0)} \lambda_1 + \xi^{(0)} Z(2\omega) (\lambda_1^2 - \lambda_2^2)); \]

\[ Z(2\omega) = \beta \frac{J + K}{4} + \Lambda_4(2\omega) + \Lambda(2\omega). \]