On the theory of ferroelectrics of the KH_2PO_4 type

V. G. Vaks and V. I. Zinenko
Physics Institute, Siberian Division, USSR Academy of Sciences

(Submitted June 26, 1972)
Zh. Eksp. Teor. Fiz. **64**, 650-664 (February 1973)

The statistics of ferroelectrics of the KH_2PO_4 type is investigated in the cluster approximation previously proposed by Blinc and Svetina[8]. By expanding into terms of small parameters of the problem it is possible to derive an analytical expression for the free energy. The calculated values and temperature dependences of the polarization, susceptibility and specific heat are compared with the experimental values for KH_2PO_4 and KD_2PO_4. Satisfactory agreement between the theory and totality of experimental data can be attained if one parameter is added to the model which takes into account the influence of anharmonic and correlation effects near T_C. The changes in parameters of the model due to deuteration are discussed and estimates of the changes are presented.

1. INTRODUCTION

The study of phase transitions in ferroelectrics of the KH_2PO_4 (usually called KDP) has been the subject of very many papers. According to the accepted interpretation, the principal role in the transition is played here by the ordering of the hydrogen ions, the effective potential $U(\xi)$ for which at the O–H–O bonds is of the form shown in Fig. 1. Above the transition, both minima of $U(\xi)$ are statistically uniformly populated, and below T_C there appears a spontaneous asymmetry of the population. A detailed description of all the data on the transition can be found, for example, in[1-5].

A qualitative feature of the thermodynamics is in this case the narrowness of the transition region: almost all the changes of the polarization and of the specific heat occur in an interval of several degrees near T_C[1-5]. This indicates immediately that the description of the statistics by the usual approximations of the molecular-field (MF) type, which is sufficient, for example, for a qualitative description of the transition in the ordinary Ising model, will not be very satisfactory here. In this connection, Slater proposed in the first paper on the theory of KDP[6] a known model that presupposes the presence of strong short-range interactions, and described an approximate method for its investigation, equivalent, as it turned out later, to the so-called "cluster approximation"[7,8]. Slater's model was generalized and developed in a number of papers, particularly in[9,10]. Blinc[11,8] emphasized the importance of taking quantum effects into account, particularly the tunneling through the potential barrier (Fig. 1); this has explained qualitatively the strong isotopic shift of T_C from 123 to 220° following deuterization. The interaction of the hydrogens of the OH bonds with the lattice vibrations, the features of the dynamics, and other aspects were also considered in a number of papers[12,13].

These crystals are of interest, on the one hand, because of the relative simplicity of the structure and because they have been fairly well studied, so that it is possible to use them as examples for the understanding and study of the general properties of ferroelectrics of the order-disordered type, many of which also have hydrogen bonds. On the other hand, transitions in these crystals have peculiarities from the point of view of the general theory of phase transitions. Thus, the transition in Slater's model turns out to be essentially different from that in the Ising model, and numerous variants of the Slater model (particularly, two-dimensional ones, for which exact solutions could be obtained), are also widely discussed in the literature (see, for example,[14]).

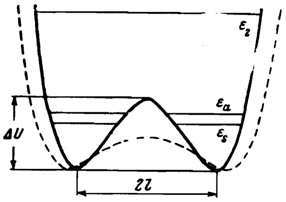

FIG. 1

The most complete discussion of the statistics of the transition in KDP with allowance for tunneling effect has been proposed by Blinc and Svetina[8]. They have developed in further detail, as applied to this problem, the cluster approximation, which is much more accurate than, say, the MF approximation. For the Slater model, the main thermodynamic results indicate exactly[15] the position of T_C, the character of the transition (of first-order with saturation of the polarization immediately at the point T_C), and the Curie-Weiss law for the susceptibility. It is natural to expect the accuracy with which the fundamental thermodynamic quantities are determined to remain high enough also in the case of not too large deviations from the Slater model (see below), so that a quantitative comparison with experiment is justified. Blinc and Svetina[8] reduced the problem of calculating the free energy to a determination of the roots of algebraic equations of sixth and third degree, but investigated these equations only numerically. Their results therefore have no lucid analytic form and it is difficult to compare them with new and noticeably more accurate data on KDP and DKDP (KD_2PO_4)[1-5], or with the data being obtained on other crystals in this family (RbH_2PO_4, KH_2AsO_4, CsH_2AsO_4, etc.). In addition, the numerical results, as seen from a comparison with the analytic ones, contain some inaccuracies. At the same time, a quantitative comparison of theory with experiment is of interest here for a number of reasons.

1. First, it is desirable to verify the correctness of the general ideas concerning the transition, including the very hypothesis that two minima exist (Fig. 1) and that the hydrogens at the bonds are ordered. To this end it is desirable to eliminate, for example, the large discrepancy (by a factor of 2–3) noted by Cochran[13] between the experimental data and the ratio of the Curie-Weiss constant to the square of the saturation polarization, a discrepancy that arises when KDP and DKDP are described by the MF approximation. When

other crystals, say $NaNO_2$, are described with the aid of this approximation, no such discrepancy arises.

2. Several papers (see, for example,[16,8]) examine whether the interaction constants of the hydrogen ions change when the hydrogen is replaced by deuterium. A determination of this change and its interpretation can greatly clarify the microscopic picture and the mechanism of the transition.

3. In a number of experimental papers[2-5] it was proposed to describe the rapid growth of the polarization P and of the specific heat c near T_c by means of unusual empirical relations such as $P \sim \tau^{1/4}$, $c \sim \tau^{-1/2}$[2], or $P \sim \tau^{1/6}$[5], where $\tau = 1 - T/T_c$. These relations differ strongly from those observed in other transitions and from those proposed theoretically[17]. For the general theory of phase transitions it is therefore very interesting to compare the observed curves with the results of the employed cluster approximation, to see whether they are described already within the framework of this simple approximation (of the self-consistent-field type) without making use of the contribution of the critical long-range correlations[17]. The latter may not be decisive in KDP, even near T_c, since this ferroelectric is uniaxial and exhibits a piezoeffect in the paraphase[18,19].

2. HAMILTONIAN AND FUNDAMENTAL APPROXIMATIONS

Following[20,7], we start from the following effective Hamiltonian for the hydrogen subsystem:

$$H = -\frac{1}{2}\sum_{\mathbf{r},\mathbf{r}'} J(\mathbf{r}-\mathbf{r}')\sigma_{\mathbf{r}}^z\sigma_{\mathbf{r}'}^z - \Gamma\sum_{\mathbf{r}}\sigma_{\mathbf{r}}^x - E_{ex}p\sum_{\mathbf{r}}\sigma_{\mathbf{r}}^z. \qquad (1)$$

Here $\mathbf{r}$ describes the position of the hydrogen bond; $\sigma_{\mathbf{r}}^{\mathrm{Z}}$ and $\sigma_{\mathbf{r}}^{\mathrm{X}}$ are Pauli matrices describing the transitions of the hydrogen ion between the lowest states in the potential (Fig. 1), namely symmetrical $\psi_s \equiv \psi_0$ and antisymmetrical $\psi_a \equiv \psi_1$. The excitation energies of the higher states are apparently large (see Sec. 6 below), and can be neglected at the considered $T \sim T_c$. The constants J and Γ, according to[20], are expressed in terms of ψ_s and ψ_a in the following fashion:

$$J(\mathbf{r}-\mathbf{r}') = \sum_{\alpha,\beta} V_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\xi_{sa}{}^{\alpha}\xi_{sa}{}^{\beta}, \qquad \xi_{sa} = \int d^3\xi\,\psi_s(\xi)\xi\psi_a(\xi), \qquad (2a)$$

$$\Gamma = \varepsilon_a - \varepsilon_s + \frac{1}{2}\sum_{\mathbf{r},\alpha,\beta} V_{\alpha\beta}(\mathbf{r})[(\xi^\alpha\xi^\beta)_{aa} - (\xi^\alpha\xi^\beta)_{ss}]. \qquad (2b)$$

Here $V_{\alpha\beta}(\mathbf{r}-\mathbf{r}')$ are structure constants characterizing the interaction of the bonds $\mathbf{r}$ and $\mathbf{r}'$; ϵ_a and ϵ_s are the energies of the states ψ_a and ψ_s, while $(\ldots)_{ss}$ and $(\ldots)_{aa}$ denote averages over the states ψ_s and ψ_a. The quantity E_{ex} in the last term of (1) denotes an electric field from external sources, i.e., the field that would exist in the absence of the polarizability of the medium and the crystal.

Expressions (1) and (2) were obtained in[20] without allowance for the lattice vibrations. It is also shown there that in the absence of tunneling, $\Gamma = 0$, allowance for these vibrations in the harmonic approximation leads only to a renormalization of the constants $V_{\alpha\beta}$. Blinc and Svetina[8] argue that even in the case of noticeable tunneling the interaction with the lattice does not lead to significant changes in the Hamiltonian (1). By the methods of[20,21] it can be shown that the effective bond dipole moment p in (1) is proportional to ξ_{sa}, i.e., to the dipole moment of the transition between the states ψ_s and ψ_a. We note also that inasmuch as in KDP the distance between the minima $U(\xi)$ is $2l \sim 0.35\,\text{Å} \ll |\mathbf{r}-\mathbf{r}'|_{\min} \sim 3.5\,\text{Å}$, the second term of (2b), generally speaking, is smaller than the first by a factor $\sim l^2|\mathbf{r}-\mathbf{r}'|_{\min}^{-2}$, and will henceforth be disregarded in the estimates. Nor will we take into account the corrections discussed by Blinc and Ribaric[21], which must be introduced in Γ and p as a result of the "polaron" mechanism of the interaction of the hydrogen with the lattice, since the influence of these corrections can, in the main, evidently also be taken into account by renormalization of the constants and of the form of the potential $U(\xi)$.

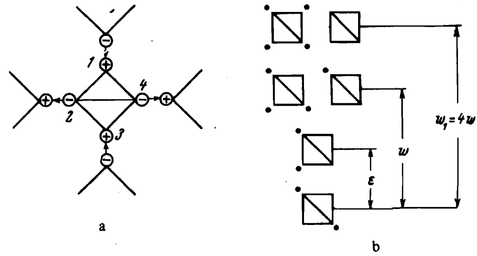

FIG. 2

A schematic diagram of the PO_4 tetrahedron with the adjacent OH bonds is shown in Fig. 2. Just as in[8,7], we choose as the principal cluster the aggregate of four spins adjacent to the given tetrahedron while the interaction with the more remote neighbors is described by the MF approximation. To simplify the formulas, we confine ourselves to the case when there is no microscopic field, E = 0, and the expressions for the dielectric constant χ in a weak field will be obtained from the thermodynamic equation

$$\frac{1}{\chi - 1} = \frac{1}{4\pi}\frac{\partial^2 F}{\partial P^2}$$

where F(P) is the free-energy density in the absence of the field and P is a polarization per unit volume (see, for example,[1]). Then the cluster Hamiltonian H_4 and the single-particle Hamiltonian H_1 can be expressed in the form[8,7]

$$\begin{aligned} H_4 = {} & -V(\sigma_1^z\sigma_2^z + \sigma_2^z\sigma_3^z + \sigma_3^z\sigma_4^z + \sigma_4^z\sigma_1^z) \\ & -U(\sigma_1^z\sigma_3^z + \sigma_2^z\sigma_4^z) - (\gamma\sigma + {}^1\!/_2\varphi)(\sigma_1^z + \sigma_2^z + \sigma_3^z + \sigma_4^z) \\ & -(\Gamma - {}^1\!/_2\eta)(\sigma_1^x + \sigma_2^x + \sigma_3^x + \sigma_4^x); \end{aligned} \qquad (3)$$

$$H_1 = -(\gamma\sigma + \varphi)\sigma_1^z - (\Gamma - \eta)\sigma_1^x. \qquad (4)$$

Here U and V are the constants of the interaction with the nearest neighbors shown in Fig. 2:

$$U = J_{13} = J_{24} = {}^1\!/_2(\varepsilon - w), \quad V = J_{12} = J_{23} = J_{34} = J_{41} = {}^1\!/_2(w - {}^1\!/_2\varepsilon). \qquad (5)$$

The quantities ϵ and w in (5), as can be verified from (3), have the meaning of differences of the interaction energies in the states shown in Fig. 2b (just as in[7], the presence of hydrogen near a given PO_4 group corresponds to values $\sigma_1^{\mathrm{Z}} = \sigma_3^{\mathrm{Z}} = +1$ and $\sigma_2^{\mathrm{Z}} = \sigma_4^{\mathrm{Z}} = -1$). The constant γ describes the sum of the interaction J(r) with the non-nearest neighbors. The quantity φ has the meaning of the average "longitudinal" field produced by the nearest neighbors and acting on the given spin, while η is the attenuation of the "transverse" field by these neighbors. The average spin $\sigma = \langle\sigma^{\mathrm{Z}}\rangle$, according to (4), is connected with φ and η by the relation

$$\sigma = \frac{\mathrm{Sp}\,\sigma_1^z\exp(-\beta H_1)}{\mathrm{Sp}\exp(-\beta H_1)} = \frac{\varphi + \gamma\sigma}{[(\varphi+\gamma\sigma)^2 + (\Gamma-\eta)^2]^{1/2}}\,\mathrm{th}\,\beta[(\varphi+\gamma\sigma)^2 + (\Gamma-\eta)^2]^{1/2}, \qquad (6)$$

where $\beta = 1/T$. In the cluster method, the effective fields φ and η are variational parameters determined from the self-consistency conditions: the average spin $\langle \sigma \rangle$ of the cluster particles should coincide with the average for any spin of the system, described by the Hamiltonian H_1:

$$\mathrm{Sp}\,\sigma_1^z\rho_1 = \mathrm{Sp}\,\sigma_1^z\rho_4, \tag{7a}$$

$$\mathrm{Sp}\,\sigma_1^x\rho_1 = \mathrm{Sp}\,\sigma_1^x\rho_4, \tag{7b}$$

$$\rho_1 = \frac{\exp(-\beta H_1)}{Z_1}, \quad \rho_4 = \frac{\exp(-\beta H_4)}{Z_4}, \quad Z_i = \mathrm{Sp}\exp(-\beta H_i). \tag{8}$$

The free energy per KH_2PO_4 molecule is given by[8]

$$F = -T(\ln Z_4 - 2\ln Z_1) + \gamma\sigma^2. \tag{9}$$

Relation (9) was derived in[8] somewhat formally, but it can be derived also in a more illustrative form by expressing the average energy $E = \langle H \rangle$, with H from (1), the exact pair distribution function $\rho(1, 2)$, in accordance with the considered approximation, by the function obtained from ρ_4 [Eq. (8)]

$$\rho(1,2) = \mathrm{Sp}_{3,4}\rho_4(1,2,3,4),$$

and integrating then the thermodynamic relation $E = \partial(\beta F)/\partial\beta$ with respect to β, we obtain formula (9) when (7) are taken into account. It is easy to verify that the consistency equations (6) and (7) coincide with the conditions (9) for the minimum of the energy F regarded as a function of σ, φ, and η:

$$\frac{\partial F}{\partial\sigma} = \frac{\partial F}{\partial\varphi} = \frac{\partial F}{\partial\eta} = 0,$$

so that these equations can be obtained also by minimizing F.

Let us recall the results of the investigation of this model without tunneling, i.e., at $\Gamma = \eta = 0$. If we neglect all the charged configurations ($w = \infty$) and put $\gamma = 0$, then we obtain Slater's model[7,6], in which the polarization changes jumpwise from zero to saturation $\sigma = 1$ at $T = T_C$, and the dielectric constant χ satisfies the Curie-Weiss law $\chi = C(T - T_0)^{-1}$, with $T_0 = T_C$. Allowance for the contribution of the long-range forces $\gamma \neq 0$, as mentioned by Silsbee et al.[10], does not change the character of the transition, but the transition point T_C now lies above the Curie-Weiss temperature T_0, so that the dielectric constant χ is finite at the transition point:

$$\exp\{-\beta_c\varepsilon\} = \exp\{\beta_c\gamma\} - {}^1/_2, \quad \exp\{-\beta_0\varepsilon\} = {}^1/_2 + \beta_0\gamma < \exp\{-\beta_c\varepsilon\} \tag{10}$$

($\beta_{0,C} = 1/T_{0,C}$). At finite energy of the charge configurations, $w \neq \infty$ and $\gamma = 0$, we obtain the Takagi model[9], in which the transition becomes of second order, but at small T/W the growth of the polarization takes place in the narrow interval

$$\Delta T \sim T_c \exp(-\beta_c w).$$

Finally, at $\gamma \neq 0$ and $w \neq \infty$, we obtain the model of Silsbee et al.[10], in which the type of transition and the value of the polarization jump ΔP_C are determined by the relation between ϵ, γ, and w. In accordance with the already mentioned limiting cases, larger values of γ/ϵ and w/ϵ favor the first-order transition, particularly the growth of $T_C - T_0$ and ΔP_C.

Silsbee et al.[10] used this model to describe DKDP. From the experimental data of[22] they estimated $w \approx 900 \pm 200^\circ$, after which a reasonable description of the thermodynamics was obtained at values $\epsilon \approx 110^\circ$ and $\gamma \approx 20^\circ$.

3. DIAGONALIZATION OF H_4 AND GENERAL EXPRESSION FOR F

In the presence of a transverse field we have Γ, $\eta \neq 0$ and the matrix of the operator H_4 in (3) is no longer diagonal; to find the sum Z_4 in (9) it is necessary to obtain its eigenvalues λ_i. Then

$$Z_4 = \sum_{i=1}^{16} \exp(-\beta\lambda_i). \tag{11}$$

Using the symmetry of H_4 relative to the permutations $1 \longleftrightarrow 3$, $2 \rightarrow 4$, and $1, 3 \rightarrow 2, 4$, we can reduce the matrix H_4 to quasidiagonal form, i.e., write it in the form of the direct product $A^{(6)} \times A^{(3)} \times A^{(3)} \times B^{(3)} \times A^{(1)}$, where

$$A^{(6)} = \begin{pmatrix} -2a & 0 & 0 & 2\nu & 0 & 0 \\ 0 & 2a & 0 & 0 & 2\nu & 0 \\ 0 & 0 & \varepsilon & 2\nu & 2\nu & 0 \\ 2\nu & 0 & 2\nu & w-a & 0 & \nu\sqrt{2} \\ 0 & 2\nu & 2\nu & 0 & w+a & \nu\sqrt{2} \\ 0 & 0 & 0 & \nu\sqrt{2} & \nu\sqrt{2} & w_1 \end{pmatrix},$$

$$A^{(3)} = \begin{pmatrix} \varepsilon & \nu\sqrt{2} & \nu\sqrt{2} \\ \nu\sqrt{2} & w-a & 0 \\ \nu\sqrt{2} & 0 & w+a \end{pmatrix}, \quad A^{(1)} = \varepsilon, \tag{12}$$

$$B^{(3)} = \begin{pmatrix} w-a & 0 & \nu\sqrt{2} \\ 0 & w+a & \nu\sqrt{2} \\ \nu\sqrt{2} & \nu\sqrt{2} & w_1 \end{pmatrix}.$$

Here

$$a = \varphi + 2\gamma\sigma, \quad \nu = \Gamma - {}^1/_2\eta, \quad w_1 = 4w - 2\varepsilon.$$

The matrices (12) are equivalent to those given by Blinc and Svetina[8], with the exception of a few elements of $A^{(6)}$. If we rewrite the corresponding matrix from[8] in the basis employed here, then we get for these elements, in place of the values 2ν and 0 obtained by us, the values

$$A_{14} = A_{41} = A_{25} = A_{52} = {}^3/_2\nu,$$
$$A_{15} = A_{51} = A_{24} = A_{42} = {}^1/_2\nu.$$

It is seen from (12) that to determine λ_i exactly it is necessary to solve one equation of sixth degree and two third-degree equations, although above T_C (at $a = 0$), these equations become one fourth-degree and quadratic or linear equations. To simplify the algebraic problem, we make use of the fact that the energy of the charged configurations w is much larger than the energies ϵ of the neutral configurations, i.e., $\alpha = \epsilon/w \sim 0.1$ is a small parameter. We therefore obtain the eigenvalues of H_4 by expansion with respect to α, confining ourselves to linear terms.

We present first expressions for the spectrum above T_C:

$$\frac{\lambda_1}{\varepsilon} = \frac{1}{2}(\rho - 2\Delta - d), \quad \frac{\lambda_2}{\varepsilon} = -\Delta, \quad \frac{\lambda_3}{\varepsilon} = \frac{\lambda_4}{\varepsilon} = (1-\delta)(1-\alpha\delta),$$
$$\frac{\lambda_5}{\varepsilon} = \frac{1}{2}(\rho - 2\Delta + d), \quad \lambda_6 = \varepsilon, \tag{13}$$
$$\lambda_7 = w(1 - {}^1/_3\alpha\delta), \quad \lambda_8 = \lambda_9 = \lambda_{10} = w,$$
$$\lambda_{11} = \lambda_{12} = \lambda_{13} = w(1 + \alpha\delta), \quad \lambda_{15} = \lambda_{16} = w_1(1 + {}^1/_{12}\alpha\delta);$$

here

$$\Delta = \delta - \alpha\delta^2, \quad \delta = (2\Gamma - \eta)^2/w\varepsilon, \quad \rho = 1 - \delta - 2\alpha\delta + {}^{25}/_4\alpha\delta^2,$$
$$d = [(1 - 3\delta - 2\alpha\delta + {}^{33}/_4\alpha\delta^2)^2 + 4\delta - 11\alpha\delta^2]^{1/2}. \tag{14}$$

The levels λ_i in (13) are numbered in increasing order, and we use for the estimates the value $\delta \approx 0.4$, which will be derived later on for KDP near T_C.

It is seen from (13) that at the considered small α and at not too large δ the six lower levels, just as in Slater's model, have an energy of the order of ϵ and lie much lower than the remaining ten levels: $\lambda_i \gtrsim w \sim 1000^\circ$. It is therefore clear that whereas in the region $T \sim T_{cD} \sim 220^\circ$ of the transition in DKDP the charged configurations still make a certain contribution to the thermodynamics, this contribution in KDP at $T \leq T_{cH} \sim 130^\circ$ is quite small and the main factor in the second-order transition is tunneling. We have therefore taken into account in the levels λ_i with $i \geq 7$ only corrections linear in α, and neglected the terms $\sim w\alpha^2\delta = \epsilon\alpha\delta$.

Below T_c, where $a \neq 0$, using as before an expansion in α up to first order, we find that λ_3, λ_4, λ_6, λ_{15}, and λ_{16} do not depend on a and are determined as before by (13). The remaining levels are bound. The higher levels $\lambda_7 - \lambda_{14}$ are obtained from the linear and quadratic equations. On the other hand, for the levels λ_1, λ_2, and λ_5, by eliminating from perturbation theory the contribution of the lowest states, we obtain a third-degree equation. By obtaining its roots with the aid of Cardan's formula and substituting them together with the other λ_i in (11), we arrive at the following expression for the free energy F in the region $T \lesssim T_c$:

$$\beta F = 2\ln Z_1 - \ln(K_0 + K_1 + L) + \gamma\beta\sigma^2. \tag{15}$$

Here

$$\begin{gathered}Z_1 = 2\operatorname{ch}\beta[(a-\gamma\sigma)^2 + (\Gamma-\eta)^2]^{1/2},\\ K_0 = 2e^{-\beta\varepsilon(1-\delta)(1-\alpha\delta)} + e^{-\beta\varepsilon} + 2e^{-\beta w_1(1-\alpha\delta/12)},\\ L = 4e^{-\beta w(1+\alpha\delta/2)}\operatorname{ch}\beta(a^2+\delta^2\varepsilon^2/4)^{1/2} + 2e^{-\beta w(1-\alpha\delta/6)}\operatorname{ch}\beta(a^2+\delta^2\varepsilon^2/36)^{1/2}\\ + 2e^{-\beta w(1+11\alpha\delta/6)}\operatorname{ch}\beta(a^2+25\delta^2\varepsilon^2/36)^{1/2},\\ K_1 = e^{-\beta\varepsilon(\rho/3-\Delta)}[e^{-2\beta\varepsilon r\cos\psi} + 2e^{\beta\varepsilon r\cos\psi}\operatorname{ch}(\beta\varepsilon r\sqrt{3}\sin\psi)],\end{gathered} \tag{16}$$

and the parameter r and ψ in K_1 are given by

$$\begin{gathered}r = \frac{1}{3}\left[\rho^2 + 6\delta^2 + \frac{3}{4}\alpha\delta^2(1-37\delta) + 12a_1^2\right]^{1/2}, \quad a_1^2 = \frac{a^2}{\varepsilon^2}(1-\alpha\delta),\\ \cos 3\psi = \frac{1}{27r^3}\left[\rho^3 + 9\rho\delta^2 + \frac{9}{8}a\delta^2(1-\delta)(1-37\delta) - 36a_1^2\left(\rho - \frac{21}{8}\alpha\delta^2\right)\right]\end{gathered} \tag{17}$$

where ρ and Δ are the same as in (14).

The last term in the sum K_0 is negligibly small in practice. We have retained it only for convenience in comparing with the results in the absence of tunneling, $\Gamma = \eta = \delta = 0$. In this case, as can be easily verified, $\tan\psi = 2a\sqrt{3}$, $r\cos\psi = a/3$, $r\sqrt{3}\sin\psi = 2a$, and (15) goes over into a well-known expression (see[10,7]).

4. INVESTIGATION OF THE PHASE-TRANSITION REGION

We consider first the region above T_c, where a and $\sigma(a)$ are equal to zero, but $\eta \neq 0$. If we denote for brevity $\Gamma - \eta = \mu$, so that (14) yields $\delta = (\Gamma + \mu)^2/w\epsilon$, then the equation $\partial F/\partial\eta = 0$ takes the form

$$\operatorname{th}\beta\mu = f_0'\frac{\Gamma+\mu}{\varepsilon w}T \quad\text{or}\quad \operatorname{th}^2\beta\mu = \alpha\delta\frac{T^2}{\varepsilon^2}(f_0')^2, \tag{18}$$

where $f_0' = \partial\ln Z_0/\partial\delta$ and $Z_0 = Z_4(\delta, a = 0)$ is given by (11) with λ_i from (13).

We see that $\beta^2\mu^2 \leq \alpha\delta$, so that $\tanh\beta\mu$ in (18) can be replaced by $\beta\mu$. We then obtain from the first equation of (18) the following expression for the determination of δ:

$$\delta(1-\alpha f_0' T^2/\varepsilon^2)^2 = \Gamma^2/\varepsilon w \equiv \delta_0. \tag{19}$$

Thus, tunneling effects are determined in the statistics by the parameter $\delta_0 = \alpha\Gamma^2/\epsilon^2$, and not by Γ/ϵ. Therefore, for sufficiently noticeable $\Gamma \gtrsim \epsilon$, for example in KDP, where $\Gamma \sim 2\epsilon$, the influence of tunneling is still not too large.

Using (18) and (19) we can obtain an equation for the Curie-Weiss temperature T_0, which is determined from the condition that the coefficient of a^2 in the expansion (15) of F in powers of a vanish (in this case $\sigma = \sigma(a)$ is determined from (6)). The obtained expression is somewhat cumbersome, and we present only its form at small values of δ:

$$\begin{gathered}K + 2L_0 - 1 - 2\gamma\beta(L_0+1) - \alpha\delta c_1 - \delta^2 c_2 = 0,\\ K = 2e^{-\beta\varepsilon} + e^{-\beta w_1}, \quad L_0 = e^{-\beta w}.\end{gathered} \tag{20}$$

Here c_1 and c_2 are certain positive functions of β, ϵ, γ, and w (which are not written out because of their complexity).

We see that in accordance with the discussion of[11,20], the tunneling makes T_0 lower. It is seen also that the expansion of T_0 in powers of δ begins with terms $\sim\alpha\delta$ and δ^2. It is seen from (15)–(17) that the same character is possessed by the expansion in powers of δ of all other quantities connected with the polarization, at all values of T. Therefore at small δ (for example, in DKDP), the results in the statistical approach hardly differ from the case $\Gamma = 0$. For KDP, however, such an expansion would already be inaccurate, owing to the large numerical factors of δ in (13), (14), and (17).

Below T_c, at nonzero a or σ, the equation for δ takes, as before, the form (19), but f_0' is replaced by $f' R \coth R$, where $R = \beta[(a - \gamma\sigma)^2 + \mu^2]^{1/2}$, and f' is determined in the same manner as f_0', except that Z_0 is replaced by the complete function $Z_4(\delta, a)$. In analogy, $\beta^2\mu^2$ is given by the right-hand side of (18) with the substitution $f_0' \to f' R \coth R$. Thus, the entire dependence of δ on T is contained in small terms of order of α, and we can verify that even at $T_c = T \sim 15^\circ$, when the KDP polarization is already close to saturation, the deviation of δ from $\delta(T_c)$ in KDP does not exceed 2–3%. We can therefore assume in practice that δ is constant in the entire region of the transition. The same pertains also to the quantity μ, since the difference (~10–20%) between the right-hand side of (18) and the value at $T = T_c$ sets in only at $R \gtrsim 1$, when the small quantity μ^2 in R becomes utterly insignificant.

Thus, to determine the thermodynamic below T_c, it remains to express σ in terms of a (or a in terms of σ), by means of (6), then substitute $\sigma(a)$ in (15) and determine a(T) at $\sigma(T)$ from (7a) or from the minimum condition $\partial F/\partial a = 0$. These transcendental equations were solved numerically, and it turned out to be simpler and clearer (in particular for the determination of T_c from the condition $F(a, T_c) = F(0, T_c)$), instead of solving the last equation, to plot F(a) at different values of T and then obtain the minimum of F(a) from these plots.

The results for a number of thermodynamic quantities are given together with the available data on DKDP and KDP in the table and in Fig. 3. We start with a discussion of DKDP. In the first line of the table are given the results for the set of parameters proposed by Silsbee et al.[10]. We see that these values on the whole describe satisfactorily the experimental data,

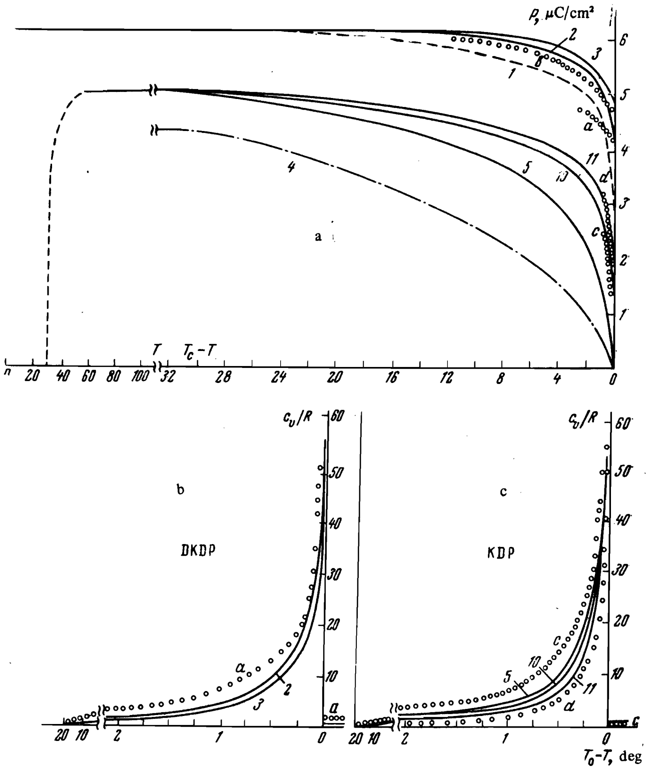

FIG. 3. Temperature dependence of the polarization (a) and of the specific heat (b, c) in DKDP and KDP. The numbers and letters marking the curves correspond to the sets of parameters and experimental data indicated in the table. Curve a was plotted for an incompletely deuterated sample (~ 80% deuterium content).

but there are certain discrepancies. The polarization jump ΔP_c is smaller, the P(T) increases more steeply, and T_c is lower than in experiment. The latter is worthy of mention because the employed approximation, like other self-consistent field approximations, as a rule overestimates T_c (see, for example,[25]), so that the exact value of T_c at the given parameters lies apparently even lower. The agreement becomes better if one chooses for w the value 1100°, which lies within the limits of the experimental error given by Schmidt and Uehling[22], and if ϵ is somewhat increased (see the set 2). The remaining small discrepancies can be attributed to inaccuracies of the model and to failure to take into account some effects which will be discussed below.

We start the discussion of KDP with set 4, in which the entire influence of the D → H substitution reduces only to the addition of tunneling Γ without a change of ϵ, w, and γ in comparison with set 2. We see that to obtain the observed lowering of T_c it would be necessary to have quite large values of Γ, at which the transition would be much more of second order, less abrupt than in experiment, and P_s would be noticeably lower than the observed value. We thus arrive, in agreement with[8,16], at the need for changing the interaction parameters ϵ, γ, and w when the hydrogen is replaced by deuterium.

Since the relative change of the lattice parameters is small on going from KDP to DKDP, ~0.2%[26], the factors $V_{\alpha\beta}$ in (2) can be naturally regarded as constant, and the change of the potentials in (2) and (5) can be ascribed to a change in the values of ξ_{sa}, which are proportional to the effective dipole moments p:

$$\frac{\varepsilon_H}{\varepsilon_D}\approx\frac{\gamma_H}{\gamma_D}\approx\frac{w_H}{w_D}\approx\frac{p_H^2}{p_D^2}\approx\frac{(\xi_{sa})_H^2}{(\xi_{sa})_D^2}. \tag{21}$$

Relations of this type were discussed earlier[8,10], and it can be assumed that they are preserved in the main even in a more accurate allowance for the interaction with the lattice vibrations than is used in models (1) and (2). We therefore confine the selection of the parameters for KDP to the condition (21). In sets 5 and 9 we have changed ϵ, γ, and w by approximately 25% in comparison with sets 4 and 2, and we have chosen Γ such as to have $T_{cH}\sim 130°$. We see that although the set 5 does indeed describe KDP satisfactorily, the transition remains of second order, and the polarization near T_c increases much more slowly than in experiment. Set 6 shows that an increase of γ, while making the agreement with T_c and C worse, has little effect on the discrepancy. It can be verified that different variations of ϵ, γ, and w (sets 7 and 8), not even those connected with condition (21), do not lead to a noticeable improvement of agreement with experiment for KDP.

5. PHENOMENOLOGICAL ALLOWANCE FOR EFFECTS OF STRICTION AND CORRELATION

We see thus that although the employed model gives perfectly reasonable description of both the general properties of KDP and DKDP and of the thermodynamics of the transition in DKDP, it is not sufficient for a quantitative description of KDP, since it does not account for the first-order character of the transition and for the sharp increase of P(T) near T_c. Let us discuss in this connection some of the made approximations. It was emphasized above that the Hamiltonians (1) and (2) were derived microscopically only for a rigid lattice or only when its vibrations are taken into account in the harmonic approximation. Anharmonic interactions, particularly electrostriction interactions and terms of fourth degree in the displacements, were not taken into account.

It is known, however, that striction interactions contribute to the conversion of the phase transition into a first-order transitoin[27-29]. Thus, if we describe this interaction with the aid of the usual expansion in the strains u_i and the polarization P, then F takes the form

$$\frac{F}{v_0}=\frac{F_0}{v_0}-\sum_i u_i q_{i1}P^2+\frac{1}{2}\sum_{i,k}c_{ik}u_iu_k, \tag{22}$$

where F and v_0 are the free energy and the volume per molecule; c_{ik} and q_{i1} are the elastic moduli and the electrostriction coefficients; F_0 is the free energy of the clamped crystal, given in our case by expressions (9) and (15). If we eliminate u_i from (22) with the aid of the equations $\partial F/\partial u_i=0$ and recognize that in our mode P is proportional to σ, then F takes in place of (9) the form

$$F=F_0-q\sigma^4, \tag{23}$$

$$q=\frac{1}{2v_0^3}(2p)^4\sum_{i,k}q_{i1}(c^{-1})_{ik}q_{k1}, \tag{24}$$

where $p=Pv_0/2\sigma$ is the same as in (1). It is seen from (23) (for example, by expanding $F_0(\sigma)$ in powers of σ), that subtraction of the term with q actually favors the first-order transition and a sharper increase of $\sigma(T)$ below T_c. To be sure, this term has the meaning of a small anharmonic correction and cannot be large. However, as already noted above and as can be seen from

Set No.	Model parameters						T_c, deg	$T_c - T_0$, deg	ΔP_c, μC/cm²	P_s, μC/cm²	σ_s	C+, deg	C−, deg	ΔS, cal/mol-deg
	ε, deg	w, deg	γ, deg	Γ, deg	p, dB	q, deg								
KD_2PO_4 (theory)														
1	110	900	23	0	0,186	0	213	0,7	3,07	6,15	1	3700	—	1
2	115	1100	23	0	0.186	0	223	1	4,45	6.15	1	3700	130	1,05
3	115	1100	23	0	0.186	0.7	224.1	2.1	4,9	6,15	1	3700	130	1,05
$K(D_xH_{1-x})_2PO_4$ (experiment)														
a	$x = 0,8 \pm 0,1$ [2, 3]						215	0,7	4,3	6,15 [23]		3800		1
b	Extrapolation to x = 1						220	0,8	4,8			4000		1
KH_2PO_4 (theory)														
4	115	1100	23	295	0.186	0	146,0	0	0	4,4	0.72	2900	—	0.49
5	80	800	16	140	0.163	0	134.8	0	0	5.05	0.94	3000	450	0.714
6	80	800	23	140	0.163	0	150.1	0	0	5.1	0.95	2800	—	0.796
7	90	800	16	140	0,163	0	144,5	0	0	5,05	0.94	3100	—	0.768
8	80	1100	16	140	0,163	0	139.6	0	0	5.05	0.94	3100	—	0.706
9	80	800	16	170	0.163	0	122.5	0	0	4,6	0.85	2800	—	0.652
10	80	800	16	140	0.163	1,9	134.8	0.04	1.41	5,05	0.94	3000	450	0.714
11	80	800	16	140	0.163	2,14	134.8	0,08	2.03	5.05	0.94	3000	450	0.714
KH_2PO_4 (experiment)														
c	[4]						122,7	0,03	1.3	5.1 [23]		3200	520 [24]	0.7
d	[5]						123	0.05	1.83					

Note. Here ΔS is the entropy of the transition, defined as $S(T_C + 0) - S(0)$. C_+ and C_- are the Curie-Weiss constants for the paraphase and ferroelectric phase. $1 dB = 4.8 \times 10^{-18}$ cgs esu is the Debye dipole-moment unit.

the table and from Fig. 3, since the transition is generally narrow and is close to the transition in the Slater model, even relatively small factors influence here strongly the behavior near T_C, although this influence decreases with increasing distance from T_C.

Besides the striction term, the other terms of second and third order in the ion displacements are of the same order in the anharmonicity (see, for example,[28]). If these terms are assumed small, then the displacements can be regarded in the first approximation, as before, as linearly connected with σ[20,12]. Expressing them in terms of σ, we again arrive at a formula similar to (23), except that q is now connected not only with the striction coefficients, but also with other anharmonic coefficients.

More appreciable deviations from (23) can result from an allowance for the correlation effect and for the growth of the long-wave fluctuations near T_C[17,18]. These effects increase as T_0 is approached, and can therefore be more strongly pronounced in KDP than in DKDP, since $T_C - T_0$ is noticeably smaller here. It is known that when these effects are taken into account the polarization and the subseptibility increase more rapidly near T_C than in the self-consistent field approximations[17,18]. This may explain, in particular, why the Curie-Weiss constants in the table are somewhat lower than in experiment. In addition, Larkin and Pikin[29] have shown that, in the region of strong correlation effects, striction coupling with the elastic forces always causes the phase transition to become of first order. When T_C is approached to be sure, the correlation effects in uniaxial ferroelectrics of the KDP type increase more slowly, logarithmically,[18], and generally speaking they never become too strong here if the piezoelectric effect in the paraphase is taken into account[19]. However, estimates of these effects are quite uncertain and do not contain a formal small parameter[18,19], so that one cannot exclude the possibility that these effects are the causes of the first-order transition and of the sharp growth of P(T) in KDP.

To obtain a quantitative idea of the total contribution of the anharmonic and correlation effects, we have attempted to describe them with the aid of expression (23), in which q is a new reconciliation parameter. In order not to complicate the calculation scheme, in the last term of (23) as well as in the term F_0, was taken to be $\sigma(a)$ as defined by (6). The values of q in sets 10 and 11 were matched to the values of ΔP_C from the papers of Strukov et al.[2] and of Benepe and Reese[5]. We see that in accordance with the foregoing remarks, sufficiently small $q \sim 0.015T_C$ have a strong effect on P(T) near T_C, almost annihilating the noted discrepancy, and that negligible changes of q alter ΔP_C strongly.

It is interesting that the values obtained thereby for the difference $T_C - T_0$, which is very small and can be assumed to be sensitive to the accuracy of the calculation, turn out to be in reasonable agreement with experiment. We have attempted to compare the value of q for KDP with the "pure striction" value q_S (24). The use of data on c_{ik}, given in the book by Iona and Shirane[1] and the data of Kobayashi et al.[30] on q_{ik}, yielded $q_S \sim 0.23°$, i.e., smaller than in the table by almost one order of magnitude. It is unclear whether it is necessary to ascribe the obtained agreement of P(T) and $T_C - T_0$ to other anharmonic terms that make a definite contribution to q, or whether formula (23) gives a sufficient interpolation also of the contribution of the remaining effects, particularly correlation effects.

Finally, Set 3 illustrates the influence of the term with q on the thermodynamics of DKDP. Since the meaning of q is not quite clear, we do not know how it should be altered by deuterization, but we see that the small $q_D \sim 0.3q_H$ seems to improve somewhat the agreement with experiment. Recognizing that the change of T_C with pressure, which is proportional to q_{ik}, is smaller in DKDP[31], and $T_C - T_0$ is larger, than in KDP, the decrease of q_D in comparison with H can be regarded as not contradicting the ideas developed above.

6. SATURATION POLARIZATION. ESTIMATES OF THE PARAMETERS OF THE OH AND OD BONDS

In the discussion of P_S, we note first that at low T and $\Gamma \neq 0$, the employed approximation, which includes the "transverse" matching equation (7b), no longer holds, since it gives a meaningless result concerning the "anti-Curie point," a vanishing of the polarization at a certain temperature T_{ac}[8]. The reason is that since σ^z and σ^x do not commute, the interaction of the particles inside the cluster (3) cannot be replaced by specifying a classical field with definite components, as in (4), and at low T, when only one, lowest quantum state is significant in H_4 and H_1, the matching conditions (6) and (7), which imply such an equivalence, have only a zero solution at $\sigma = a = 0$. If we do not insist on transverse matching, i.e., assume $\eta = 0$, then no anti-Curie point arises, and σ tends to a finite limit as $T \to 0$, for example to $\sigma_s = 1 - \Gamma^2/2w^2$ at $\Gamma^2 \ll w^2$. However, in the description of the transition, where the thermal fluctuations are more important than the quantum fluctuations, the absence of a transverse matching would make the accuracy of F worse, as can be seen from variational considerations.

It can be shown, however, that at small δ_0 the region of the fictitious decrease of polarization and of T_{ac} lies quite low, $T_{ac} \lesssim \delta_0^2 T_c$. For the parameters used in KDP, this is illustrated by the left-hand side of Fig. 3. Actually, however, the saturation of P(T) to P_s occurs already near T_c. We shall therefore take P_s, just as Blinc and Svetina do[8], to mean precisely this value, which, as can be seen from Fig. 3, is practically constant in a wide interval of T. The values of σ_s obtained in this case are shown in the table. We see that in spite of the noticeable tunneling, the values of σ_s in KDP differ from unity by only several percent. Therefore the observed decrease of P_s in comparison with DKDP is connected not so much with the tunneling Γ as with the change of the coupling moment p in accordance with (21).

An interpretation of this change of p and of the interaction constants is important for the understanding of the microscopic picture of the transition. Blinc and Svetina[8] have assumed that this change is due to the strong lengthening of the O—H—O bond upon deuteration, $\Delta L = L_D - L_H = 0.14$ Å, as cited in the unpublished paper by Garret (see[32]). This value is much larger than the known L of compounds with OH bonds[33], namely $\Delta L \sim 0.01$–0.04 Å. In addition, the assumption[8] that ΔL coincides with the change of the distance $2l$ between the minima (see Fig. 1) is likewise not very obvious. We wish to note in this connection that the relative small change of p and ξ_{sa}, which in accordance with (21) and the table is necessary for the description of deuteration ($p_D - p_H \approx 0.15\, p_D$), may be connected to a considerable degree simply with the change of the amplitudes of the zero-point oscillations in the potential (Fig. 1), even without a change in its parameters (as is noted also in[8]). Indeed, for hydrogen, in view of the smaller mass, the levels ϵ_s and ϵ_a lie higher than for deuterium. Therefore, if it is assumed in accordance with Fig. 1 and the accepted models of the OH bond[33] that the outer edge of each of the $U(\xi)$ wells is steeper than the inner edge, then it is clear that with increasing mass the average distance to the center and the dipole moment of the transition ξ_{sa} increase.

For quantitative estimates we can use the calculations of[34], in which the coupling potential $U(\xi)$ was approximated by the expression

$$U(\xi) = \frac{8\hbar^2}{ml^2} A \left(-\frac{\xi^2}{l^2} + \frac{\xi^4}{2l^4} \right). \tag{25}$$

Assuming for the OH bond in accordance with[1] $2l \sim 0.35$ Å and in accordance with the table $\Gamma = \epsilon_a - \epsilon_s \approx 140°$, we obtain from[34] $A \approx 2.95$ and $(\xi_{sa})_H \sim 0.9 l_H$. If it is assumed that when the bond is lengthened the barrier ΔU increases in proportion to the elongation:

$$\Delta U_H : \Delta U_D = l_H / l_D,$$

then to obtain the values $(\xi_{sa})_H : (\xi_{sa})_D \approx 0.85$ given in the table and in (21) it suffices to assume $2l_D - 2l_H \approx 0.023$ Å; in this case $\Gamma_D \approx 4°$. If we assume that the shape of the potential remains unchanged and $l_H = l_D$, then the change of ξ_{sa} by deuteration would be ~6% and Γ_D would be ~ 10°. We note also that the distance to the next excited level $\epsilon_2 - \epsilon_a$ is of the order of 13,000°, thereby justifying the neglect of these states.

Actually, the shape of the potential along the OH bond differs apparently strongly from (25). This is seen, in particular, from the fact that in the presented estimate the height of the barrier, $\Delta U \sim 10{,}000°$, is apparently too large for such small l_H (see, for example,[33,35]). More reasonable, in accordance with the assumed concepts concerning the interatomic interactions, is the form of the potentials shown in Fig. 1 dashed, with a more gently sloping and broader barrier. It is seen from the figure that in such a potential the distance between the minima can be noticeably larger than the distance between the average positions of the H ions (~0.35 Å), which was identified above with $2l_H$. Therefore the effect of the change of ξ_{sa} upon deuteration is apparently larger here than in (25) and may be sufficient to account for the observed change in the parameters (21) even without a change in the distance between the minima of $U(\xi)$.

The authors are deeply grateful to V. M. Osadchiev for hints and help during the numerical calculations, to B. A. Strukov for numerous discussions that have stimulated this work, and to N. D. Sokolov for valuable remarks.

---

[1] F. Iona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962 (Russ. transl., Mir, 1965), Chap. III.

[2] B. A. Strukov, A. Baldur, and I. A. Velichko, Fiz. Tverd. Tela 13, 2484 (1971) [Sov. Phys.-Solid State 13, 2085 (1972)].

[3] B. A. Strukov, M. Amin, and A. S. Sonin, ibid. 9, 2421 (1967) [9, 1894 (1968)].

[4] B. A. Strukov, M. A. Korzhuev, A. Baldur, and V. A. Koptsik, ibid. 13, 1872 (1971) [13, 1569 (1972)]. B. A. Strukov, M. Amin, and V. A. Kopcik, Phys. Stat. Sol. 27, 741 (1968).

[5] W. Benepe and W. Reese, Phys. Rev., B3, 3032 (1971).

[6] J. C. Slater, J. Chem. Phys., 9, 16 (1941).

[7] M. Tokunaga and T. Matsubara, Prog. Theor. Phys., 35, 581 (1966).

[8] R. Blinc and S. Svetina, Phys. Rev., 147, 430 (1966).

[9] U. Takagi, J. Phys. Soc. Japan, 3, 271 (1948).

[10] H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev., 133, A165 (1964).

[11] R. Blinc, J. Chem. Phys. Sol., 13, 204 (1960).

[12] J. Villain and S. Stamenkovic, Phys. Stat. Sol., 15, 585 (1966). K. Kobayashi, J. Phys. Soc. Japan, 24, 497 (1968).

[13] W. Cochran, Adv. Phys., 18, 157 (1969).

[14] E. H. Lieb, Phys. Rev. Lett., 19, 108 (1967). B. Sutherland, C. N. Yang, and C. P. Yang, Phys. Rev. Lett., 19, 588 (1967).

[15] H. Takahashi, Proc. Phys. Math. Soc. Japan, 23, 1069 (1941).
[16] V. Kopsky, Phys. Stat. Sol., 5, 69 (1971).
[17] V. L. Pokrovskiĭ, Usp. Fiz. Nauk 94, 127 (1968) [Sov. Phys.-Usp. 11, 66 (1968)].
[18] A. P. Levanyuk, Izv. AN SSSR 29, 879 (1965). V. G. Vaks, A. I. Larkin, and S. A. Pikin, Zh. Eksp. Teor. Fiz. 51, 361 (1966) [Sov. Phys.-JETP 24, 240 (1967)].
[19] A. P. Levanyuk and A. A. Sobyanin, ZhETF Pis. Red. 11, 540 (1970) [JETP Lett. 11, 371 (1970). J. Villain, Sol. Stat. Commun. 8, 295 (1970).
[20] V. G. Vaks and A. I. Larkin, Zh. Eksp. Teor. Fiz. 49, 975 (1965) [Sov. Phys.-JETP 22, 678 (1966)].
[21] R. Blinč and M. Ribaric, Phys. Rev., 130, 1816 (1963).
[22] V. H. Schmidt and E. A. Uehling, Phys. Rev., 126, 447 (1963).
[23] J. Azoulay, J. Grinberg, I. Pelah, and E. Wiener, J. Chem. Phys. Sol., 29, N5, 813 (1968).
[24] S. Tsunekawa, Y. Yshibashi, and Y. Takagi, J. Phys. Soc. Japan, 27, 918 (1969).
[25] T. L. Hill, Statistical Mechanics, McGraw, 1956, Secs. 44–46.
[26] B. J. Isherwood and J. A. James, J. de Phys., 33, N4, Suppl., C-91, 1972.
[27] A. F. Devonshire, Phil. Mag., 42, 1065 (1951).
[28] V. G. Vaks, Zh. Eksp. Teor. Fiz. 54, 910 (1968); 58, 296 (1970) [Sov. Phys.-JETP 27, 486 (1968), 31, 161 (1970)].
[29] A. I. Larkin and S. A. Pikin, ibid. 56, 1664 (1969) [29, 891 (1969)].
[30] Y. Kobayashi, Y. Uesu, I. Mizutani, and Y. Enomoto, Phys. Stat. Sol., (a), 3, 63 (1970).
[31] R. Blinc and B. Zekš, Phys. Lett., 26A, 468 (1968).
[32] B. S. Garret, US Oak Ridge Nat. Lab. Rep., ORNL-1745, 149 (1954).
[33] W. C. Hamilton and J. A. Ibers, Hydrogen Bonding in Solids, W. A. Benjamin, 1968.
[34] R. J. Somorjai and O. F. Hornig, J. Chem. Phys., 36, 1980 (1962).
[35] V. A. Savel'ev and N. D. Sokolov, Teor. i Eksp. Khim. 6, 174 (1970).

Translated by J. G. Adashko
72