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The Dynamics of Ionic Lattices of Ferroelectric Crystals in Limiting Cases

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In this article a method is proposed for the investigation of the motion of the ions of a ferroelectric which is not limited by the magnitude of the anharmonic forces. A ferroelectric is considered whose ferroelectric ions vibrate as a rigid lattice, and coupled vibrations of two rigid lattices are also considered. The temperature dependence of the displacements and of their dispersions is obtained in qualitative agreement with experiment. Criteria are established for the number of phase transitions and their nature. Results of the investigation of a model anharmonic vibrator are made more precise, in which a possibility of a transition of the first kind is demonstrated. A model study is proposed of a ferroelectric which contains diatomic ferroelectric molecules. Criteria are established for the number and nature of phase transitions.

THE existing theories of ferroelectricity, except for the early work of Slater[1], assume that the motions of ferroelectric ions in the absence of polarization take place statistically independently of one another, so that the phase integral of the translational lattice breaks up into a product of the phase integrals of the ions. In studying problems of the polarization of liquids such theories are referred to as model theories. In a solid state there exists a greater correlation between the motions of the ions, so that it is useful to investigate another limiting case in which the ferroelectric ions form a rigid lattice (infinite wavelength). To this case belong inorganic crystals of simple structure, whose ferroelectric ions are situated relatively near to one another and the predominant wavelengths of whose vibrations are much larger than the interatomic distances. The theory of melting based on the analysis of the vibrations of a rigid lattice has turned out to be satisfactory[2]. The realization of model representations may be expected to occur in complex organic crystals with relatively large distances between ferroelectric ions, for example, in Rochelle salt.

An important role in the phenomena of ferroelectricity is played by the anharmonicity of the forces acting on the ferroelectric ions. It makes it possible to introduce normal coordinates not coupled to one another, and to define space-time trajectories of ions as is done in Born's theory[3]. Statistical methods of the determination of observed average characteristics of the motion are also complicated, and up to the present time have been applied only on the assumption of the smallness of the anharmonic terms, which imposed certain limitations. In this article we start out by assuming that the randomness in the motion of the ions of a solid is relatively small, and that it is not necessary, in order to take it into account, to utilize the apparatus of statistical mechanics which is more suitable for the treatment of liquids and gases[4]. The observed average characteristics of motion can be determined from certain dynamic principles without computing space-time trajectories. Inasmuch as the deBroglie wavelength of the ion of a solid is of the order 0.1-0.5 A, one can consider that space-time trajectories do not exist. In the present article we examine by a similar method of averaged parameters the vibrations of the rigid lattice of a ferroelectric, model theories, coupled vibrations of two rigid lattices and a model theory of a ferroelectric with diatomic ferroelectric molecules. The last case is realized in the case of Rochelle salt whose ferroelectric ions-protons are located in the lattice in pairs relatively distant from one another, so that a correlation exists only between the motion of the ions of a single pair.

1. THE BASIS OF THE METHOD OF AVERAGED PARAMETERS

Hamilton's variational principle is written in the form

$$\delta\left(\frac{1}{t_2-t_1}\int_{t_1}^{t_2} L\,dt\right)=0 \qquad (1.1)$$

under the condition $\delta q(t_1)=\delta q(t_2)=0$. In the case of statistical equilibrium it is useful to work with the limit of the expression being varied under the condition $t_1\to-\infty$, $t_2\to\infty$ which exists in the case of bounded motion, and which is equal to the average value of the Lagrangian function $\overline{L}$. If we demand that the variations in the coordinates and the velocities should be bounded functions of time, and if we take into account the fact that the motion is bounded, we may go over from (1.1) to Hamilton's principle in the form[5] $\delta \overline{L} = 0$.

We shall apply this principle using Ritz's method. The true and quite complicated dependence of the coordinates on time we shall represent in the form of functions which contain parameters which define the average characteristics of the motion. The values of these parameters are found from the conditions that $\overline{L}$ should be an extremum. As such parameters we shall take the average value of the coordinate af the ion and its dispersion:

$$\overline{q}_k = s_k, \quad \overline{(q-\overline{q}_k)^2} = u_k^2. \tag{1.2}$$

Representing q_k in the form

$$q_k = s_k + u_k\theta_k(t), \tag{1.3}$$

we shall obtain on the basis of (1.2):

$$\overline{\theta}_k = 0, \quad \overline{\theta_k^2} = 1. \tag{1.4}$$

The manifold of bounded functions which satisfy conditions (1.4) represents the manifold of microscopic motions with the same average coordinate and dispersion. The relationship to the temperature is given by the relation $\overline{w}_k = kT/2$, where $\overline{w}_k$ is the average kinetic energy associated with some one generalized coordinate.

A less general method is obtained if one starts out from Hamilton's equations

$$\dot{p}_k = -\partial H/\partial q_k, \quad \dot{q}_k = \partial H/\partial p_k. \tag{1.5}$$

Averaging these equations over an infinite time interval we shall obtain

$$\overline{\partial H/\partial q_k} = 0, \quad \overline{\partial H/\partial p_k} = 0. \tag{1.6}$$

From (1.5) it follows that

$$\dot{p}_k q_l + \dot{q}_l p_k = \frac{d}{dt}(p_k q_l)$$
$$= -q_l \frac{\partial H}{\partial q_k} + p_k \frac{\partial H}{\partial p_l}.$$

Averaging over time we obtain

$$\overline{q_l \partial H/\partial q_k} = \overline{p_k \partial H/\partial p_l}. \tag{1.7}$$

Expressions (1.6) and (1.7) form the required group of equations. The connection with the temperature is given in the same way as before.

2. ONE-DIMENSIONAL ANHARMONIC VIBRATIONS OF A RIGID LATTICE

The Lagrangian function of a single ion of the rigid lattice is equal to

$$L = \frac{m}{2}\left(\dot{\xi}^2 - \omega_0'^2\xi^2 - \frac{a^2}{2}\xi^4\right), \tag{2.1}$$

where $\omega_0'^2 = c'/m$, $a^2 = b/m$. Using (1.3) and (1.4) we find

$$\overline{\xi^4} = s^4 + 6s^2u^2 + 4su^3\overline{\theta^3} + u^4\overline{\theta^4}.$$

We shall take $\overline{\theta^3} = 0$, assuming that the function $\theta(t)$ takes on with equal probability both the value $+\theta$, and the value $-\theta$. In view of the condition $\overline{\theta^2} = 1$, we may consider that $\overline{\theta^4}$ is equal to unity in order of magnitude. Averaging (2.1) we obtain

$$\frac{2}{m}\overline{L} = \dot{u}^2\overline{\dot{\theta}^2} - \omega_0'^2(s^2+u^2) \tag{2.2}$$
$$-\frac{a^2}{2}(s^4 + 6s^2u^2 + u^4\overline{\theta^4}).$$

Using the extremal conditions $\partial\overline{L}/\partial s = 0$, $\partial\overline{L}/\partial u = 0$ and eliminating $\overline{\dot{\theta}^2}$ by means of the relationship $mu^2\overline{\dot{\theta}^2} = kT$ we shall obtain two equations:

$$s(a^2s^2 + \omega_0'^2 + 3a^2u^2) = 0, \tag{2.3}$$

$$\overline{\theta^4}a^2u^4 + 3a^2s^2u^2 + \omega_0'^2u^2 - kT/m = 0. \tag{2.4}$$

From (2.3) it follows that if $\omega_0'^2 > 0$, then only a single real solution $s = 0$ is possible which corresponds to the absence of spontaneous polarization. If $\omega_0'^2 < 0$, then for a sufficiently small u spontaneous polarization is possible. Since the dispersion u is certainly an increasing function of temperature, then above a certain temperature only the solution $s = 0$ will turn out to be possible. In the case $\omega_0'^2 < 0$, the substance is a ferroelectric. Equation (2.4) with $s = 0$ determines the dispersion of the oscillations of an ion of a paraelectric or a ferroelectric at high temperature.

In the case of a paraelectric we obtain

$$u^2 = \frac{2kT}{m\omega_0'^2}\left[1 + \sqrt{1 + \frac{4\overline{\theta^4}a^2}{m\omega_0'^4}kT}\right]^{-1} \tag{2.5}$$

For a ferroelectric (2.4) gives

$$u^2 = -\frac{2kT}{m\omega_0'^2}\left[\sqrt{1+\frac{4\overline{\theta^4}a^2}{m\omega_0'^4}kT}-1\right]^{-1} \tag{2.6}$$

We now proceed to investigate a ferroelectric at temperatures which correspond to the existence of spontaneous polarization. Eliminating s^2 from Eqs. (2.3) and (2.4) we obtain the equation for the dispersions

$$(9-\overline{\theta^4})\,a^2u^4 + 2\omega_0'^2u^2 + kT/m = 0. \tag{2.7}$$

From this we obtain, choosing in front of the radical that sign which gives $u^2 = 0$ at $T = 0$,

$$u^2 = -\frac{kT}{m\omega_0'^2}\left[1+\sqrt{1-\frac{(9-\overline{\theta^4})\,a^2}{m\omega_0'^4}kT}\right]^{-1}. \tag{2.8}$$

At low temperatures we obtain the formula for the dispersion of a harmonic vibrator

$$u^2 = -kT/2m\omega_0'^2 = -kT/2c'$$

with the coefficient of elasticity equal to $-2c'$. This is the coefficient of elasticity in the region of the minimum of the curve (Fig. 1) where the ion is located at low temperatures. As the temperature increases the dispersion grows faster than in accordance with a linear law. The formula (2.8) is not applicable for temperatures $T > T' = m\omega_0'^4/(9-\overline{\theta^4})ka^2$.

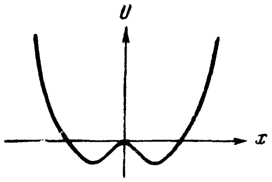

FIG. 1

On the basis of (2.3) and (2.8) we obtain the spontaneous displacement

$$s^2 = -\frac{\omega_0'^2}{a^2}\left\{1-\frac{3a^2kT}{m\omega_0'^4}\times\left[1+\sqrt{1-\frac{(9-\overline{\theta^4})\,a^2}{m\omega_0'^4}kT}\right]^{-1}\right\}. \tag{2.9}$$

This equation may cease to hold at temperatures less than T', if its right-hand side becomes negative at $T = T'$. Making this substitution we obtain

$$s_{T'}^{(2)} = -(\omega_0'^2/a^2)\,[1-3/(9-\overline{\theta^4})]. \tag{2.10}$$

The right-hand side is positive if $\overline{\theta^4} < 6$. In the case of sinusoidal vibrations, $\theta(t) = \sqrt{2}\sin(\omega t + \psi)$ and $\overline{\theta^4} = 1.5$, which is appreciably less than 6.

In the case of anharmonic vibrations $\frac{2}{3}\,\overline{\theta^4}$ apparently exceeds unity by only a small amount, and consequently,

$$T' = m\omega_0'^4/(9-\overline{\theta^4})ka^2 \tag{2.11}$$

is the temperature of a phase transition of the first kind.

We then find other quantities of interest. The spontaneous displacement at absolute zero is

$$s_{T=0}^2 = -\omega_0'^2/a^2. \tag{2.12}$$

The limit of the displacement, when $T \to T'$ from below is

$$s_{T'-0}^2 = -(\omega_0'^2/a^2)(6-\overline{\theta^4})/(9-\overline{\theta^4}). \tag{2.13}$$

The limit of the dispersion, when $T \to T'$ from below is

$$u_{T'-0}^2 = -(\omega_0'^2/a^2)/(9-\overline{\theta^4}). \tag{2.14}$$

The limit of the dispersion, when $T \to T'$ from above is

$$u_{T'+0}^2 = -\frac{2}{9-\overline{\theta^4}}\left[\sqrt{1+\frac{4\overline{\theta^4}}{9-\overline{\theta^4}}}-1\right]^{-1}\frac{\omega_0'^2}{a^2}. \tag{2.15}$$

Assuming $\overline{\theta^4} = 2$, we obtain

$$T' = 0.143\,m\omega_0'^4/ka^2; \tag{2.16}$$

$$s_{T'-0} = 0.75\,|\omega_0'|/a;$$

$$u_{T'-0} = 0.38\,|\omega_0'|/a;$$

$$u_{T'+0} = 0.78\,|\omega_0'|/a.$$

Figure 2 shows the variations of s and u with temperature. Analogous relationships had been established experimentally by Könzig[6] for $BaTiO_3$ by methods of X-ray analysis. Although in the case of $BaTiO_3$ two lattices are displaced, and moreover they oscillate in space, the qualitative dependences remain fundamentally analogous to those of Fig. 2.

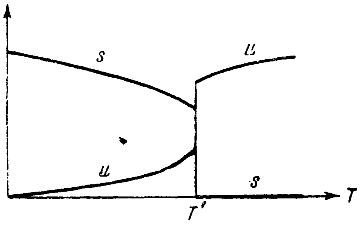

FIG. 2

We note that $m\omega_0'^4/4a^2 = U_m$ is the height of the potential barrier which separates the minima of the curve of Fig. 1. In accordance with (2.16), $kT' = 0.57\ U_m$. The quantity kT is, roughly speaking, the total energy of the oscillator at the transition point if one equates the average values of the kinetic and potential energies. It is evident that the equality $kT' = \gamma U_m$, where $\gamma \approx 1$, must hold for a barrier of arbitrary shape, and not only for that special shape which has been investigated above. The existence of the dependence of the phase transition point on the height of the potential barrier distinguishes the theory outlined above from the model theory of local minima[7]. Another difference is the existence of a discontinuity in the temperature dependence of the displacement. This also distinguishes the theory of the rigid lattice from the model theory of the anharmonic oscillator.

Let us make some numerical estimates. From (2.11) and (2.12) we have

$$kT' = bs_{T-0}^4/(9 - \overline{\theta^4}).$$

For $BaTiO_3$ it is known that $T' = 400°$, $s_{T=0.1}$A. Assuming $\overline{\theta^4} = 2$ we shall obtain $b = 4 \times 10^{23}$, $c' = 4 \times 10^5$. Values close to these can be obtained by a direct calculation using the known parameters of the ions.

3. PHASE TRANSITIONS IN A FERROELECTRIC WITH TWO LATTICES CAPABLE OF DISPLACEMENT

The present investigation can be applied to certain ferroelectrics which have more than two transitional lattices. In particular, one should note the field of solid solutions of ferroelectric components. Restricting ourselves to one-dimensional vibrations we shall characterize the positions of the ions of the two lattices by the coordinates ξ_1 and ξ_2, which are measured from the symmetrical positions in which the forces acting on the ions are equal to zero. The Lagrangian function for a molecule has the form

$$L = \frac{m_1}{2}\dot{\xi}_1^2 + \frac{m_2}{2}\dot{\xi}_2^2 - \frac{c_1'}{2}\xi_1^2 \qquad (3.1)$$

$$- \frac{c_2'}{2}\xi_2^2 - c_{12}'\xi_1\xi_2 - \frac{b_1}{4}\xi_1^4 - \frac{b_2}{4}\xi_4^2.$$

Terms of the form $\xi_1^3\xi_2, \ldots$ are omitted. The coefficients c_1', c_2', c_{12}' are the direct and the mutual coefficients of elasticity which take into account the polarization of the ions. The coefficients b_1 and b_2 are taken to be positive.

Averaging (3.1), we obtain

$$\overline{L} = \frac{m_1}{2}u_1^2\overline{\dot{\theta}_1^2} + \frac{m_2}{2}u_2^2\dot{\theta}_2^2 \qquad (3.2)$$

$$- \frac{c_1'}{2}(s_1^2 + u_1^2) - \frac{c_2'}{2}(s_2^2 + u_2^2)$$

$$- c_{12}'s_1s_2 - \frac{b_1}{4}(s_1^4 + 6\,s_1^2u_1^2 + \overline{\theta_1^4}u_1^4)$$

$$- \frac{b_2}{4}(s_2^4 + 6s_2^2u_2^2 + \overline{\theta_2^4}u_2^4).$$

Equating to zero the derivatives with respect to s_1, s_2, u_1, u_2 and introducing temperature into these equations, we shall obtain

$$s_1^3 + 3s_1u_1^2 + (c_1'/b_1)s_1 + (c_{12}'/b_1)s_2 = 0; \qquad (3.3)$$

$$s_2^3 + 3s_2u_2^2 + (c_2'/b_2)s_2 + (c_{12}'/b_2)s_1 = 0; \qquad (3.4)$$

$$3s_1^2 + \overline{\theta_1^4}u_1^2 + c_1'/b_1 - kT/b_1u_1^2 = 0; \qquad (3.5)$$

$$3s_2^2 + \overline{\theta_2^4}u_2^2 + c_2'/b_2 - kT/b_2u_2^2 = 0. \qquad (3.6)$$

It is not possible to solve this system in the general case, and we shall undertake a qualitative investigation of it. From (3.3) and (3.4) it follows that if $s_1 = 0$, then also $s_2 = 0$, and conversely, so that the displacements may appear and disappear only simultaneously. Since the dispersions increase indefinitely with increasing temperature it may be shown that at sufficiently high temperature, $s_1 = s_2 = 0$. Indeed, if we assume the converse, and factor s_1 and s_2 outside the brackets in (3.3) and (3.4), we rewrite these equations in the form

$$s_1\varphi_1(T) + (c'_{12}/b_1)s_2 = 0;$$
$$(c'_{12}/b_2)s_1 + s_2\varphi_2(T) = 0,$$

where φ_1 and φ_2 increase indefinitely with temperature. The determinant of this system $\varphi_1\varphi_2 - c'^2_{12}/b_1b_2$ is positive at sufficiently high temperature, which is incompatible with the assumption that $s_1 \neq 0$ and $s_2 \neq 0$. Thus, if the substance is not a pyroelectric for which the melting point lies lower than the temperature of disappearance of spontaneous polarization, then at high temperature only the nonpolar phase exists. In this phase the dispersions are determined by the equation

$$u_1^2 + c'_1/\overline{\theta_1^4}b_1 - kT/\overline{\theta_1^4}b_1u_1^2 = 0. \tag{3.7}$$

in agreement with (3.5) and (3.6) (and similarly for u_2^2); conversely, the fulfillment of one of these equations characterizes the nonpolar phase. The solution of (3.7) has the form

$$u_1^2 = \frac{2kT}{|c'_1|}\left[\frac{c'_1}{|c'_1|} + \sqrt{1 + \frac{4\overline{\theta_1^4}b_1}{c'^2_1}kT}\right]^{-1}. \tag{3.8}$$

Let us suppose that we have the polar phase. Multiplying (3.5) by s_1, (3.3) by 3, subtracting term by term and carrying out the same operations on (3.6) and (3.4), we shall obtain the system of equations:

$$[(9 - \overline{\theta_1^4})u_1^2 + 2c'_1/b_1 + kT/b_1u_1^2]s_1 + 3(c'_{12}/b_1)s_2 = 0;$$
$$3(c'_{12}/b_2)s_1 + [(9 - \overline{\theta_2^4})u_2^2 + 2c'_2/b_2 + kT/b_2u_2^2]s_2 = 0.$$

From this it follows that the determinant

$$\Delta = \left[(9 - \overline{\theta_1^4})u_1^2 + 2\frac{c'_1}{b_1} + \frac{kT}{b_1u_1^2}\right] \times \left[(9 - \overline{\theta_2^4})u_2^2 + 2\frac{c'_2}{b_2} + \frac{kT}{b_2u_2^2}\right] - 9\frac{c'^2_{12}}{b_1b_2} \tag{3.9}$$

is equal to zero.

Let us for the sake of brevity denote the manifold of all those values of the temperature for which $s_1 = s_2 = 0$ by the term paramanifold. Let us denote the left-hand parts of (3.7) by D_1 and D_2; they are equal to zero everywhere within the paramanifold, and differ from zero outside it. The determinant Δ is equal to zero everywhere outside the paramanifold and, conversely, where $\Delta \neq 0$, there we have the paramanifold. Let us denote by the manifold M that submanifold of those points of the paramanifold in which $\Delta = 0$, and let us show that the manifold M is not generally empty. Over this manifold the following conditions hold: $D_1 = 0$, $D_2 = 0$, $\Delta = 0$. Substituting (3.8) into the equation $\Delta = 0$, we shall obtain for the temperature an irrational equation, the solutions of which are roots of a certain algebraic equation. From this it follows that the manifold M is finite. Let us investigate the question as to the kind of points of which this manifold may be composed. Let the point A be an isolated point of the paramanifold (Fig. 3); consequently, as T approaches T_A $s_1 \to 0$, $s_2 \to 0$. Transposing [in Eqs. (3.3) and (3.4)] s_1^3 and s_2^3 into the right-hand side and solving the equations with respect to s_1 and s_2 as linear equations, we obtain

$$s_1 = -\frac{(3u_2^2 + c'_2/b_2)s_1^3 - (c'_{12}/b_2)s_2^3}{(3u_1^2 + c'_1/b_1)(3u_2^2 + c'_2/b_2) - c'^2_{12}/b_1b_2} \tag{3.10}$$

and similarly for s_2. The determinant of this system vanishes at the point A. As may be seen from (3.7) and (3.9) it is equal to the value of Δ over the paramanifold reduced ninefold, and consequently, Δ vanishes at isolated points of the paramanifold, and these points belong to the manifold M.

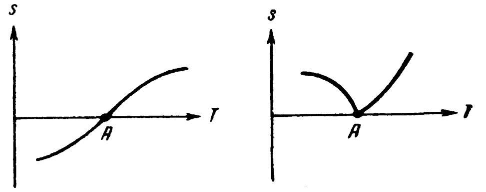

FIG. 3

Let the point C be the upper or the lower bound of the paramanifold, or the Curie point (Fig. 4). By reasoning similar to the above, but letting s_1 and s_2 approach zero from one side, we conclude that the bounds of the paramanifold belong to the manifold *M*. In addition to the bounds of the paramanifold and the isolated points one may also have points of discontinuity, but these are outside the scope of the present investigation. We shall deal with them only indirectly.

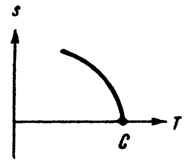

FIG. 4

Let us now proceed to a geometrical investigation of the Eqs. (3.3) and (3.4). We note that Eqs. (3.3)-(3.6) are satisfied if one replaces s_1 and s_2 by $-s_1$ and $-s_2$. The change of sign of c'_{12} leads to a change of sign of one of the displacements. Since the dispersions are monotonic, although possibly discontinuous functions of the temperature, the dependence of the solutions of the Eqs. (3.3) and (3.4) on the parameters u_1^2 and u_2^2 qualitatively represents their dependence on the temperature. Without loss of generality one may take $c'_{12} < 0$ and distinguish the following three cases: 1) $c_1' > 0$, $c_2' > 0$; 2) $c_1' > 0$, $c_2' < 0$; 3) $c_1' < 0$; $c_2' < 0$.

We shall consider the rigid lattice to be ferroelectric only in the case when its own coefficient of elasticity is negative. The usual stability conditions at the temperature of absolute zero

$$\frac{\partial^2 U}{\partial s_1^2} > 0; \quad \frac{\partial^2 U}{\partial s_2^2} > 0; \quad \frac{\partial^2 U}{\partial s_1^2}\frac{\partial^2 U}{\partial s_2^2} - \left(\frac{\partial^2 U}{\partial s_1 \partial s_2}\right)^2 > 0$$

show that the state $s_1 = s_2 = 0$ is stable only in the first case if

$$c_{12}'^2 < c_1' c_2' . \qquad (3.11)$$

First Case. Neither of the two lattices is ferroelectric.

The graphs of Eqs. (3.3) and (3.4) are shown in Fig. 5. As the temperature is increased the point *C* approaches the origin, and at sufficiently high temperature the curves intersect only at the origin. However, it is possible that the curves intersect only at the origin at all temperatures; in such a case the substance is paraelectric. In this case the criterion for ferroelectric behavior is the inequality

$$(ds_2/ds_1)_3 (ds_1/ds_2)_4 < 1 \quad \text{for} \quad u_1 = u_2 = 0,$$

which leads to the inequality

$$|c_{12}'| > \sqrt{c_1' c_2'}. \qquad (3.12)$$

The spontaneous polarization in this case is entirely due to the interaction of the lattices, while each lattice separately does not have any tendency for a spontaneous displacement.

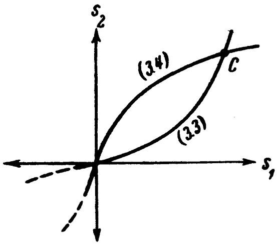

FIG. 5

Second Case. Only one of the two lattices is ferroelectric.

The corresponding graphs for a low and for a somewhat higher temperature are shown in Fig. 6. In this case the substance is a ferroelectric.

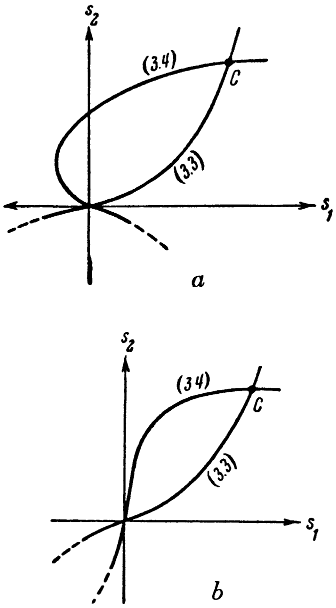

FIG. 6. a-$3u_2^2 + c_2'/b_2 < 0$, b-$3u_2^2 + c_2'/b_2 > 0$.

Third Case. Both lattices are ferroelectric ones.

The corresponding graphs for increasing temperatures are shown in Fig. 7. In this case at low temperatures not one but two nonzero intersections and two phase transitions are possible at low temperatures, but for this, the fulfillment of condition (3.11) is necessary. Thus, if the interaction between lattices is small, then at low temperatures such spontaneous displacements are established which correspond to the "natural" tendencies of the ferroelectric lattices for the production of spontaneous displacements. At still higher temperature the spontaneous displacements are determined by the interaction of the lattices. With a still further increase of temperature the spontaneous displacements disappear.

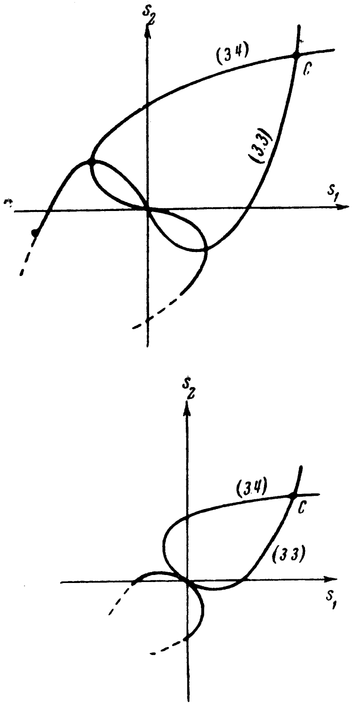

FIG. 7

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We now proceed to the investigation of the nature of the phase transitions in all cases and for this we shall determine the corresponding Curie points or the isolated points. If the corresponding temperatures turn out to be negative, then even though phase transformations may occur, nevertheless they must be discontinuous. We equate expression (3.9) to zero, using (3.7), which yields the following equation:

$$\left(\frac{c_1'|c_1'|}{6b_1}+kT_\mathrm{C}\Big/\left[\sqrt{1+\frac{4\overline{\theta_1^4}b_1}{c_1'^2}kT_\mathrm{C}}+\frac{c_1'}{|c_1'|}\right]^{-1}\right)$$
$$\times\left(\frac{c_2'|c_2'|}{6b_2}+kT_\mathrm{C}\Big/\left[\sqrt{1+\frac{4\overline{\theta_2^4}b_2}{c_2'^2}kT_\mathrm{C}}+\frac{c_2'}{|c_2'|}\right]^{-1}\right)$$
$$=\frac{c_{12}'^2|c_1'||c_2'|}{36b_1b_2}. \tag{3.13}$$

The solutions of this irrational equation can be found from the solutions of the complete algebraic equation of the fourth degree. Since we are seeking only the qualitative relationships we shall assume for simplicity

$$b_1=b_2=b;\ |c_1'|=|c_2'|=c'; \tag{3.14}$$
$$\overline{\theta_1^4}=\overline{\theta_2^4}=\overline{\theta^4}.$$

First Case. Using the notation $c'^2/6b=a$; $4\overline{\theta^4}b/c'^2=\varkappa$; $c'^2_{12}c'^2/36b^2=m$, $kT_c=\chi$, (3.13) may be written in the form

$$a+\chi/(\sqrt{1+\varkappa\chi}+1)^2=m. \tag{3.15}$$

Setting $1+\varkappa\chi=y^2$ with the condition $y>0$, we obtain

$$y=-(a\varkappa-1)\pm\varkappa\sqrt{m} \tag{3.16}$$
$$=1-{}^2/_3\,\overline{\theta^4}(1\mp|c_{12}'|/c').$$

Since ${}^2/_3\ \overline{\theta^4}\geq 1$, we must take the upper sign in (3.16) in order to obtain $y>0$.

The Curie temperature is equal to

$$T_\mathrm{C}=\frac{c'^2}{3bk}\left(\frac{|c_{12}'|}{c'}-1\right) \tag{3.17}$$
$$\times\left[1+\frac{1}{3}\overline{\theta^4}\left(\frac{|c_{12}'|}{c'}-1\right)\right].$$

It is positive if the condition (3.12) is satisifed, i.e., if in the first case a phase transition is possible at all, then it will be a phase transition of the second kind.

Second Case. Equation (3.13) has the form

$$\left(a+\frac{\chi}{\sqrt{1+\varkappa\chi}+1}\right)\times\left(-a+\frac{\chi}{\sqrt{1+\varkappa\chi}-1}\right)=m. \tag{3.18}$$

In analogy with the preceding we shall obtain $y^2 = m\varkappa^2 + (a\varkappa - 1)^2$ and

$$kT_{\mathrm{C}}=\frac{\overline{\theta^4}}{9b}c'^2\left[\left(\frac{c'_{12}}{c'}\right)^2+1-\frac{3}{\overline{\theta^4}}\right].$$

We have a phase transition of the first kind if the mutual coefficient of elasticity is small in comparison with the direct ones, and of the second kind if this coefficient is large.

Third Case. Equation (3.13) has the form

$$(-a+\chi/[\sqrt{1+\varkappa\chi}-1])^2=m. \tag{3.19}$$

From this we obtain

$$y=a\varkappa-1\pm\varkappa\sqrt{m}={}^2/_3\overline{\theta^4}(1\pm|c'_{12}|/c')-1.$$

If condition (3.11) is not satisfied, i.e., if only one transition exists, then $y > 0$ only corresponding to the upper sign. For sufficiently small $|c'_{12}|/c'$ the lower sign is also possible,

Further,

$$\varkappa\chi=y^2-1=\frac{2}{3}\overline{\theta^4}\left(1\pm\frac{|c'_{12}|}{c'}\right)\left[\frac{2}{3}\overline{\theta^4}\left(1\pm\frac{|c'_{12}|}{c'}\right)-2\right]. \tag{3.20}$$

If condition (3.11) is satisfied then (3.20) does not have any positive values, and both phase transitions are of the first kind. If condition (3.11) is not fulfulled, then the phase transition is of the second kind with a Curie temperature:

$$T_{\mathrm{C}}=\frac{c'^2}{3bk}\left(\frac{|c'_{12}|}{c'}+1\right)\times\left[\frac{\overline{\theta^4}}{3}\left(\frac{|c'_{12}|}{c'}+1\right)-1\right]. \tag{3.21}$$

On the basis of the above one may establish the general regularity that the domination of the mutual coefficient of elasticity over the direct ones leads to a phase transition of the second kind. The dependence of the displacements and of the total polarization on the temperature in the first and in the second cases is quite evident; one should only note that the total polarization determined by both displacements may be equal to zero, and in such a case the polar phase will be antiferroelectric. The thermodynamic theory of antiferroelectrics was developed in Ref. 8. The dependence of the displacements and of the polarization on the temperature in the third case in the presence of two phase transitions is shown in Fig. 8.

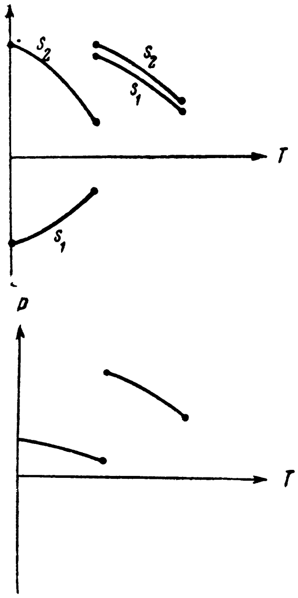

FIG. 8

We note that after the lower phase transition one of the displacements changes sign, so that in a special case one may have here a transition from a ferroelectric state into an antiferroelectric state.

4. MODEL INVESTIGATION OF THE ANHARMONIC VIBRATOR IN A SPHERICALLY SYMMETRIC POTENTIAL WELL

The calculations of this section are applicable to a vibrator both with a positive coefficient of elasticity (the model of Ginzburg-Devonshire) and also with a negative coefficient of elasticity which corresponds to the local minima model of Pauling-Slater. In this work we improve the results which were obtained not quite rigorously in Ref. 9, as it was assumed there that the effective field has no effect on the dispersion of the ion. The potential energy for a single anharmonic vibrator has the form

$$U = \frac{c}{2}\,(\xi^2 + \eta^2 + \zeta^2) \tag{4.1}$$

$$+ \frac{b}{4}\,(\xi^2 + \eta^2 + \zeta^2)^4 - \frac{1}{2}\,e^*A\,(\xi s_x + \eta s_y + \zeta s_z).$$

The coefficient ½ in front of the last term is introduced in order that the interaction of the ions will not be taken into account twice when the average potential energy of the whole lattice $N\bar{U} = -\frac{1}{2} Ne^*As^2 + \ldots$ is being calculated.

The Lagrangian function of a given ion is

$$L = \frac{m}{2}\,(\dot{\xi}^2 + \dot{\eta}^2 + \dot{\zeta}^2) - U. \tag{4.2}$$

Averaging (4.2), we shall obtain a system of equations for the average values of the coordinates of the ion s_x, s_y, s_z and of their dispersions u_x, u_y, u_z.

$$s_x\,[s_x^2 + s_y^2 + s_z^2 + 3u_x^2 \tag{4.3}$$

$$+ u_y^2 + u_z^2 + (c - e^*A)\,/\,b] = 0;$$

$$3s_x^2 + s_y^2 + s_z^2 + \overline{\theta_x^4}u_x^2$$

$$+ \overline{\theta_x^2\theta_y^2}u_y^2 + \overline{\theta_x^2\theta_z^2}u_z^2 + c\,/\,b = kT\,/\,bu_x^2;$$

$$s_y\,[s_x^2 + s_y^2 + s_z^2 + 3u_y^2$$

$$+ u_z^2 + u_x^2 + (c - e^*A)\,/\,b] = 0;$$

$$3s_y^2 + s_z^2 + s_x^2 + \overline{\theta_y^4}u_y^2$$

$$+ \overline{\theta_y^2\theta_z^2}u_z^2 + \overline{\theta_y^2\theta_x^2}u_x^2 + c\,/\,b = kT\,/\,bu_y^2;$$

$$s_z\,[s_x^2 + s_y^2 + s_z^2 + 3u_z^2$$

$$+ u_x^2 + u_y^2 + (c - e^*A)\,/\,b] = 0;$$

$$3s_z^2 + s_x^2 + s_y^2 + \overline{\theta_z^4}u_z^2$$

$$+ \overline{\theta_z^2\theta_x^2}u_x^2 + \overline{\theta_z^2\theta_y^2}u_y^2 + c\,/\,b = kT\,/\,bu_z^2.$$

From these equations it may be seen that spontaneous polarization is possible only if $e^*A > c$. Insofar as the direction in space of the displacement in a spherically symmetric potential well has no physical significance, we shall set $s_x = s_y = s_z$, $u_x = u_y = u_z$; then also $\overline{\theta_x^4} = \overline{\theta_y^4} = \overline{\theta_z^4} = \vartheta_1$ and $\overline{\theta_x^2\,\theta_y^2} = \overline{\theta_x^2\theta_z^2} = \overline{\theta_y^2\theta_z^2} = \vartheta_2$.. Equations (4.3) then reduce to the following:

$$s_x\,(3s_x^2 + 5u_x^2 + (c - e^*A)\,/\,b) = 0; \tag{4.4}$$

$$5s_x^2 + \vartheta u_x^2 + c\,/\,b = kT\,/\,bu_x^2, \tag{4.5}$$

where $\vartheta = \vartheta_1 + 2\vartheta_2$. An important difference between Eq. (4.5) and Eq. (2.5) of Ref. 9 is the presence of a term which consains s_x^2. In the region in which spontaneous polarization is absent we obtain

$$u_x^2 = \frac{2kT}{c}\left[\sqrt{1 + \frac{4\vartheta b}{c^2}\,kT} + 1\,\right]^{-1}, \tag{4.6}$$

if $c > 0$,

$$u_x^2 = -\frac{2kT}{c}\left[\sqrt{1 + \frac{4\vartheta b}{c^2}\,kT} - 1\,\right]^{-1}, \tag{4.7}$$

if $c < 0$.

In the region of spontaneous polarization by eliminating s^2 from (4.4) and (4.5), and taking into account that $Se^*A > 2c$, we obtain

$$u_x^2 = \frac{6kT}{5e^*A - 2c} \tag{4.8}$$

$$\times\left[1 + \sqrt{1 - 12\,\frac{25 - 3\vartheta}{(5e^*A - 2c)^2}\,bkT}\,\right]^{-1}$$

This expression ceases to be real if $T > T'$, where

$$T' = (5e^*A - 2c)^2\,/\,12\,(25 - 3\vartheta)\,bk. \tag{4.9}$$

If for $T \to T'$ from below the displacement tends to a real value different from zero, then at the transition through the point T' a discontinuous transition into the nonpolar state will occur, while in the opposite case the transition will be continuous. From (4.4), (4.8) and (4.9) we obtain

$$\lim_{T\to T'} s^2 = 3\lim_{T\to T'} s_x^2 \tag{4.10}$$

$$= \frac{1}{2\,(25 - 3\vartheta)\,b}\,[5\,(5e^*A - 8c) - 6\vartheta\,(e^*A - c)].$$

Thus, the transition will be of the first kind if

$$5\,(5e^*A - 8c) > 6\vartheta\,(e^*A - c), \tag{4.11}$$

and of the second kind if

$$5\,(5e^*A - 8c) \leqslant 6\vartheta\,(e^*A - c). \tag{4.12}$$

The equals sign corresponds to the critical case when the phase transition remains continuous, but acquires a number of special properties.

The condition (4.11) is fulfilled only if $c \leq 0$, i.e., in the model of the minima, and in the model of the purely anharmonic vibrator, we have a phase transition of the first kind. As long as ϑ lies within the limits 3-4½, then from (4.11) it follows that the phase transition will be of the first kind also in the model with one minimum if e^*A is much larger than c. In the case of a phase transition of the second kind the Curie point may be found from (4.4) and (4.5) if one take into account that from $T = T_C$ the dispersion satisfies both these equations with $s = 0$:

$$T_C = \frac{\vartheta}{25bk}(e^*A - c)\left(e^*A + \frac{5-\vartheta}{\vartheta}c\right). \quad (4.13)$$

Expression (4.13) agrees with expression (2.11) of Ref. 9, if one sets $\vartheta = 3$.

In the neighborhood of the Curie point s^2 is proportional to $T_C - T$ and, differentiating (4.4) and (4.5), we find

$$s^2 = -\frac{25k}{5(5e^*A - 8c) - 6\vartheta(e^*A - c)}(T_C - T) + \ldots \quad (4.14)$$

As we appraoch the fulfillment of the condition for a phase transition of the first kind the coefficient of $T_C - T$ increases, and in the critical case becomes infinite. On the basis of the data obtained above one may also determine the discontinuity in the specific heat for the transition through the Curie point. The average value of the Hamiltonian function for a single ion is determined by the formula

$$\frac{2}{3}\bar{H}_1 = kT - (e^*A - c)s_x^2 + cu_x^2 + \frac{b}{2}(3s_x^4 + \vartheta u_x^4 + 10s_x^2u_x^2). \quad (4.15)$$

The specific heat for a single ion in the neighborhood of the Curie point is given by

$$\frac{2}{3}C_1 = k - (e^*A - c)\frac{ds_x^2}{dT} + c\frac{du_x^2}{dT} + \vartheta bu_x^2\frac{du_x^2}{dT} + 5bu_x^2\frac{ds_x^2}{dT}. \quad (4.16)$$

Close by and below the Curie point we obtain from the above expression

$$\frac{2}{3}C_1 - k = \frac{15k}{6\vartheta(e^*A - c) - 5(5e^*A - 8c)}\left[c + \frac{1}{5}(e^*A - c)\right]. \quad (4.17)$$

As we approach the region of validity of the inequality (4.11) this quantity grows indefinitely. In the neighborhood of the upper Curie point the specific heat is determined by the formula

$$^2/_3\,C_1 - k = k[\vartheta(e^*A - c) + 5c]/[2\vartheta(e^*A - c) + 5c]. \quad (4.18)$$

This quantity remains angular as the region of validity of the inequality (4.11) is approached. Thus, the present investigation shows that in the model of the minima the phase transition must be of the first kind; in the model with the single minimum it must be also of the first kind if e^*A is much larger than c, and of the second kind if e^*A is smaller than c. The sharpness of the transition of the second kind may vary within wide limits, depending on the relationships between the force parameters e^*A and c. The one-dimensional case does not qualitatively differ from the case discussed above.

5. MODEL THEORY OF A FERROELECTRIC WITH DIATOMIC MOLECULES

The potential energy of the atoms forming the molecule taking into account their mutual polarization, but not taking into account the polarization of the medium, is given by

$$\frac{c_1'}{2}\xi_1^2 + c_{12}'\xi_1\xi_2 + \frac{c_2'}{2}\xi_2^2 + \frac{b_1}{4}\xi_1^4 + \frac{b^2}{4}\xi_2^4,$$

where ξ_1 and ξ_2 are the displacements of the atoms measured from their equilibrium positions. The potential energy of the molecule in the electric field determined by the polarization of the medium may be written in the form

$$-{}^1/_2\,e_1^*E_{ef_1}\xi_1 - {}^1/_2\,e_2^*E_{ef_2}\xi_2 \quad (5.1)$$

with the following expressions for the effective fields[10]:

$$E_{ef_1} = A_{11}'s_1 + A_{12}'s_2;\ E_{ef_2} = A_{21}'s_1 + A_{22}'s_2. \quad (5.2)$$

The primes on A_{ik} denote that in the calculation of the corresponding structural sums one must omit the neighboring ion present in the molecule under investigation. The potential energy per molecule is thus equal to

$$U = \frac{c'_1}{2}\xi_1^2 + c'_{12}\xi_1\xi_2 + \frac{c'_2}{2}\xi_2^2 \tag{5.3}$$
$$+ \frac{b_1}{4}\xi_1^4 + \frac{b^2}{4}\xi_2^4 - {}^1/_2\, \overset{*}{e}_1 (A'_{11}s_1 + A'_{12}s_2)\,\xi_1 - {}^1/_2\, \overset{*}{e}_2$$
$$\times (A'_{21}s_1 + A'_{22}s_2)\,\xi_2.$$

The average value of the Lagrangian function is found in the usual way

$$\overline{L} = \frac{m_1}{2} u_1^2\overline{\dot{\theta}_1^2} + \frac{m_2}{2} u_2^2\overline{\dot{\theta}_2^2} \tag{5.4}$$
$$- \frac{c'_1}{2}(s_1^2 + u_1^2) - \frac{c'_2}{2}(s_2^2 + u_2^2) - c'_{12}s_1s_2$$
$$- \frac{b_1}{4}(s_1^4 + 6s_1^2u_1^2 + \overline{\theta_1^4}u_1^4)$$
$$- \frac{b_2}{4}(s_2^4 + 6s_2^2u_2^2 + \overline{\theta_2^4}u_2^4) + \frac{1}{2}\overset{*}{e}_1A'_{11}s_1^2$$
$$+ \frac{1}{2}\overset{*}{e}_2A'_{22}s_2^2 + \frac{1}{2}(\overset{*}{e}_1A'_{12} + \overset{*}{e}_2A'_{21})\,s_1s_2.$$

The conditions for $\overline{L}$ to be an extremum after the temperature has been introduced into them have the form

$$s_1^3 + 3s_1u_1^2 + s_1(c'_1 - \overset{*}{e}_1A'_{11})/b_1 \tag{5.5}$$
$$+ s_2[c'_{12} - {}^1/_2(A'_{12} + A'_{21})]/b_1 = 0;$$

$$s_2^3 + 3s_2u_2^2 + s_2(c'_2 - \overset{*}{e}_2A'_{22})/b_2 \tag{5.6}$$
$$+ s_1[c'_{12} - {}^1/_2(A'_{12} + A'_{21})]/b_2 = 0;$$

$$3s_1^2 + \overline{\theta_1^4}u_1^2 + c'_1/b_1 - kT/b_1u_1^2 = 0; \tag{5.7}$$
$$3s_2^2 + \overline{\theta_2^4}u_2^2 + c'_2/b_2 - kT/b_2u_2^2 = 0. \tag{5.8}$$

These equations turn out to be similar in many respects to the corresponding equations for a crystal composed of two rigid lattices, but there are also differences which lead to a large variety of possible cases. This is connected with the fact that the ferroelectric ion (for example, $e_1^* A'_{11} > c'_1$) may exist either in a potential well with two minima ($c'_1 < 0$), or with one minimum ($c'_1 > 0$). Let us examine the possible variants very briefly, since the corresponding discussion is in many respects analogous to the case of rigid lattices.

1. Neither ion is ferroelectric: $e_1^* A'_{11} < c'_1$ and $e_2^* A'_{22} < c_2$. In this case only $c'_1 > 0$ and $c'_2 > 0$ are possible since $e_1^* A'_{11} > 0$ and $e_2^* A'_{22} > 0$ (the polarization forces determined by the displacement of the ion aid its further displacement, but do not hinder it). The substance is a paraelectric if

$$|c'_{12} - {}^1/_2(\overset{*}{e}_1A'_{12} + \overset{*}{e}_2A'_{21})| \tag{5.9}$$
$$< [(c'_1 - \overset{*}{e}_1A'_{11})(c'_2 - \overset{*}{e}_2A'_{22})]^{1/2}.$$

In the opposite case only one phase transition exists.

2. Only one ion is ferroelectric: $e_1^* A'_{11} > c'_1$, $e_2^* A'_{22} < c'_2$ or, conversely, $e_1^* A'_{11} < c'_1$, $e_2^* A'_{22} > c'_2$. The substance is a ferroelectric and there exists one phase transition.

3. Both ions are ferroelectric. In this case there are two phase transitions if condition (5.9) is satisfied, and one phase transition in the opposite case.

In order to draw conclusions in regard to the nature of the phase transitions one must examine the equation which determines the Curie points or the isolated points. In order to simplify calculations this investigation is carried out under the assumption

$$|c'_1| = |c'_2|;\ b_1 = b_2;\ \overline{\theta_1^4} = \overline{\theta_2^4};$$
$$|c'_1 - \overset{*}{e}_1A'_{11}| = |c'_2 - \overset{*}{e}_2A'_{22}|$$

and leads to the following results:

First Case. If condition (5.9) is not fulfilled, then a positive Curie temperature is obtained. Thus, if a phase transition is possible it will be of the second kind.

Second Case. $e_1^* A'_{11} > c'_1$ and $e_2^* A'_{22} < c_2$. Here, two subcases are possible: $c'_1 < 0$ and $c'_1 > 0$. The first subcase is analogous to the second case of rigid lattices, so that the transition will be of the first kind if the interaction forces are small in comparison with the self-forces, or to be more precise, if $|c'_{12} - ½(e_1^* A'_{12} + e_2^* A'_{21})|$ is small in comparison with $|e_1^* A'_{11} - c'_1|$ or $|e_2^* A'_{22} - c'_2|$. In the opposite case the transition will be of the second kind. If $c'_1 > 0$, then the phase transition will be of the second kind.

Third Case. Both ions are ferroelectric. Here three subcases are possible:

a) $c'_1 < 0$ and $c'_2 < 0$. Analysis shows that if condition (5.9) is fulfilled, then both phase transitions are of the first kind. If this condition is not fulfilled, then only a single phase transition of the second kind is possible.

b) $c_1' > 0$ and $c_2' > 0$. In this subcase if condition (5.9) is satisfied, then both phase transitions are of the second kind. If condition (5.9) is not satisfied, then only a single phase transition of the second kind is possible.

c) $c_1' < 0$ and $c_2' > 0$. In this subcase there is at least one phase transition of the second kind which will also be the only one if condition (5.9) is not fulfilled. The nature of the other phase transition in the case that condition (5.9) is fulfilled is to a large extent determined by the relationships between the force parameters of the vibrators.

From the above it is possible to draw the conclusion that a phase transition of the first kind is favored by the negative sign of the direct coefficients of elasticity, and by a small value of the interaction forces between the two ions.

One may also note that the total polarization determined by the displacements of both ions may turn out to be equal to zero, and then the third case apparently describes a crystal of the type of Rochelle salt. Here a change in sign of one of the displacements after the lower phase transition leads to the disappearance of the macroscopic spontaneous polarization, and it turns out to be possible only within a certain temperature interval.

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