Investigation of ferroelectric order-disorder type compounds with asymmetric double-well potential

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June 18, 2001

Abstract

The Mitsui model for the order-disorder type ferroelectrics is studied within the mean field approximation. The phase diagram of the model is obtained, its dependence on the transverse field is obtained. A scheme of setting the values of the model parameters is proposed; all the dielectric characteristics of Rochelle salt are calculated with the found parameters. Within the Mitsui model we study the physical characteristics of RbHSO₄ type crystals; the found values of the model parameters provide a good description of both dielectric and thermodynamic properties of these compounds.

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1 Introduction

The Mitsui model proposed for description of Rochelle salt turned out to be suitable for description of the dielectric properties of other ferroelectric crystals (for instance of RbHSO$_4$ type) as well. This model is based on the assumption that the ordering structure elements move in double-minima potential wells. Due to the existing in these ferroelectrics internal electric field, directed to the opposite sides at the neighboring sites, this potential is asymmetric. In the case of Rochelle salt, spontaneous polarization is most likely caused by the hydroxyl group (OH)$_3$, whereas in NH$_4$HSO$_4$ and RbHSO$_4$ spontaneous dipole moments are related to ordering of sulphate groups.

For the first time, the pseudospin formalism for the Mitsui model was used in. The values of the effective interaction parameters were found, which enabled a description of certain characteristics of Rochelle salt in the mean field approximation. It should be noted that the Mitsui model can have qualitatively different behavior depending on the values of the parameters; this dependence was explored in. Influence of the model parameters on its thermodynamic properties was analysed; the phase diagram of the model was obtained; a region of possible values of the model parameters suitable for Rochelle salt was found. The dielectric properties of Rochelle salt were studied in within the mean field approximation; however a description of the static dielectric susceptibility and the Curie-Weiss constant was not good. In the Mitsui model was treated within the two-particle cluster approximation; satisfactory results were obtained. On the other hand, in approximations of the interacting chains for the Mitsui model were proposed.

The Mitsui model was also used for description of NH$_4$HSO$_4$ and RbHSO$_4$ crystals. Relaxation dynamics of these compounds was studied in within the mean field approximation. Unfortunately, within the mean field approximation it is impossible to obtain such values of the model parameters which would predict the low-temperature first order paraelectric-ferroelectric phase transition in NH$_4$HSO$_4$ crystals. It was shown that the temperature dependence of polarization in these crystals can be described with the temperature dependent model parameters. A more rigorous theory was developed in, where exact taking into account of interaction between neighboring chains allowed to reproduce the correct temperature dependence of polarization in NH$_4$HSO$_4$.

An important problem is to take into account tunneling of the ordering elements through the potential barrier (a transverse field in the
Hamiltonian of the Mitsui model \[4\]. This problem was studied in \[5, 6, 21, 22, 23\]. In \[6\] the isotopic effect in deuterated Rochelle salt was described by changing tunneling only. In \[21\] the spontaneous polarization and static dielectric susceptibility of the Mitsui model are calculated for several values of tunneling integral; a dynamic susceptibility from the Bloch type equation is obtained.

It should be mentioned that in Rochelle salt a strong piezoelectric effect is present; hence for a correct description of all its characteristics we should take into account an interaction of the ordering structure elements with a phonon subsystem. The pseudospin-phonon interaction was taken into account in \[24, 25\].

The aim of the present paper was to develop a fitting procedure for the ferroelectrics described by the Mitsui model and to find out whether their physical characteristics could be described within the mean field approximation.

2 Thermodynamics of the Mitsui model in the mean field approximation

Let us consider a Hamiltonian of ferroelectrics placed in external electric field and described by the Mitsui model \[4, 5, 6\]:

\[
H = -\frac{1}{2} \sum_f \sum_{ij} J_{ij} S^z_i(f) S^z_j(f) - \sum_{ij} K_{ij} S^z_i(1) S^z_j(2)
- \Delta \sum_i (S^z_i(1) - S^z_i(2)) - \mu E \sum_f S^x_i(f) - \Omega \sum_f S^y_i(f), \quad (2.1)
\]

where \(S^\alpha_i(f) = \frac{1}{2} \sigma^\alpha_i(f)\) is the \(\alpha\)-component of the pseudospin operator, \(J_{ij}\) and \(K_{ij}\) are interactions between the spins of the same and of different sublattices; \(\mu\) is the effective dipole moment of the ordering structure elements; \(\Delta\) is the magnitude of asymmetry of the double-well potential; the transverse field \(\Omega\) characterises a finite height of the potential barrier.

Neglecting quadratic in fluctuations terms, we obtain the corresponding Hamiltonian of the mean field approximation \([3]\):

\[
H = \sum_i \left\{ \frac{J + K}{4} \xi^2 + \frac{J - K}{4} \sigma^2 - \sum_f \left[ E(f) \frac{\sigma^x_i(f)}{2} - \Omega \frac{\sigma^y_i(f)}{2} \right] \right\}, \quad (2.2)
\]

\[
E(1, 2) = \frac{J + K}{2} + \mu E + \left( \frac{K - J}{2} - \Delta \right).
\]
Here $\xi = \langle S_z^i(1) \rangle + \langle S_z^i(2) \rangle$ is the parameter of a ferroelectric ordering, whereas $\sigma = \langle S_z^i(1) \rangle - \langle S_z^i(2) \rangle$ is the parameter of an antiferroelectric ordering; $J, K$ are the Fourier transforms of the interaction constants at $q = 0$.

In order to calculate the partition function, we need to exclude the terms in the Hamiltonian containing the operators $\sigma_i^z(f)$. With the help of the rotation transformation for the spin operators

$$\tilde{\sigma}_i^z(f) = \sigma_i^z(f) \cos \phi_f + \sigma_i^x(f) \sin \phi_f,$$

$$\tilde{\sigma}_i^x(f) = -\sigma_i^z(f) \sin \phi_f + \sigma_i^x(f) \cos \phi_f,$$

(2.3)

where

$$\sin \phi_f = \frac{\Omega}{\sqrt{E^2(f) + \Omega^2}}, \quad \cos \phi_f = \frac{E(f)}{\sqrt{E^2(f) + \Omega^2}},$$

we get the transformed Hamiltonian

$$H = \sum_i \left\{ \frac{J + K}{4} \xi^2 + \frac{J - K}{4} \sigma^2 - \sum_f \sqrt{E^2(f) + \Omega^2} \tilde{\sigma}_i^z(f) \right\}. \quad (2.4)$$

Now we can easily obtain the free energy per site

$$\frac{F}{N} = -\frac{1}{N \beta} \ln \text{Sp} e^{-\beta H} = \frac{J + K}{4} \xi^2 + \frac{J - K}{4} \sigma^2$$

$$- \frac{1}{\beta} \sum_f \ln 2 \cosh \frac{\beta \sqrt{E^2(f) + \Omega^2}}{2}, \quad (2.5)$$

where $\beta = \frac{1}{k_B T}$ is the inverse temperature. In the subsequent calculations it is convenient to use the free energy normalized per $\frac{i + \tilde{J}}{4}$:

$$f = \frac{4}{J + K} \frac{F}{N} = \xi^2 - a \sigma^2 - t \left[ \ln \left( 2 \cosh \frac{K_1}{t} \right) + \ln \left( 2 \cosh \frac{K_2}{t} \right) \right]. \quad (2.6)$$

Here we introduce the notations $K_1 = \sqrt{(\xi - a \sigma + \gamma + e)^2 + \omega^2}$, $K_2 = \sqrt{(\xi + a \sigma - \gamma + e)^2 + \omega^2}$, $a = \frac{K_1 - J}{K_1}$, $\gamma = \frac{2 \Delta}{K_1}$, $t = \frac{\Omega}{K_1}$, $e = \frac{2 \mu E}{K_1}$, $\omega = \frac{2 \Omega}{K_1 + J}$; the parameters with tildes, like $\tilde{J} = J/k_B$, are in temperature units.

Unknown parameters $\xi, \sigma$ are determined from the condition of extremum of the free energy as a function of $\xi, \sigma$. This yields the following system of equations

$$\xi = \frac{1}{2} \left[ \frac{\xi - a \sigma + \gamma + e}{K_1} \tanh \frac{K_1}{t} + \frac{\xi + a \sigma - \gamma + e}{K_2} \tanh \frac{K_2}{t} \right],$$

$$\sigma = \frac{1}{2} \left[ \frac{\xi - a \sigma + \gamma + e}{K_1} \tanh \frac{K_1}{t} - \frac{\xi + a \sigma - \gamma + e}{K_2} \tanh \frac{K_2}{t} \right]. \quad (2.7)$$
Here it is required that its solution \((\xi_0, \sigma_0)\) is a saddle point of the function \(f\), that is, this function should have a maximum in the parameter of an antiferroelectric ordering \(\sigma (\frac{\partial^2 f}{\partial \sigma^2} < 0)\) and a minimum in the parameter of a ferroelectric ordering \(\xi (\frac{\partial^2 f}{\partial \xi^2} < 0)\) [20].

Using the known thermodynamic relations, we can calculate the other thermodynamic functions: entropy

\[
s = \frac{S}{N} = -\frac{1}{N} \frac{dF}{dT} = -k_B \frac{df}{dt} = \ln \left( 2 \cosh \frac{K_1}{t} \right) + \ln \left( 2 \cosh \frac{K_2}{t} \right) - \frac{1}{t} \left( K_1 \tanh \frac{K_1}{t} + K_2 \tanh \frac{K_2}{t} \right),
\]

(2.8)

and internal energy

\[
u = \frac{4}{f + K N} = f + ts = \xi^2 - a\sigma^2 - \sum_f K_f \tanh \frac{K_f}{t}.
\]

(2.9)

To calculate the specific heat

\[
c_v = t \frac{ds}{dt} = t \left\{ \frac{\partial s}{\partial t} + \frac{\partial s}{\partial \xi} \frac{\partial \xi}{\partial t} + \frac{\partial s}{\partial \sigma} \frac{\partial \sigma}{\partial t} \right\}
\]

we need to solve the system of equations for \(\frac{\partial \xi}{\partial t}\) and \(\frac{\partial \sigma}{\partial t}\):

\[
2 \frac{\partial \xi}{\partial t} = \left( \frac{\partial \xi}{\partial t} - a \frac{\partial \sigma}{\partial t} \right) M_1 - N_1 + \left( \frac{\partial \xi}{\partial t} + a \frac{\partial \sigma}{\partial t} \right) M_2 - N_2,
\]

\[
2 \frac{\partial \sigma}{\partial t} = \left( \frac{\partial \xi}{\partial t} - a \frac{\partial \sigma}{\partial t} \right) M_1 - N_1 - \left( \frac{\partial \xi}{\partial t} + a \frac{\partial \sigma}{\partial t} \right) M_2 + N_2,
\]

where \(M_i = \frac{1}{K_i^2} \left( \frac{K_i^2 - \omega^2}{t \cosh^2 \frac{K_i}{t}} + \omega^2 \frac{K_i}{t} \tanh \frac{K_i}{t} \right),\) \(N_i = \sqrt{\frac{K_i^2 - \omega^2}{t^2 \cosh^2 \frac{K_i}{t}}} \). Solution of this system reads

\[
\frac{\partial \sigma}{\partial t} = \frac{N_2 (M_1 - 1) - N_1 (M_2 - 1)}{(M_1 - 1)(1 + aM_2) + (M_2 - 1)(1 + M_1)};
\]

\[
\frac{\partial \xi}{\partial t} = \frac{N_2 (1 + aM_1) + N_1 (1 + aM_2)}{(M_1 - 1)(1 + aM_2) + (M_2 - 1)(1 + M_1)}.
\]

From this we obtain the specific heat:

\[
c_v = t \left\{ \frac{1}{t^2} \left( \frac{K_1^2}{\cosh^2 \frac{K_1}{t}} + \frac{K_2^2}{\cosh^2 \frac{K_2}{t}} \right) - \frac{1 - a}{a} (N_1 + N_2)^2 + 2a (M_2 N_1^2 + M_1 N_2^2) \right\}.
\]

(2.10)
Polarization of a crystal is calculated from the following thermodynamic relations:

\[ P = \frac{\partial F}{\partial E} = \mu N \xi. \]

Experimentally, polarization per unit volume is measured:

\[ p = \frac{P}{V} = \mu \xi \frac{1}{v}, \quad (2.11) \]

where \( v \) is the unit cell volume. Hence, the static susceptibility is obtained in the following form:

\[ \chi = \frac{dp}{dE} = \frac{2 \mu^2}{v} \frac{1}{k_B(K + J)} \frac{d\xi}{de}, \quad (2.12) \]

where \( \frac{d\xi}{de} = \frac{M_2(1 + aM_1)}{(1 - M_1)(1 + aM_2) + (1 - M_2)(1 + aM_1)}. \)

If we neglect tunneling (\( \Omega = 0 \)), the expressions for the thermodynamic quantities and the system of equations for \( \xi \) and \( \sigma \) simplify. The system of equations for the order parameter now reads:

\[ \xi = \frac{1}{2} \left[ \tanh \frac{K_1'}{t} + \tanh \frac{K_2'}{t} \right], \]

\[ \sigma = \frac{1}{2} \left[ \tanh \frac{K_1'}{t} - \tanh \frac{K_2'}{t} \right], \quad (2.13) \]

where \( K_1' = \xi - a \sigma + \gamma + e, \ K_2' = \xi + a \sigma - \gamma + e. \)

The expressions for the thermodynamic functions simplify as well. Entropy:

\[ s = \ln \left( 2 \cosh \frac{K_1'}{t} \right) + \ln \left( 2 \cosh \frac{K_2'}{t} \right) - \frac{1}{t} \left[ 2(\xi + e)\xi - 2(a \sigma - \gamma)\sigma \right], \quad (2.14) \]

internal energy:

\[ u = -(\xi + 2e)\xi + (a \sigma - 2\gamma)\sigma. \quad (2.15) \]

### 3 Phase diagram of the Mitsui model

It could be easily verified that the Hamiltonian and thermodynamics functions of the Mitsui model can be expressed via the dimensionless parameters \( a, \gamma, t, e, \omega \). Depending on the values of these parameters, the model has different types of temperature behavior.
the case $\Omega = 0$ ($\omega = 0$).

In order to explore the phase diagram in this case we use the scheme proposed by Vaks \[5\]. To find possible second order phase transitions in the system, we expand the system (2.13) in $\xi$ up to the linear terms:

$$
\xi = \left(1 - \tanh^2 \frac{-a\sigma + \gamma}{t}\right) \frac{\xi}{t},
$$

$$
\sigma = \tanh \frac{-a\sigma + \gamma}{t}.
$$

(3.1)

We obtain a system of equations for temperature of the second order phase transition. From the second equation we find that $t = \frac{-a\sigma + \gamma}{\text{arcth}\sigma}$ and reduce (3.1) to a single equation for $\sigma$:

$$
\frac{-a\sigma + \gamma}{\text{arcth}\sigma} = 1 - \sigma^2.
$$

(3.2)

Let us introduce the notation $\sigma = \tanh \alpha$ and rewrite this equation as

$$
f(\alpha) = -\gamma + a\tanh \alpha + \alpha(1 - \tanh^2 \alpha) = 0,
$$

(3.3)

$\alpha$ varies from 0 to $\infty$; the values of $f(\alpha)$ in the limiting points are $f(\alpha = 0) = -\gamma$, $f(\alpha \to \infty) = -\gamma + a$. Since

$$
f'(\alpha) = \frac{\partial f}{\partial \alpha} = (a + 1 - 2\alpha \tanh \alpha)(1 - \tanh^2 \alpha)
$$

(3.4)

is a monotonic function, it turns to zero only at one point $\alpha_0$ and has an extremum at this point.

Let us consider the case $\gamma > a$ ($f(\alpha \to \infty) < 0$). The $f(\alpha)$ is an increasing function at small $\alpha$ and a decreasing one at large $\alpha$. Hence, it has a maximum at certain $\alpha_0$. If $f(\alpha_0) < 0$, the model cannot undergo the second order phase transitions, whereas at $f(\alpha_0) > 0$ there could be two phase transitions in the system. The line on the phase diagram ($a, \gamma$), separating these two characteristic types of behavior (with two phase transitions and with none) is determined from the following system of equations

$$
f(\alpha_0) = -\gamma + a\tanh \alpha_0 + \alpha_0(1 - \tanh^2 \alpha_0) = 0,
$$

$$
f'(\alpha_0) = (a + 1 - 2\alpha_0 \tanh \alpha_0)(1 - \tanh^2 \alpha_0) = 0.
$$

(3.5)

An equation for this line can be written in implicit form

$$
\frac{\gamma + \sqrt{\gamma^2 + 1 - a^2}}{2} \tanh \frac{\gamma + \sqrt{\gamma^2 + 1 - a^2}}{2} = \frac{a + 1}{2}.
$$

(3.6)
On increasing $a$, when $a = \gamma$ one of the second order phase transitions disappears, and the system goes to the region with a single second order phase transition. At $T = 0$ the system can be in two states: the ordered ($\xi = 1$, $\sigma = 0$) or anti-ordered ($\xi = 0$, $\sigma = 1$) one. Which of the two states is realised depends on the corresponding energies

$$U(\xi = 1, \sigma = 0) = 1, \quad U(\xi = 0, \sigma = 1) = a - 2\gamma. \quad (3.7)$$

In the region

$$a - 2\gamma > 1 \quad (3.8)$$

the system is in the ordered ground state since its energy is the lowest, whereas in the region

$$a - 2\gamma < 1$$

the system is in the disordered state.

The phase diagram of the model is depicted in fig.3.1. The line $AB$ corresponds to the case $a = \gamma$, $CED$ corresponds to equation (3.6), $CEB$ corresponds to conditions (3.7) and (3.8). According to the obtained above results, in the region V of the model parameters values, the ferroelectric order in the system is absent at any temperature. In the region IV the ground state of the system in not ordered ($\xi = 0$); however, here two phase transitions with the order parameter $\xi$ are possible. This means that $\xi \neq 0$ in a limited interval of temperatures, as shown in fig.3.2 for $a = 0.5$, $\gamma = 0.77$. In the region II the system still can undergo two second order phase transitions, but its ground state is ordered. In this region several types of the system behavior are possible; they will be considered later. In the region I the system undergoes a single first order phase transition. We fail to obtain simple expressions for temperature of this transition and restrict our consideration by numerical analysis of temperature behavior of $\xi$, in order to find new types of the temperature behavior of the model. The results of this analysis at different $a$, $\gamma$ (along the lines $a = const$ at the phase diagram) are shown in figs.3.2-3.8. We find that in a narrow layer IIa of the region II there emerges an additional first order phase transition at low temperature. The temperature dependence of $\xi$ and other thermodynamic functions of the model in this region is shown in figs.3.4, 3.5 for the curves corresponding to $a = 0.3$, $\gamma = 0.642$. In the region IIb the lower second order phase transition becomes of the first order. Qualitatively, the lines $a = 0.3$, $\gamma = 0.645$ in figs.3.4, 3.5 illustrates the model behavior in this
Figure 3.1. (a) Phase diagram of the Mitsui model.
Figure 3.1. (b) Phase diagram of the Mitsui model.
Figure 3.2: Temperature behavior of $\xi$ at $a = 0.5$ and different values of $\gamma$.

Figure 3.3: Temperature dependence of $(d\xi/de)^{-1}$ at $a = 0.5$ and different values of $\gamma$. 
Figure 3.4: Temperature dependence of $\xi$ at $a = 0.3$ and different values of $\gamma$.

Figure 3.5: Temperature dependence of $(d\xi/de)^{-1}$ at $a = 0.3$ and different values of $\gamma$. 
Figure 3.6: Temperature dependence of $\xi$.

Figure 3.7: Temperature dependence of $\xi$ at $a = -0.3$ and different values of $\gamma$. 
regions. Deeper in the region II, the first order phase transition disappears, because the corresponding transition temperatures become equal ($a = 0.3, \gamma = 0.652$ in figs. 3.4, 3.5). On going from the region III to the region II, the first order phase transition persists up to the boundary of the region IIc. The jump of the order parameter at this boundary turns to zero. At all other points of the phase diagram, the system undergoes a single second order phase transition.

**b) the case $\Omega \neq 0$.** As in the case $\Omega = 0$, in order to find possible second order phase transitions at $\Omega \neq 0$ we expand the system (2.7) in $\xi$ up to the linear terms. After some transformations, it can be presented as

$$
t = \frac{\omega^2 t}{[(\gamma - a\sigma)^2 + \omega^2]^{3/2}} \tanh \frac{\sqrt{(\gamma - a\sigma)^2 + \omega^2}}{t} \frac{\sqrt{(\gamma - a\sigma)^2 + \omega^2}}{t}
$$

$$
+ \frac{(\gamma - a\sigma)^2}{(\gamma - a\sigma)^2 + \omega^2} \left( 1 - \tanh^2 \frac{\sqrt{(\gamma - a\sigma)^2 + \omega^2}}{t} \right),
$$

$$
\sigma = \frac{\gamma - a\sigma}{\sqrt{(\gamma - a\sigma)^2 + \omega^2}} \tanh \frac{\sqrt{(\gamma - a\sigma)^2 + \omega^2}}{t}. 
$$

(3.9)
Excluding $t$, we obtain the system (3.9) in the form $f(\sigma) = 0$, where
\[
\begin{align*}
    f(\sigma) &= \frac{\text{arcth}[\sigma\sqrt{1+\tilde{\omega}^2}(1-\sigma^2(1+\tilde{\omega}^2))]}{1+\tilde{\omega}^2}\left[1 - \sigma^2(1+\tilde{\omega}^2)\right] \\
    &\quad - \sqrt{1+\tilde{\omega}^2} \left[(\gamma - a\sigma) - \frac{\tilde{\omega}^2\sigma}{1+\tilde{\omega}^2}\right].
\end{align*}
\] (3.10)
Here $\tilde{\omega} = \omega/(\gamma - a\sigma)$, $\sigma$ changes from 0 up to $1/\sqrt{1+\tilde{\omega}^2}$. Let us find $f(\sigma)$ in the limiting points
\[
\begin{align*}
    f(\sigma = 0) &= -\sqrt{\gamma^2 + \omega^2} < 0, \\
    f(\sigma = 1/\sqrt{1+\tilde{\omega}^2}) &= -\gamma + a\sigma + \sigma(1-\sigma^2). \\
\end{align*}
\] (3.11)
Hence, the line delimiting the region with a single possible second order phase transition is a solution of the equation $f(\sigma_{max}) = 0$. We obtain the following equation for $a$, $\gamma$:
\[
-\gamma + a\sigma + \sigma(1-\sigma^2) = 0; \quad (3.12)
\]
we also should solve the equation for $\sigma$: $\sigma = 1/\sqrt{1+\tilde{\omega}^2}$. An equation for the line delimiting the regions with two possible second order phase transitions is obtained from the system of two equations $\frac{\partial f(\sigma)}{\partial \sigma} = 0$, $f(\sigma) = 0$. The expression for the derivative $\frac{\partial f(\sigma)}{\partial \sigma}$ is too cumbersome to be presented here. The equations are solved numerically; the calculation results are shown in fig.3.9. The line separating regions with ferroelectric ground state and a disordered ground state is found from the condition
\[
U(\xi \neq 0) = U(\xi = 0). \quad (3.13)
\]
This equation is also solved numerically. The phase diagram of the quantum Mitsui model at the value of tunneling $\omega = 0.4$ is shown in fig.3.9 by dashed lines. From this figure one can see that the boundary of existence of the ordered ground state in raised up and now goes along the line $CE'\,D'$. The line of the two phase phase transitions corresponds to $CE'B'$, whereas the line of a single phase transition corresponds to $A'B'$.

### 4 Thermodynamics of Rochelle salt and deuterated Rochelle salt.

The ordered phase in the Rochelle salt type crystals exists in a certain temperature interval: from $T_1 = 255K$ to $T_2 = 297K$ for a regular
Figure 3.9: The phase diagram of the quantum Mitsui model (solid and dashed lines correspond to $\omega = 0$ and $\omega = 0.4$, respectively.)
Rochelle salt and from $T_1 = 251K$ to $T_2 = 307K$ for deuterated Rochelle salt. The transitions to the ordered phase are of the second order in both crystals. According to the phase diagram (fig.3.1) the possible parameters for Rochelle salt should be taken from the region IV. A difference between the transition temperatures $\delta_{Rs} = (T_2 - T_1)/(T_2 + T_1) = 0.076$ is small; therefore, the feasible values of the parameters for Rochelle salt are close to the line $ED$. In fig.4.1 the line which corresponds to the sets of the theory parameters for Rochelle salt is depicted; above it there lies a line for deuterated Rochelle salt at which $\delta_{dRs} = 0.1$.

The parameters are chosen as follows: for the chosen at the phase diagram values of $a$, $\gamma$, we find such $K$, $J$, $\Delta$ for which the theoretical transition temperatures coincide with the experimental values; the effective dipole moment $\mu$ is chosen such as the theoretical and experimental maximal values of polarization coincide. In figs.4.2-4.5 we plot the examples of calculated polarization and inverse static dielectric susceptibility for Rochelle salt and deuterated Rochelle salt at several different sets of the parameters. One can see, that the best fit for the susceptibility is obtained at the small values of $a$ and $\gamma$ from the curves $Rs$ and $dRs$ (fig.4.1). Hence, the set of the model parameters which provides the best description of temperature behavior of Rochelle salt is: $a = 0.29506, \gamma = 0.648 (K = 1473.59 K, J = 802.12 K, \Delta = 737.33 K)$. The unit cell volume $v = 5.24 \times 10^{-22} \text{cm}^3$ of the model is twice smaller than the real one, since the full unit cell contains four ordering elements, whereas the Mitsui model corresponds only to two ordering elements per unit cell. The effective dipole moment $\mu$ for Rochelle salt is found from the experimental value of polarization is $\mu = 3.04 \times 10^{-18}$. For the deuterated Rochelle salt the best set of the fitting parameters is: $a = 0.29952, \gamma = 0.65 (K = 1502.83 K, J = 8102.07 K, \Delta = 751.69 K, \mu = 3.6 \times 10^{-18})$.

It should be noted that the Rochelle salt was studied in the mean field approximation by other authors too. The parameters values for $Rs$ and $dRs$ obtained in these papers are given in Table 4.1.

In order to explore the character of isotopic effect in Rochelle salt, we studied the influence of transverse field on the thermodynamic properties of the model. Another fitting procedure for the Rochelle salt was to include tunneling into the model with the chosen already parameters for deuterated Rochelle salt, since deuterated mainly decreases the tunneling of the ordering structure elements. The calculation results are shown in figs. 4.6, 4.7. They indicate that it is impossible to describe the present isotopic effect by changing the transverse field only. A thorough
Figure 4.1: The phase diagram of the Mitsui model in region of possible values of the parameters for Rochelle salt.
Table 4.1: The sets of the parameters for regular and deuterated Rochelle salt obtained in the mean field approximation (the sets 4 and 5 are found in the present work).

| No | compound | $K$, K  | $J$, K   | $\Delta$, K | $a$   | $\gamma$ |
|----|----------|---------|----------|--------------|-------|----------|
| 1  | $Rs$     | 1599.84 | 764.64   | 815.9        | 0.353 | 0.69     |
| 2  | d$Rs$    | 1563.84 | 790.85   | 789.7        | 0.328 | 0.671    |
| 3  | d$Rs$    | 1480    | 800      | 740          | 0.298 | 0.649    |
| 4  | $Rs$     | 1473.59 | 802.12   | 737.3        | 0.295 | 0.648    |
| 5  | d$Rs$    | 1502.83 | 810.07   | 751.7        | 0.299 | 0.65     |

Figure 4.2: Temperature dependence of polarization of Rochelle salt at different sets of the model parameters ( ■ are experimental points [2]).
Figure 4.3: Temperature dependence of inverse static dielectric susceptibility of Rochelle salt at different sets of the model parameters (■ are experimental points [2]).

Figure 4.4: Temperature dependence of polarization of deuterated Rochelle salt at different sets of the model parameters (■ are experimental points [2]).
numerical study of transverse field effects on the thermodynamic characteristics of the model has shown that taking into account of tunneling does not improve an agreement between the theory and experiment. For a fixed $\gamma$, an increase in $\omega$ only increases the static susceptibility.

The performed calculations of spontaneous polarization and static dielectric susceptibility for $Rs$ and $dRs$ have shown that it is impossible to find such sets of the microparameters $K$, $J$, $\Delta$, and $\mu$, which would provide a simultaneous good description of both characteristics. Therefore, the statements of other authors that the Mitsui model is adequate to $Rs$ or $dRs$ and properly describes the physical characteristics of these crystals are incorrect. Within the model (2.1) either with tunneling or without it, this is not possible.

5 Relaxation dynamics of $Rs$ and $dRs$.

It has been mentioned in several papers that as indicated by measurements of dielectric dispersion, tunneling effects do not play an important role in Rochelle salt crystals. Therefore, the time correlations are believed to be caused by interaction with a phonon subsystem. A phenomenologic description of this interaction is performed within the
Figure 4.6: Temperature dependence of polarization of Rochelle salt and deuterated Rochelle salt for different sets of the parameters: lines for Rs and dRs correspond to sets of parameters 4, 5 in table 4.1, dashed line is the model with the set of parameters 5 and $\Omega = 50$.

Figure 4.7: Temperature dependence of inverse static susceptibility of Rochelle salt and deuterated Rochelle salt for the same sets of the parameters as in previous figure.
Glauber method \( [32] \). A master equation for \( \xi, \sigma \) in this approach can be presented as \( [9] \):

\[
- \alpha \frac{d}{dt} \xi = \xi - \frac{1}{2} \left[ \tanh \frac{K'_1}{t} + \tanh \frac{K'_2}{t} \right],
\]
\[
- \alpha \frac{d}{dt} \sigma = \sigma - \frac{1}{2} \left[ \tanh \frac{K'_1}{t} - \tanh \frac{K'_2}{t} \right],
\]
(5.1)

where \( \alpha \) is the parameter of the spin-phonon relaxation.

Considering a weakly non-equilibrium system, we expand \( \xi, \sigma \) near their equilibrium values \( \xi, \sigma \):

\[
\xi = \xi + \xi(t), \quad \sigma = \sigma + \sigma(t).
\]

From (5.1) we obtain that \( \xi, \sigma \) satisfy equation (2.13), whereas \( \xi(t), \sigma(t) \) can be found from the following system of equations

\[
- \alpha \frac{d}{dt} \xi(t) = M_{11} \xi(t) + M_{12} \sigma(t) - M_1 e(t),
\]
\[
- \alpha \frac{d}{dt} \sigma(t) = M_{21} \xi(t) + M_{22} \sigma(t) - M_2 e(t),
\]
(5.2)

where

\[
M_{11} = 1 - \frac{1}{2} \left( 1 - \xi^2 - \sigma^2 \right), \quad M_{12} = -\frac{2 \alpha}{t} \xi \sigma, \quad M_{21} = 2 \frac{\xi \sigma}{t}, \quad M_{22} = 1 + \frac{1}{2} \left( 1 - \xi^2 - \sigma^2 \right).
\]

In a frequency representation, a linear response of \( \xi(t) \) to a small field \( e(t) \) is obtained in the following form

\[
\xi(\omega) = \chi_0(\omega) e(\omega),
\]
(5.3)

\[
\chi_0(\omega) = \frac{w_1 \tau_1}{1 + \omega^2 \tau_1^2} + \frac{w_2 \tau_2}{1 + \omega^2 \tau_2^2} + i \omega \left[ \frac{w_1 \tau_1^2}{1 + \omega^2 \tau_1^2} + \frac{w_2 \tau_2^2}{1 + \omega^2 \tau_2^2} \right],
\]
(5.4)

\[
w_1 = \frac{M_1 (M_{11} - \frac{M_{12}}{\tau_1}) + M_2 M_{12}}{\alpha^2 (\tau_1^{-1} - \tau_2^{-1})},
\]
\[
w_2 = \frac{M_1 (M_{11} - \frac{M_{12}}{\tau_2}) + M_2 M_{12}}{\alpha^2 (\tau_1^{-1} - \tau_2^{-1})},
\]

where \( \tau_{1,2}^{-1} = \frac{M_{11} + M_{22} \pm \sqrt{(M_{11} - M_{22})^2 + 4M_{12}M_2}}{2\alpha} \) are the inverse relaxation times of the model. Relations (5.3), (5.4) for polarization \( P \) and electric field \( E \) now read

\[
P(\omega) = \chi(\omega) E(\omega),
\]
\[
\chi(\omega) = \frac{2 \mu^2}{v (K + J)} \chi_0(\omega).
\]
(5.5)

The dielectric permittivity is related to the corresponding susceptibility as

\[
\varepsilon(\omega) = 1 + 4 \pi \chi(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega),
\]
(5.6)
where \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) are the real and imaginary parts of the dielectric permittivity.

In figs. 5.1-5.6 we depicted the calculated dielectric permittivity of Rochelle salt. In calculations we use the parameters found above: \( K = 1473 \), \( J = 802.12 \), \( \Delta = 737.33 \) for Rochelle salt and \( K = 1502 \), \( J = 810.07 \), \( \Delta = 751.69 \) for deuterated Rochelle salt. Unfortunately, at the already set values of \( \mu \) we are unable to find a value of the relaxation parameter \( \alpha \) such as to obtain a satisfactory description of the experimental points for the dynamic permittivity. Therefore, in this case we take \( \mu = 1.8427 \times 10^{-18} \) for Rochelle salt and \( \mu = 2.0 \times 10^{-18} \) for deuterated Rochelle salt. Polarization and static susceptibility calculated with the new values of \( \mu \) are shown in figs. 5.7, 5.8.

As one can see in figs. 5.1-5.6, the mean field approximation yields a fair description of the temperature behavior of the dynamic dielectric permittivity of Rochelle salt at all temperatures except for the vicinity of the phase transitions, where the real part of the permittivity tends to \( \varepsilon_\infty \). This is due to the divergence of the relaxation times of the model at the transition temperatures (fig. 5.9).
Figure 5.2: Temperature dependence of $\varepsilon''$ for Rochelle salt.

6 Thermodynamics and relaxational dynamics of RbHSO$_4$.

Ferroelectric properties of RbHSO$_4$ were discovered in 1960 [43]. This crystal undergoes a single second order phase transition ($T_c = 265$ K). A microscopic theory of RbHSO$_4$ for the first time was proposed in [16, 3]. The studied model was based on the assumption that the phase transition in RbHSO$_4$ is related to ordering of sulphate groups, which in a high-temperature phase move in asymmetric double-well potentials. Hence, RbHSO$_4$ can be described within the Mitsui model [1] (see (2.1)). In [3, 10, 16, 17, 18, 19] the thermodynamic and dielectric properties of RbHSO$_4$, RbDSO$_4$ and disordered mixtures RbH$_{1-x}$D$_x$SO$_4$ were studied. Unfortunately, the found in these papers values of the microparameters do not provide a proper description of the experimentally observed jump of the specific heat at the transition point ($\Delta c = 9.02$ J/Mol K).

Since RbHSO$_4$ and related disordered mixtures undergo a single second order phase transition, the possible values of the model parameters for these compounds should be taken from the regions I, II of the phase diagram. Also, since the specific heat of the studied model depends only on the dimensionless parameters $a$ and $\gamma$, the values of these parameters were chosen such as to fit the theoretical jump of specific heat to the ex-
Figure 5.3: The frequency dependence of the real part of dynamic dielectric permittivity $\varepsilon'(\nu)$ at different temperatures $T$ (K): a) – 235, b) – 245, c) – 265, d) – 285, e) – 305, f) – 315. Solid lines are the results from [29], dashed line is the result of present paper, experimental points are taken from ■ – [30], ○ – [33, 34], ▼ – [35], + – [36], • – [38], × – [39], △ – [40], ○ – [41].
Figure 5.4: The frequency dependence of the imaginary part of dynamic dielectric permittivity $\varepsilon''(\nu)$ at different temperatures $T$ (K): a) – 235, b) – 245, c) – 265, d) – 285, e) – 305, f) – 315. Solid lines are the results from [29], dashed line is the result of present paper, experimental points are taken from ■ [30], ○ [33, 34], ▼ [35], + [36], ○ [37], × [38], □ [42].
Figure 5.5: Temperature dependence of $\varepsilon'$ for deuterated Rochelle salt; lines are theoretical results for $\alpha = 0.8 \times 10^{-13}$, $\mu = 2.00457 \times 10^{-18}$; symbols are experimental points [31].

Figure 5.6: Temperature dependence of $\varepsilon''$ for deuterated Rochelle salt.
Figure 5.7: Temperature dependence of polarization of regular (solid line) and deuterated (dashed line) Rochelle salt for sets of parameters 4, 5 of table 4.1; $\mu_{Rs} = 1.8487 \times 10^{-18}$, $\mu_{dRs} = 2.0046 \times 10^{-18}$.

Figure 5.8: Temperature dependence of inverse static dielectric susceptibility of regular (solid line) and deuterated (dashed line) Rochelle salt for the same sets of parameters as in previous figure.
Figure 5.9: Temperature dependence of inverse relaxation times of regular (solid line) and deuterated (dashed line) Rochelle salt. Symbols are experimental points of [31]).

Experimental value. Then the parameters $K$, $J$, $\Delta$ were determined from $a$ and $\gamma$ using the condition that the calculated transition temperature should coincide with the experimental one. Finally, for RbHSO$_4$ we obtained the following set of the parameters $K = 880.64$ K, $J = 780.9$ K, $\Delta = 398.8$ K, $\mu = 0.425276 \times 10^{-18}$. Here we took into account the fact that for RbHSO$_4$ $v = 2.105 \times 10^{-22}$ cm$^3$.

Thermodynamic and dielectric characteristics of the disordered compounds RbH$_{1-x}$D$_x$SO$_4$ were calculated in the mean field approximation under assumption that the corresponding model parameters are given by

$$K_x = K_H (1 - x) + K_D x,$$
$$J_x = J_H (1 - x) + J_D x,$$
$$\Delta_x = \Delta_H (1 - x) + \Delta_D x. \quad (6.1)$$

Here $K_H$, $J_H$, $\Delta_H$ and $K_D$, $J_D$, $\Delta_D$ are the model parameters, corresponding to RbHSO$_4$ and RbDSO$_4$, respectively. We took into account the fact that for RbDSO$_4$ $T_c = 252$ K. Analogously to the case of RbHSO$_4$, we obtained the values of the model parameters for RbH$_{0.3}$D$_{0.7}$SO$_4$, and then using (6.1) found the parameters for RbDSO$_4$. 29
Table 6.1 contains values of the model parameters for RbHSO$_4$ and RbDSO$_4$, obtained in the present and previous [3, 16, 17, 18] works. Using equation (6.1) and the presented in Table 6.1 values of the model parameters for RbHSO$_4$ and RbDSO$_4$, we calculated the physical characteristics of the mixed compounds RbH$_{1-x}$D$_x$SO$_4$. The obtained results for polarization, inverse dielectric susceptibility, and contribution of the ordering structure elements to the specific heat of RbH$_{1-x}$D$_x$SO$_4$ along with the available experimental data are shown in figs. 6.1-6.3. The fig.6.4 illustrates the calculated specific heat and the experimental points for RbHSO$_4$. In figs.6.5-6.9 we plotted the calculated $\varepsilon'(\nu, T)$, $\varepsilon''(\nu, T)$ for RbHSO$_4$ and the inverse relaxation time RbH$_{1-x}$D$_x$SO$_4$. A good quantitative fit of the obtained theoretical results to experimental data for the studied characteristics of RbHSO$_4$ is obtained. If figs.6.10-6.13 we show that the proposed theory also well describes the experimental data of [17] for temperature and frequency dependences of $\varepsilon'(\nu, T)$, $\varepsilon''(\nu, T)$ for RbH$_{0.3}$D$_{0.7}$SO$_4$. Hence, a good agreement between the theoretical results and experimental data is obtained for thermodynamic and dynamic characteristics of the RbHSO$_4$ RbH$_{0.3}$D$_{0.7}$SO$_4$ ferroelectrics. We can maintain that the Mitsui model (2.1) is totally adequate to these crystals.

### Table 6.1: The sets of the model parameters for RbHSO$_4$ and RbDSO$_4$, obtained within the mean field approximation (the sets 5 and 6 are found in the present work).

| No | compound          | $K$, K | $J$, K | $\Delta$, K | $a$  | $\gamma$ |
|----|-------------------|--------|--------|-------------|------|----------|
| 1  | RbHSO$_4$        | 616    | 784    | 245         | -0.12| 0.35     |
| 2  | RbHSO$_4$        | 1040   | 228    | 468         | 0.64 | 0.738    |
| 3  | RbHSO$_4$        | 616    | 777.2  | 244         | -0.116| 0.35    |
| 4  | RbHSO$_4$        | 616    | 784    | 244         | -0.12| 0.348    |
| 5  | RbHSO$_4$        | 880.64 | 780.9  | 398.8       | 0.6  | 0.48     |
| 6  | RbDSO$_4$        | 842.4  | 747.1  | 381.5       | 0.6  | 0.48     |

7 Concluding remarks

In this paper we calculated thermodynamic and dynamic characteristics of ferroelectric order-disorder type compounds described by the pseudospin model with asymmetric double-well potential. For the first time, a role of tunneling on the systems described by this model is studied thoroughly; its influence on the phase diagram is shown. Possible phase
Figure 6.1: Temperature dependence of polarization of Rb$_x$D$_{1-x}$SO$_4$ for $x = 1, 0.7, 0.5, 0.25, 0$; □ are the experimental points taken from [47].

Figure 6.2: Temperature dependence of the inverse static susceptibility of Rb$_x$D$_{1-x}$SO$_4$ for $x = 1, 0.7, 0.5, 0.25, 0$; Symbols are the experimental points taken from [47].
Figure 6.3: Contribution of the ordering elements to the specific heat as a function of temperature for RbH$_x$D$_{1-x}$SO$_4$ at $x = 1, 0.7, 0.5, 0.25, 0$.

Figure 6.4: Specific heat of RbHSO$_4$ as a function of temperature (the solid line represents theoretical results obtained within the mean field approximation, the symbols are experimental points [3]).
Figure 6.5: Temperature dependence of $\varepsilon'$ of RbHSO$_4$ ($\alpha = 0.48 \times 10^{-13}$): the solid line represents theoretical results; the symbols are experimental points [17].

Figure 6.6: Temperature dependence of $\varepsilon''$ of RbHSO$_4$ ($\alpha = 0.48 \times 10^{-13}$): the solid line represents theoretical results; the symbols are experimental points [17].
Figure 6.7: $\varepsilon'$ of RbHSO$_4$ as a function of frequency; the solid lines represent theoretical results; the symbols are experimental points [17].

Figure 6.8: $\varepsilon''$ of RbHSO$_4$ as a function of frequency; the solid lines represent theoretical results; the symbols are experimental points [17].
Figure 6.9: Temperature dependence of the inverse relaxation times of RbHSO$_4$ (solid line) and RbDSO$_4$ (dashed line), □ - [17], ◆ - [20].

Figure 6.10: Temperature dependence of $\varepsilon'$ for RbH$_{0.3}$D$_{0.7}$SO$_4$ ($\alpha = 0.54 \times 10^{-13}$): the solid lines represent theoretical results; the symbols are experimental points [17].
Figure 6.11: Temperature dependence of $\varepsilon''$ for RbH$_{0.3}$D$_{0.7}$SO$_4$ ($\alpha = 0.54 \times 10^{-13}$): the solid lines represent theoretical results; the symbols are experimental points [17].

Figure 6.12: $\varepsilon'$ of RbH$_{0.3}$D$_{0.7}$SO$_4$ as a function of frequency; the solid lines represent theoretical results; the symbols are experimental points [17].
transitions are analysed at different values of the model parameters; at these values the physical characteristics of the model are calculated. Interesting results are obtained for compounds undergoing three phase transitions, like \((\text{NH}_4)_3\text{H(SO}_4)_2\)\(_{1-x}\)\(\{(\text{ND}_4)_3\text{D(SO}_4)_2\}_x\) \[18\]. Because of a limited number of experimental data available for these crystals, we cannot draw final conclusions about the model adequacy for these crystals. We also calculated the physical characteristics of the \((dRs)_xRs_{1-x}\) and RbH\(_{1-x}\)D\(_x\)SO\(_4\) type ferroelectrics.

Our study has shown that within the studied model it is most likely impossible to describe the phase transition and physical characteristics of NH\(_4\)HSO\(_4\) crystal. Interesting results are obtained for the RbHSO\(_4\) and Rs type ferroelectrics. The first crystal is not piezoelectric in the paraelectric phase, whereas the piezoelectric effect determines the physical characteristics of the second one \[29\]. The considered here model does not take into account the piezoelectric interaction.

It should be also noted that in the mentioned ferroelectrics, an interaction of the ordering structure elements with phonons is rather important. Corresponding studies for these crystals were performed in \[23\, 24\, 25\].

Hence, despite a great attention to the crystals described by the Mitsui model, especially to Rochelle salt and of RbHSO\(_4\) type, it still

Figure 6.13: \(\varepsilon''\) RbH\(_{0.3}\)D\(_{0.7}\)SO\(_4\) as a function of frequency; the solid lines represent theoretical results; the symbols are experimental points \[17\].
unclear whether this model provides a quantitative description of the entire spectrum of physical characteristics for these crystals. Indeed, in practically all earlier paper, the microparameters were chosen by fitting to only a few characteristics of the crystals, whereas other quantities were not calculated with these parameters. Naturally, the incorrectly chosen values of the $K$, $J$, $\Delta$ parameters led to the incorrect values of $\mu$ and $\alpha$ as well. The aim of the present paper was to calculate all physical characteristics of the Mitsui model, study their dependences on the microparameters, explore the tunneling effects on these characteristics. We also intended to develop a fitting procedure for regular and deuterated Rochelle salt and RbHSO$_4$ type ferroelectrics, which would provide a good fit to the available experimental data for these crystals and help to establish the adequacy (or inadequacy) of the considered model to the specific crystals.

In [49] it has been shown that an important characteristics in the fitting procedure for ferroelectric materials is a specific heat. In the present paper at setting the microparameters $K$, $J$, $\Delta$ we used the data for the specific heat of the studied crystals. However, it should be mentioned that for specific heat $Rs$ and $dRs$ reliable data are most likely absent.

The performed calculations yielded the values of the microparameters for the RbHSO$_4$ crystals, with which we calculated the physical characteristics of the disordered ferroelectrics RbH$_{1-x}$D$_x$SO$_4$. The proposed consistent fitting scheme provides a good quantitative description of experimental data for pure crystals; we also present the results for disordered crystals RbH$_{1-x}$D$_x$SO$_4$ which can be experimentally verified.

For $Rs$ and $dRs$ crystals it is impossible to find such values of the model parameters, which would provide a simultaneous fit to the experimental data for $P_s(T)$ and $\varepsilon(0, T)$. An agreement could be somewhat improved by taking into account the piezoelectric interaction. This is also indicated by calculations of the dynamic characteristics of the crystals for which a satisfactory agreement with experimental data is obtained. It is clear that with increasing frequency, the effects of piezoelectric interaction in $Rs$ type crystals become unimportant. The crystals become clamped, and we obtain a good agreement with experimental data for $\varepsilon'(\nu, T)$ and $\varepsilon''(\nu, T)$.

Another important point is, if we choose the values of the microparameters $K$, $J$, $\Delta$ at which (see the phase diagram) the third low-temperature phase transition in $Rs$ emerges, an agreement with the experimental data simultaneously for $P_s(T)$ and $\varepsilon(0, T)$ could be much improved. However, the question about the low-temperature transition in $Rs$ is still open, even though such a transition was reported in some
papers.

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