# Thermodynamics of interacting linear spin chains with an asymmetric potential

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An exact solution is obtained for a statistical model consisting of two interacting Ising chains located in an asymmetric magnetic field. It is shown that phase "quasitransitions" are possible in this model, i.e., changes in the magnetic moment $M$ and the susceptibility $\chi$ can occur in a narrow range of temperatures, $\Delta T$, and fields, $\Delta H'$. The results are used to explain the various types of transitions that occur in ferroelectrics, and are compared with both the approximate calculations that have been performed on the basis of the Mitsui model and the experimental data on the polarization of ferroelectrics.

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## 1. INTRODUCTION

The problems of the statistics of phase transitions in ferroelectrics in which the ions that become ordered have two nonequivalent equilibrium positions in the high-symmetry phase have of late been attracting attention. The potential curve $U(r)$ along the straight line joining these sites is nonsymmetric: in one of the sublattices the deeper minima of $U(r)$ are located "to the right," while in the other sublattice they are located "to the left."[1] Although the mean dipole moment, $P$, in each of the sublattices is nonzero, there exist regions in which the resultant polarization in the crystal is zero, and the phase transition is connected with the appearance of a state with $P \neq 0$. One of the problems then is to study the effect of the asymmetry parameter $\Delta'$, which is equal to the difference between the right and left minima of $U(r)$, on the temperature dependences of the thermodynamic functions in the vicinity of the transition.

The most successful microscopic model that reflects the effect of the asymmetry on the nature of the transition is Mitsui's model[2] (see also Refs. 1 and 3), which is based on the structural data for Rochelle salt (RS). The mean-field (MF) approximation studies[2-4] of the thermodynamics of ferroelectrics have made possible the elucidation of many of the principal features of the transitions that occur in these crystals. In particular, it has been established that the ferroelectric phase can disappear at temperatures below $T_{c2}$, i.e., that $P \neq 0$ in the range $T_{c2} < T < T_{c1}$, when certain relations exist between the model parameters. At the same time, certain experimental data, such as the abrupt disappearance of the polarization observed at $T = T_{c2}$ in $NH_4HSO_4$ crystals[5] and the change in sign of $P$ observed in a number of crystals,[6] have defied explanation on the basis of the Mitsui model.[2-4]

In view of this, it was found desirable to look for more accurate methods of describing phase transitions in systems with an asymmetric potential. Thus, Vaks and Zeĭn[7] succeeded in analyzing on the basis of a modified Mitsui model with the aid of the cluster approximation (see, for example, Refs. 1 and 8) all the main distinctive features of the statistics of the transitions that occur in $NaH_3(SeO_3)_2$ crystals, whereas the MF method was found to be totally useless.

In the present paper we consider an exactly soluble statistical model consisting of two interacting spin chains located in an asymmetric potential with two minima, which is, in fact, a one-dimensional analog of the Mitsui model. The proposed model not only admits of an exact solution, but also enables us to describe all the principal distinctive features of ferroelectric transitions, in particular, the occurrence of an abrupt change in the polarization, the disappearance of the dipole moment $P$ when the temperature is lowered, the change in sign of the polarization.

It should be noted that the abrupt change in the thermodynamic functions is, in our model, in contrast to the noninteracting-chain model,[9] due to an almost exact compensation of the competing interactions. It is interesting that a similar compensation of interactions of unlike signs, which is characteristic of structural phase transitions, may be the cause of the appearance of many distinctive phenomena—from the manifestation of tricriticality[10] to transition "splitting."[11]

Let us emphasize that there exist for the application of the proposed model physical prerequisites connected with the quasi-one-dimensional character of the interaction of the ordered structure elements in a number of ferroelastic and ferroelectric crystals, e.g., in $KH_3(SeO_3)_2$, $NH_4HSO_4$ and $RbHSO_4$. According to Refs. 4, 12, and 13, the ordered ions ("pseudospins")—the hydrogen atoms in $KH_3(SeO_3)_2$ and the $SO_4$ tetrahedra in $NH_4HSO_4$ and $RbHSO_4$—are joined into double chains aligned along the direction of the $c$ axis in $KH_3(SeO_3)_2$ and along the $b$ axis in $NH_4HSO_4$ and $RbHSO_4$.

In Sec. 4 we compare the computed temperature dependences $P(T)$ with the experimental curves. The analysis performed allows us to compare our results with the results obtained earlier by approximate methods.

## 2. THERMODYNAMICS

In spite of the fact that the obtained results will be used below primarily to describe ferroelectric trans-

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itions, we shall use the conventional "magnetic" terminology. Let us write the Hamiltonian of two interacting one-dimensional Ising chains in an asymmetric magnetic field in the form

$$\mathcal{H}=-\sum_{i=1}^{N}[J_1's_is_{i+1}+J_2'\sigma_i\sigma_{i+1}+J_3's_i\sigma_i+H'(s_i+\sigma_i)+\Delta'(s_i-\sigma_i)]. \quad (1)$$

Here $N$ is the number of units in a chain, $J_1'$ and $J_2'$ are the interaction constants within each chain, $J_3'$ is the interchain interaction constant, $H'$ is the external magnetic field, and $\Delta'$ is the asymmetry parameter. The spins $s_i \equiv s_i^{\varepsilon}$ and $\sigma_i \equiv \sigma_i^{\varepsilon}$ satisfy the periodicity boundary conditions $s_{N+1}=s_1$, $\sigma_{N+1}=\sigma_1$. Our model is a one-dimensional analog of the Mitsui model[1] when $J_1'=J_2'$.

In the statistical limit $N\to\infty$, the partition function, $Z$, is defined as follows:

$$Z(T,\ H',\ \Delta')=\lambda_m^N, \quad (2)$$

where $\lambda_m$ is the largest eigenvalue of the matrix $A_{ij}$ given by

$$\begin{bmatrix} e^{J_1+J_2+J_3+2H} & e^{J_1-J_2+H+\Delta} & e^{J_2-J_1+H-\Delta} & e^{J_3-J_1-J_2} \\ e^{J_1-J_2+H+\Delta} & e^{J_1+J_2-J_3+2\Delta} & e^{-J_1-J_2-J_3} & e^{J_2-J_1-H+\Delta} \\ e^{J_2-J_1+H-\Delta} & e^{-J_1-J_2-J_3} & e^{J_1+J_2-J_3-2\Delta} & e^{J_1-J_2-H-\Delta} \\ e^{J_2-J_1-J_3} & e^{J_2-J_1-H+\Delta} & e^{J_1-J_2-H-\Delta} & e^{J_1+J_2+J_3-2H} \end{bmatrix}. \quad (3)$$

Here $J_i=J_i'/T, H'/T$, and $\Delta=\Delta'/T$; $T$ is here and below expressed in energy units. The thermodynamic potential per spin $\Phi$, the magnetic moment $M$, the antiferromagnetic moment $\tilde{M}$, and the magnetic and the antiferromagnetic susceptibilities $\chi$ and $\tilde{\chi}$ are equal to

$$\Phi=-\frac{T}{2}\ln\lambda_m, \quad M=\frac{\langle s\rangle+\langle\sigma\rangle}{2}=\frac{1}{2}\frac{d\ln\lambda_m}{dH},$$
$$\tilde{M}=\frac{\langle s\rangle-\langle\sigma\rangle}{2}=\frac{1}{2}\frac{d\ln\lambda_m}{d\Delta}, \quad (4)$$
$$\chi=\partial M/\partial H', \quad \tilde{\chi}=d\tilde{M}/d\Delta';$$

$\langle\ldots\rangle$ indicates a mean value. It follows from the expressions (3) and (4) that the quantities $M$ and $\tilde{M}$ are connected by the relation

$$M(J_3,\ H,\ \Delta)=\tilde{M}(-J_3,\ \Delta,\ H). \quad (5)$$

To find $\lambda_m$ in the general case, when $H\neq 0$ and $\Delta\neq 0$, it is necessary to solve a fourth-order algebraic equation for the eigenvalues of the matrix (3). Its roots can be found, for example, with the aid of the Ferrari formulas. However, in view of the unwieldiness of these expressions, we present here only the important limiting cases of critical variation of the thermodynamic functions with temperature or magnetic field. As a preliminary, let us introduce the following convenient dimensionless parameters and variables:

$$j_3=1+\alpha=J_3/J_1, \quad j_3=J_3/J_1, \quad \varepsilon=\Delta/J_1,$$
$$h=H/J_1, \quad t=\beta^{-1}=T/J_1', \quad \xi=\varepsilon-j_3, \quad (6)$$
$$\delta=h-\varepsilon+j_3, \ K_{1,2}=\exp(-2J_{1,2}).$$

1. The critical variation of $M$, $\tilde{M}$, $\chi$, and $\tilde{\chi}$ occurs in the case when at low temperatures $t\gg 1$ the strong magnetic field $h$ and the strong antiferromagnetic interaction $j_3$ almost compensate each other and the asymmetric of the potential $\varepsilon\ll 1$. The reason for this is that the magnetic field tends to align the spins of both sublattices in the same direction, while the antiferromagnetic interaction tends to align them in the opposite direction.

Using the fact that $\exp(-2h)$, $\varepsilon$, $K_{1,2}$ and $\rho=h+j_3$ are small, we find the largest eigenvalue of the matrix $A_{ij}$. The thermodynamic functions for positive and negative values of $\rho$ have the following form.

a) For $\rho>0$

$$M=\tfrac{1}{2}[1+\rho(\rho^2+f)^{-1/2}], \quad |\tilde{M}|\ll 1; \quad (7)$$
$$\chi=f(\rho^2+f)^{-3/2}(2J_1')^{-1}, \ f=t^2(K_1^2+K_2^2). \quad (8)$$

For $\alpha=0$ and $\varepsilon=0$, the formulas (7) and (8) go over into the corresponding expressions of Ref. 14. In this case it follows from the formulas (7) and (8) that the system is in a ferromagnetic state with $M\sim 1$ at $t<t_0$, where $t_0\sim 2/|\ln\delta|$. The moment $M$ decreases "discontinuously" at a temperature $t\sim t_0$ by an amount $\Delta M\sim 0.5$ with a relative diffusion-region width $\Delta t/t_0\sim|\ln^{-1}\delta|\ll 1$. It is clear that $\Delta t/t_0$ can be decreased by decreasing $\delta$. In this range, $\chi$ has a sharp peak $\chi_m\sim(J_1'\delta)^{-1}$, while the thermal capacity has a weak singularity (a kink). When the magnetic field is varied (with $t$ fixed), there occurs in the system a transition smeared over $h$ by an amount $\Delta h/h\sim tK_1$. The susceptibility has a peak at $\delta=0$, and its height is $\chi_m\sim(TK_1)^{-1}$. It follows from (7) and (8) that the nature of the behavior of $M$, $\tilde{M}$, $\chi$, and $\tilde{\chi}$ remains the same as in the case when $\alpha\neq 0$, $J_1\sim J_2$, and $\varepsilon\ll 1$.

b) For $\rho<0$, the quantities $M$ and $\tilde{M}$ are given in the region of temperatures $t\gg t_0'\sim|\ln^{-1}\varepsilon|$ by the formulas (7). At $t\lesssim t_0'$ "antiferromagnetic" ordering sets in the system: $\tilde{M}\sim 1, M\ll 1$. The transition at $t_0'$, like the transition at $t_0$, occurs in a narrow interval $\Delta t_0'\sim\ln^{-2}\varepsilon$.

2. Using the formula (5), we can extend the above-presented results to the case when a strong ferromagnetic interchain interaction $j_3\gg 1$ is almost compensated by a strong potential asymmetry $\varepsilon\gg 1$, $|\xi|\ll 1$ in weak magnetic fields $h\ll 1$. In this case the expressions for the thermodynamic quantities $\varepsilon$ for $h\ll\varepsilon$ are obtained from (7) and (8) in accordance with (5) by the substitution

$$M\rightleftarrows\tilde{M}, \ \varepsilon\rightleftarrows h, \ j_3\to -j_3, \ \chi\rightleftarrows\tilde{\chi}. \quad (9)$$

Interesting results are obtained in the case when $h\sim|\xi|$ in the presence of a strong intrachain-interaction asymmetry $\alpha$, i.e., for $J_2\gg J_1$ (for the $\alpha\lesssim 1$ case; see Fig. 1). Neglecting the terms of the order of $K_2$, we can easily find the roots of the characteristic equation. The roots that are essential for the subsequent analysis have the form

$$\tilde{\lambda}_1=1-\beta\xi+2\beta h,$$
$$\tilde{\lambda}_2=1-\beta h+\beta[(h+\xi)^2+t^2K_1^2]^{1/2}, \quad (10)$$
$$\tilde{\lambda}=\exp[-\beta(2+\alpha+\varepsilon)]\lambda,$$

where $\lambda$ is an eigenvalue of the matrix $A_{ij}$. For $\delta<0$ we always have $\tilde{\lambda}_2>\tilde{\lambda}_1$; therefore,

$$(M,\ \tilde{M})=\tfrac{1}{2}\{\mp 1+(\xi+h)[(\xi+h)^2+t^2K_1^2]^{-1/2}\}. \quad (11)$$

Here and below the lower sign pertains to $\tilde{M}$. Let us note that in this case $M<0$.

When $\delta>0$ and $t\sim t_{01}=4/|\ln h\delta|$, the roots are equal:

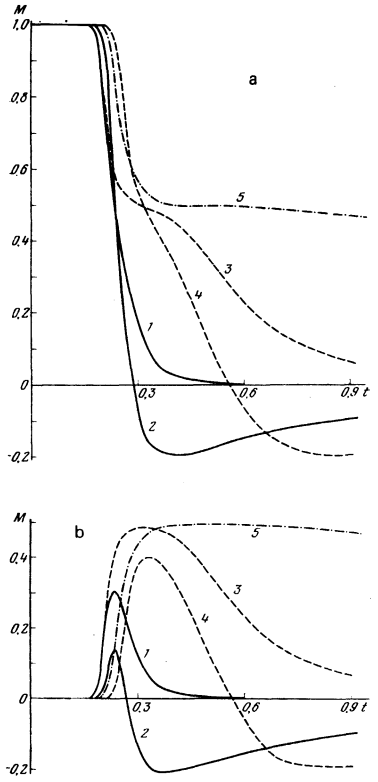


FIG. 1. The effect of the effective interaction $\xi$ and the interaction asymmetry $\alpha$ on the temperature dependence of the magnetic moment $M$: $\delta = 10^{-5}$, b) $\delta = 10^{-5}$. The continuous curves are for $\xi = 5\times10^{-5}$; the dashed curves, for $\xi = 5\times10^{-3}$; the dot-dash curves, for $\xi = 0.2$; $j_3 = 0.7$. The curves 1), 3), and 5) correspond to $\alpha = 0$; the curves 2), to $\alpha = 0.1$; the curves 4), to $\alpha = 0.3$.

$\tilde{\lambda}_1 = \tilde{\lambda}_2$. When $t > t_{01}$, we have $\tilde{\lambda}_2 > \tilde{\lambda}_1$, and $\tilde{M}$ and $M$ are determined as before by (11). When $t < t_{01}$, we shall have $\tilde{\lambda}_1 > \tilde{\lambda}_2$, and then $M = 1$ and $\tilde{M} = 0$. Thus, the moment changes its sign at the point $t_{01}$, the change in the moment occurring "abruptly." In reality, of course, this occurs in a narrow temperature range (see Fig. 1). In order to determine the behavior in this range, it is necessary to retain the terms of the order of $K_2$, and solve the standard separation problem. Let us note that, in contrast to the case (7) and (8), in which the temperature $t_0$ decreases with decreasing $\Delta t_0$, in the present case the width of the interval where the moment changes abruptly $\Delta t \sim t_{01}^{3/2}\exp(-2J_2)$ and $t_{01}$ are independent parameters.

By making the substitutions (9) in the formulas (10), (11), and the following expressions, we can obtain a change in the sign of $\tilde{M}$ in the case considered in Subsec. 1.

3. An abrupt change in the moment occurs also in the case when the difference between the strong magnetic field and the large asymmetry $\varepsilon$ (the two being almost equal to each other) is almost compensated by the weak interaction $j_3 > 0$. This means that the effective field acting on the chain $s_i$ almost orders this chain, while the effective field acting on the chain $\sigma_i$ is weak, i.e., $|\delta| \ll 1$. If in this case the interaction in the second chain is not weak, i.e., if $j_2 \gg 1$, then only the elements with $i, j = 1, 2$ are important in the matrix $A_{ij}$, and $\lambda_m$ can easily be found. As a result, we have

$$(M, \tilde{M}) = {}^1/_2\{1 \pm \delta(\delta^2 + t^2K_1^2)^{-1/2}\}. \quad (12)$$

In conclusion, let us note that $M$ and $\tilde{M}$ decrease at high temperatures. Therefore, in certain cases the behavior of both $M$ and $\tilde{M}$ is "bell-shaped" in character.

It is also easy to verify that the inequality $M \ll 1$ is always fulfilled in the case when $\varepsilon > j_3 \gg h, \alpha$. In particular, the moment $M \to 0$ in the limit as $\alpha \to 0$ and $h \to 0$, even when $j_3 \neq 0$.

## 3. NUMERICAL ANALYSIS OF THE MODEL

As we have already noted, although it is possible to write out the analytic solution to the problem in the general case, this solution is extremely unwieldy. Therefore, it is of interest to give, besides the analytic solutions obtained above for some limiting cases, numerical solutions obtained on a computer for other values of the parameters and establish some trends in the behavior of $M(\xi, \delta, \alpha, t)$.

As follows from the relation (5), it is sufficient to investigate only the case $j_3 > 0$. Figure 1 plots of the dependence $M(t)$ for $\delta = 10^{-5}$ and $-10^{-5}$ and various values of $\xi$ and $\alpha$. As can be seen from this figure, regardless of the value of $\xi$, in the region $t \lesssim 0.2$ the system is in a ferromagnetic state when $\delta > 0$ and in an antiferromagnetic state when $\delta < 0$. As $\xi$ is increased ($\alpha = 0$), the quantity $M$ tends both in the case when $\delta > 0$ and in the case when $\delta < 0$ to a limiting value $M \sim 0.5$ (the curve 5). As $\xi$ is decreased, the magnetic moment gradually deviates from the value 0.5 and approaches zero, the maximum value $M_m(\delta < 0)$ decreasing at the same time (the curves, 5, 3, and 1). At very low values of $\xi$ and $\delta$ there arises in the behavior of $M$ ($\delta > 0$) a situation that is close to a limiting case of the Slater model for crystals of the $KH_2PO_4$ type.[1] For example, for $\xi = 2\times10^{-11}$ and $\delta = 10^{-11}$ ($j_3$ and $\varepsilon$ being arbitrary), the region $\Delta t/t_0$ in which $M$ varies from zero to its saturation value is $\sim 10^{-2}$. It can also be seen from Fig. 1 that, as the parameter $\alpha$, which is equal to the difference between the two intrasublattice-interaction constants, is increased, the magnetic moment becomes negative. When $t$ is lowered further, the moment changes its sign, passing through zero at $t_c > t_0$, and the "transition" (of $M$) into the negative region being such that the smaller $\xi$ is, the smaller $\alpha$ must be in order for it to occur (the curves 2 and 4). As has already been noted, there arises at $\alpha \gg 1$ a situation close to a Slater situation: the moment changes from the value $M = -0.5$ to 0 ($\delta < 0$) or 1 ($\delta > 0$) almost at the "transition" point $t_0$.

Thus, the behavior of $M(t)$ at $\alpha = 0$ is wholly determined by the strengths of the effective field $\delta = h - \xi$ and the effective interaction $\xi$. This is connected with the fact that two types of competing parameters exist in the system: $h$ and $j_3$ strive to align the sublattice spins in one direction, while $\varepsilon$ strives to make them antiparallel. Therefore, it is natural that it is advantageous for the system to become as $t \to 0$ antiferromag-

netic when $\varepsilon > h + j_3$ and ferromagnetic when $\varepsilon < h + j_3$. The antiferromagnetic moment $\tilde{M}(j_3 > 0)$ does not, however, undergo significant changes; $\tilde{M} \neq 0$ for any $\xi, \delta \neq 0$ in the range from sufficiently high temperatures to $t_0$. In the region $t \leq t_0$ we have $\tilde{M} = 1 - M$.

We analyzed both analytically and numerically such characteristics of the behavior of the system as the abrupt change in the magnetic moment and the change in the sign of the moment. Let us now discuss in greater detail the moment's interesting—from the standpoint of experiment—"dome-shaped" behavior that obtains at $\alpha = 0$. The results of the analysis are schematically represented in Fig. 2.

1. The magnetic moment and the susceptibility undergo their main changes in the temperature range $\Delta t = t_1 - t_3$. At $t \sim t_0$ $(t_1 < t_0 < t_3)$, $\chi$ has a strongly pronounced peak $\chi_m(t_0)$, which rises and shifts toward the region of smaller $t$ as $\delta$ decreases.

2. As $\xi$ decreases, $t_1 \to t_2$, while the interval $t_2 - t_3$ remains almost constant. As $|\delta|$ decreases, the plot of $M(t)$ shifts uniformly toward the region of low $t$, with the difference $t_2 - t_3$ decreasing at the same time, while the magnitude of the interval $t_1 - t_2$ is conserved.

3. The parameter $\xi$ roughly speaking determines the magnitude of the range $t_1 - t_2$, while $|\delta|$ determines the magnitude of $t_2 - t_3$, or, in other words, the sharpness of the change in $M, \chi$. Then, it is natural that the necessary condition for the Slater situation to arise is that $t_1 \to t_3$, which is possible at sufficiently small values of $\delta > 0$, $\xi$, i.e., when there is almost complete compensation of the competing "interactions" $h, j_3$, and $\varepsilon$.

4. The abrupt disappearance of the magnetic moment at $\delta < 0$ in the region $t_2 - t_3$, when $t_1 - t_2 \gg t_2 - t_3$, is possible only when $|\delta| \ll 1$. When $\delta < 0$, $|\delta| \sim \xi \to 1$, the shape of the plot of $M(t)$ is almost symmetric about $t_m$, the temperature at which $M = M_m$.

## 4. COMPARISON WITH THE APPROXIMATE METHODS AND EXPERIMENT

In view of the one-dimensional nature of our model, the character of the singularities of the thermodynamic quantities in the neighborhood of the "phase-transition" points differs, of course, from that of really existing phase transitions. However, our results pertaining to the region outside the narrow region around the transition point can be compared with the experimental data. The one-dimensional nature of the model leads in this case to a finite value for $\chi_m(t_0)$, the spreading of the "tails" of the magnetization in the vicinity of $t_1$ and $t_3$ (Fig. 2), and to an exponentially small $(\sim t^2 e^{-4\beta})$ deviation of $M$ from unity when $\delta > 0$ and zero when $\delta < 0$ in the region $t < t_3$. At the same time, the anomalous behavior of $\chi(t)$ and the critical variation of $M(t)$, which are characteristic of true transitions survive here.

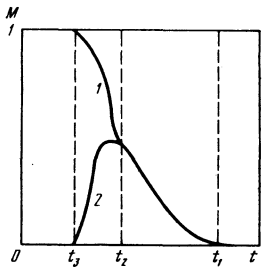


FIG. 2. The temperature behavior of the magnetization $M$ as a function of the sign of the effective field $\delta$: for the curve 1) $\delta > 0$, while for the curve 2) $\delta < 0$.

As has already been noted, (1) is a one-dimensional analog of the Mitsui model. Let us recall the results of the investigations, performed in the MF approximation, of this model. Depending on the parameters $a$ and $\gamma$ (in our notation $a = (j_3 - 1)/(j_3 + 1)$, $\gamma = \varepsilon/(j_3 + 1)$] the appearance of the ferroelectric phase $(M \neq 0)$ is possible in the following regions:

a) If $j_3 > \varepsilon$, then the ferroelectric phase, arising at some temperature $T_c$, survives down to $T = 0$,

b) If $j_3 \sim \varepsilon$, then the ferroelectric phase exists only at intermediate $T$ (a more exact relation between $a$ and $\gamma$ given in Ref. 1),

c) If $\varepsilon > j_3$, then the ferroelectric phase does not arise at any value of $T$.

In the region a) the system can undergo second- or first-order transitions,[1] while in the region b) it undergoes second-order transitions.[4] As can be seen from the above-performed investigation, three similar regions arise in the model (1) for $\alpha = 0$ (evidently, a comparison with the Mitsui model makes sense only in the case when $h \ll 1$). The condition for the appearance of the region a) implies that $\delta > 0$, and always leads to the existence of a ferroelectric phase down to absolute zero. The approach to a first-order transition with a small smearing is also possible at very small values of $\xi$ and $\delta$. The region a) arises in the model (1) also when $\varepsilon > j_3$, but then it is necessary that $h > \varepsilon - j_3$. The region b) appears when $h < \varepsilon - j_3$ and $\varepsilon > j_3$, and, what is more, the occurrence of first-order transitions is possible here when $|h - \varepsilon + j_3| \ll \varepsilon - j_3 \ll 1$, in contrast to the MF results. Finally, the region c) appears in our model when $\varepsilon \gg j_3$.

It is interesting that the same three qualitatively different regions exist when $J_3 < 0$; but now the antiferromagnetic moment $\tilde{M}$ changes during a "transition" in these regions [the relations (5) and (9)]. In the Mitsui model this would correspond to the case $|a| > 1$.

In crystals of deuterated Rochelle salt (DRS) and ammonium hydrosulfate $NH_4HSO_4$, a spontaneous polarization, $P_s$, exists in a temperature region bounded by two Curie points: $T_{c1} = 308$ K, $T_{c2} = 251$ K in DRS and $T_{c1} = 270$ K, $T_{c2} = 154$ K in $NH_4HSO_4$ (Ref. 5). In DRS the phase transition is of second order; in $NH_4HSO_4$ the polarization $P_s$ decrease abruptly at $T = T_{c2}$ from the maximum value to zero. The thermodynamics of the transitions in these crystals were investigated on the basis of the Mitsui model in the MF approximation, and these investigations led to a reasonable description of the peculiarities of DRS,[1] in contrast to ammonium hydrosulfate, in whose case the observed behavior could not be accounted for.[4]

In Fig. 3 we show the $\tau = (T_{c1} - T)/T_{c1}$ dependences of $P_s = pM$ computed from the exact expressions (3) and

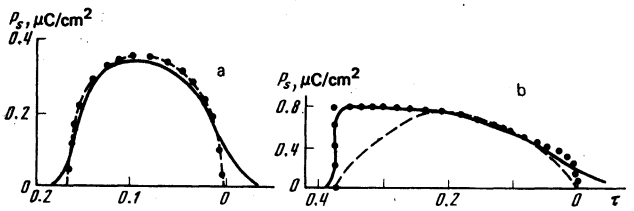


FIG. 3. The dependence $P_s(\tau)$: a) for DRS, $j_3 = 1.85$, $\alpha = 0$, $\xi = 4\times10^{-7}$, $\delta = -2\times10^{7}$, $p = 2\times10^{-6}$ C/cm²; b) for $NH_4HSO_4$, $\alpha = 0$, $j_3 = 3.69$, $\xi = 3\times10^{-6}$, $\delta = -10^{-11}$, $p = 1.8\times10^{-6}$ C/cm². The points indicate experimental values for DRS from Ref. 1 and for $NH_4SO_4$ from Ref. 5; the dashed curves were taken respectively from Refs. 1 and 4.

(4) for the two crystals. We also indicate in the same figure by a dashed curve the data for DRS ($\varepsilon = j_3 = 1.85$),[1] and for $NH_4HSO_4$ ($\varepsilon = 3.83$, $j_3 = 3.69$).[4] It can be seen from Fig. 3 that the dependence $P_s(\tau)$ obtained by us for $NH_4HSO_4$ agrees better with experiment than does the MF approximation.

The ferroelectrics $RbHSO_4$ and $NaNH_4SeO_4 \cdot 2H_2O$ and the ferroelastic substance $KH_3(SeO_3)_2$ undergo one second-order phase transition. According to estimates made in Ref. 4, $\varepsilon = 0.625$, $j_3 = 0.785$ for $RbHSO_4$ and $\varepsilon = 0.215$, $j_3 = 0.37$ for $NaNH_4SeO_4 \cdot 2H_2O$, which corresponds for both crystals to $\xi < 0$ (the region a). Since the values of the parameter $\xi$ for $RbHSO_4$ and $NaNH_4SeO_4 \cdot 2H_2O$ are roughly the same, it follows from the results of the model (1) that the changes that occur in the thermodynamic properties of these compounds during the transition will be close to each other. In particular, as indicated by the experiments performed by Blat and Zinenko,[4] the main change in the polarization occurs in these crystals in temperature intervals, $\Delta T/T_0$, that are equal in order of magnitude.

In Figs. 4 and 5 we show respectively the dependence $P_s(T)$ for $RbHSO_4$ and the function $M(\tau) \equiv \varphi(\tau)/\varphi_s$ for $KH_3(SeO_3)_2$ as computed from (3) and (4) ($\varphi$ is the angle of rotation of the optical indcatrix; $\varphi_s$ its magnitude at saturation[16]). The dashed curve in Fig. 4 indicates the result of computations performed for $RbHSO_4$ in the MF approximation.[4]

It is also interesting to compare the dependences obtained for $M(t)$ in the case when $J_1' \neq J_2'$. The inequality of the interaction constants $J_1'$ and $J_2'$ can arise if the ions that become ordered are of different chemical composition ($NH_4$ and $SO_4$), or (if they are identical) when the distortions of the radicals of one sublattice are different from the distortions of the radicals of

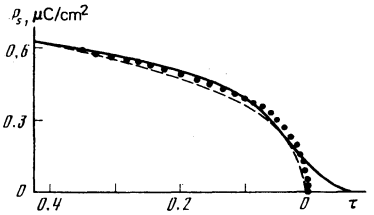


FIG. 4. The dependence $P_s(\tau)$ for the $RbHSO_4$ crystal for $j_3 = 0.785$, $\xi = 8\times10^{-5}$, $\delta = 10^{-6}$, $\alpha = 0$, $p = 0.61\times10^{-6}$ C/cm². The points represent experimental data[15]; the dashed curve was taken from Ref. 4.

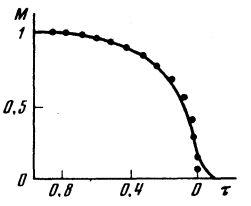


FIG. 5. The dependence $M(\tau)$ for $KH_3(SeO_3)_2$ for $j_3 = 0.8$, $\xi = 4\times10^{-3}$, $\alpha = 0$, $\delta = 10^{-5}$. The points represent experimental data.[16]

the other sublattice. The latter possibility is apparently realized in the ferroelectric $(NH_4)SO_4$ (see, for example, Ref. 11), in which a polarization-compensation point has been experimentally observed.[6] On the other hand, $P_s$ has been observed to change its sign in $RbH_3(SeO_3)_2$ and ammonium Rochelle salt[6] when the crystals are subjected to a weak shear stress.

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