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A model for a phase transition due to nonlinear resonance of lattice vibrations

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It is shown that a structural transition in a crystal can be due to a nonlinear resonance "capture" of different lattice vibration modes. The condition for capture is $\alpha > \epsilon$ (α is a dimensionless anharmonicity parameter and ϵ is a dimensionless coupling constant for the modes). A phase transition model is constructed on the basis of new experimental data for the group of isomorphous crystals of the triglycinsulfate type. It is shown that a coherent state of the orientational vibrations of the heavy-atom groups is formed below the transition point, and the thermodynamic characteristics of this state are found. The connection between the dynamical approach developed and the models for the ferroelectric type of ordering is discussed.

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INTRODUCTION

Structural lattice instability is one of the mechanisms that can lead to a phase transition of the ferroelectric type. From the dynamical point of view, such a transition may be accompanied by the appearance of the so-called "soft mode," whose frequency tends to zero as $T \to T_c$.[1] However, the dynamical approach allows us to look at the problem of instability of lattice structures from a somewhat more general point of view. Indeed, if the variation of some parameter (e.g., the temperature) leads to a situation in which some characteristic frequencies of the system turn out to be close (i.e., in resonance), then the structure of the system should also be reconstructed, and the soft mode corresponds to the particular case of such a resonance.

In[2] the possibility was discussed of the occurrence of a structural phase transition because of a resonance-type instability arising as a result of the interaction of certain types of degrees of freedom of the lattice. The present paper is devoted to a detailed analysis of this question. Underlying it are a number of experimental data on the analysis of the spectra of the Raman scattering (RS) of low-frequency optical lattice vibrations in the vicinity of a ferroelectric phase transition. These data have now been obtained for the family of isomorphous crystals of the TGS group (triglycinsulfate, triglycinselenate, triglycinfluoroberyllate),[3] for ammonium fluoroberyllate (AFB),[4] dihydrate of sodium ammonium selenate,[5] etc. It is customarily assumed that the phase transition occurring in the enumerated crystals is of the order-disorder type.[1] The RS data allow us, however, to obtain a more detailed picture of the phase transition. The reason for this consists, on the one hand, in the fact that there can exist in complex lattices individual structural atomic groups which are relatively weakly coupled to the remaining lattice and which execute motions almost independent of the other groups. Therefore, it may turn out to be possible to indicate that atomic group whose critical behavior determines (primarily) the phase transition. Thus, in all the above-enumerated crystals the isotopic substitution of hydrogen by deuterium does not lead to a significant change in the Curie temperature. This leads to the conclusion that the ordering is undergone by the relatively heavy elements: the glycine ions in TGS or the tetrahedral groups in the other crystals. On the other hand, the width of the line and its intensity in the RS spectra

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essentially depend on the coherence properties of the vibrations of the atomic groups in different lattice unit cells. Thus, the RS data may allow us to take a new view of a ferroelectric transition as a transition with a critical variation in the temperature dependence of the coherence properties of the vibrations of the atomic groups in the lattice that undergo the ordering.

If we introduce some effective potential in which the atomic groups vibrate, then the coherence factor for these vibrations in different unit cells is determined by the phase correlation of the vibrating groups (trajectory or orbit correlation). To the establishment of a long-range order below T_c should correspond an infinite correlation length of the phases of the trajectories belonging to different unit cells. A similar analysis, which underlies the present work, differs from the existing theories of the appearance of spontaneous polarization in having the dynamics of the trajectories of the atomic groups undergoing the ordering introduced more exactly into the microscopic model. Indeed, usually the atomic orbits are replaced by an equilibrium position in a potential well, and the phase transition arises as a result of the distortion of, or a shift in, the equilibrium positions. Such an approach is equivalent to an effective averaging over the orbits (i.e., over the oscillations in the potential well), and leads to the loss of the concept of coherence of the orbits in different cells of the lattice.

As will be shown below, our analysis enables us to establish the appearance below T_c of not only spontaneous polarization, but also of spontaneous coherence of the vibrations of the atomic groups in different cells of the lattice. A nicer question is the question of the formation of bound states below T_c. For classical vibrations we can indicate only one type of interaction that leads to the formation of a bound state—nonlinear resonance.[6] Owing to resonance, the vibration amplitude varies, which leads to the variation of the vibration frequency because of anharmonicity. The latter leads to the detuning of the resonance condition and to the saturation of the resonance. The effective Hamiltonian under the conditions of nonlinear resonance is analyzed in detail in §2.

The above-presented arguments are developed in the present paper for a somewhat simplified model for crystals of the TGS type, for which a comparison of the theoretical results with the experimental RS data can be carried out. In this model the ordering occurs as a result of the interaction of two low-frequency lattice vibration modes. Below T_c a bound state of the vibrations of the various structural units of the crystal is formed which leads to the occurrence of shifts in the equilibrium positions of the structure elements. A significant role in the formation of the bound state is played by the anharmonicity of at least one of the vibration branches. Owing to anharmonicity, there occurs a "capture" of the vibrations into a nonlinear-resonance state, which determines a new equilibrium structure of the lattice at $T<T_c$.

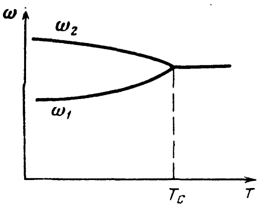

FIG. 1.

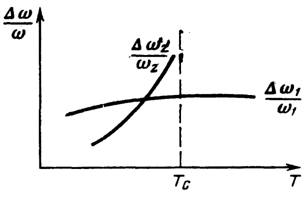

FIG. 2.

§1. DESCRIPTION OF THE MODEL

It is convenient to start with some experimental data for crystals of the TGS group, data which underlie the phase transition model considered below. Analysis of the RS spectra led to the discovery of two low-lying vibration branches with anomalous behavior of the frequency near T_c.[2] A typical example is schematically shown in Fig. 1. Simultaneously with the critical behavior of the ω_1 and ω_2 lines as T_c was approached there was observed a broadening of the second line (Fig. 2). An investigation of the spectra of the isomorphous (including the deuterated) crystals enabled us to establish the fact that the ω_1 branch is primarily due to the translational vibrations (of the SO_4 and SeO_4 groups for triglycinsulfate and triglycinselenate respectively), while the ω_2 branch is due to the orientational vibrations of glycine.

In Fig. 3 we schematically show the relative disposition of the SO_4 groups and the glycine-I ions[7] responsible for the critical branches of the ω_1 and ω_2 vibrations. The coupling between the SO_4 groups is realized through the glycine-II and glycine-III ions (not shown in the figure) by means of hydrogen bonds.[7] The glycine-I groups execute orientational vibrations conditionally (indicated in the figure by an arrow).

The two curves in Fig. 1 pertain to the same symmetry class (B), which does not correspond to the symmetry class of the soft mode in the ferroelectric phase. Furthermore, far from T_c the quantity $\Delta\omega=\omega_2-\omega_1\sim\omega_1$, ω_2, and, consequently, the interpretation of the results shown in Fig. 1 as the splitting of the vibration frequencies of one and the same group of atoms in a double-minimum potential is to be excluded.

It seems more natural to use the idea of resonance between the corresponding vibration modes. A qualitative

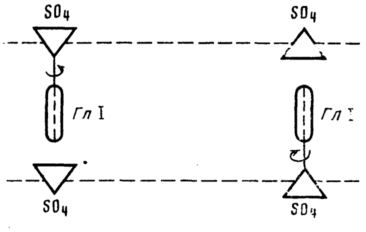

FIG. 3.

model for the lattice dynamics is based on the following. The glycine groups execute orientational vibrations that can be assumed to be largely localized. They are coupled to each other primarily via the SO_4 groups. On the other hand, the translational vibrations of the SO_4 groups are collective vibrations. We shall be interested only in the optical branch of these vibrations, which branch can be close in frequency to the orientational vibrations of glycine. Thus, the system's Hamiltonian describing only the dominant critical components of the motion can be represented in the form

$$H=H_l+H_c+V,$$
$$H_l=\sum_j H_{lj}(I_{lj}),\quad H_c=\sum_k H_{ck}(I_{ck}),\tag{1.1}$$
$$V=\sum_{j,k} V_{jk}(I_{lj},I_{ck}),$$

where I_{lj} is the action of the atomic group executing localized vibrations near the coordinate r_j, I_{ck} is the action of the collective mode having the wave vector k, and the V_{jk} are the components of the interaction energy. The orientational-vibration amplitude can attain a considerable magnitude near T_c,[8] and therefore H_{lj} describes anharmonic vibrations; $\omega_{lj}=\partial H_{lj}/\partial I_{lj}=\omega_{lj}(I_{lj})$. The collective translational vibrations can be assumed to be linear. Since the amplitude of the l-vibrations (the anharmonicity notwithstanding) is relatively small, the magnitude of the momentum Δk that can be exchanged by the l- and c-vibrations is also small, and the spread in magnitude of the momenta for the c-modes effectively interacting with the l-vibrations is small. In the small-k region (which makes the dominant contribution near T_c) the frequency difference arising when k changes by Δk because of the dispersion of the optical branch can be neglected. Hence we arrive at the single-frequency approximation for the c-vibrations:

$$H_c=\omega_c I_c,\quad V=\sum_j V_j(I_{lj},I_c),\tag{1.2}$$

where the index k on I_c has been dropped and averaging over the angles has been carried out in V.

At sufficiently high temperatures the glycine groups execute random vibrations about the centers r_j, and are weakly coupled (because of the intense temperature fluctuations) to the c-vibrations (i.e., with the SO_4 groups). If, as T approaches T_c, the variation of, for example, ω_c (or ω_{lj}) can lead to resonance ($\omega_l\approx\omega_c$), then the formation of bound $l-c$ vibrational states is possible below T_c. As will be seen below, the nonlinearity of at least one of the branches is a necessary condition for the existence of the phase transition.

§2. DETERMINATION OF THE EFFECTIVE HAMILTONIAN

As has already been noted, we considered the case when the critical behavior of the lattice is due to the resonance interaction of two anharmonic modes. To determine the form of the Hamiltonian, let us, following[6], first consider the phenomenon of nonlinear resonance between two arbitrary degrees of freedom. The Hamiltonian of such a system has the form

$$H=H_1(I_1)+H_2(I_2)+\varepsilon V(I_1,I_2;\vartheta_1,\vartheta_2),\tag{2.1}$$

where I_1, ϑ_1 and I_2, ϑ_2 are the action and angle of the corresponding degrees of freedom and εV is the interaction, whose magnitude is characterized by the dimensionless parameter ε. In the zeroth approximation the vibration frequencies are equal to

$$\omega_i=dH_i/dI_i,\quad i=1,2.\tag{2.2}$$

Let us write down the condition for resonance:

$$n_{1r}\omega_1(I_{1r})=n_{2r}\omega_2(I_{2r}),\tag{2.3}$$

where n_{1r}, n_{2r} are fixed integral numbers, while I_{1r} and I_{2r} are the oscillator-action values at which the resonance (2.3) arises.

Let us expand V in a Fourier series:

$$V=\sum_{n_1,n_2} V_{n_1n_2}(I_1,I_2)\exp i(n_1\vartheta_1+n_2\vartheta_2)+\text{c.c.},\tag{2.4}$$

and, using (2.1), (2.2), and (2.4), let us write down the equations of motion:

$$\dot I_1=-\frac{\partial H}{\partial\vartheta_1}=-i\varepsilon\sum_{n_1,n_2} n_1V_{n_1n_2}\exp i(n_1\vartheta_1+n_2\vartheta_2)+\text{c.c.},$$
$$\dot I_2=-\frac{\partial H}{\partial\vartheta_2}=-i\varepsilon\sum_{n_1,n_2} n_2V_{n_1n_2}\exp i(n_1\vartheta_1+n_2\vartheta_2)+\text{c.c.},$$
$$\dot\vartheta_1=\frac{\partial H}{\partial I_1}=\omega_1(I_1)+\varepsilon\sum_{n_1,n_2}(\partial V_{n_1n_2}/\partial I_1)\exp i(n_1\vartheta_1+n_2\vartheta_2)+\text{c.c.},\tag{2.5}$$
$$\dot\vartheta_2=\frac{\partial H}{\partial I_2}=\omega_2(I_2)+\varepsilon\sum_{n_1,n_2}(\partial V_{n_1n_2}/\partial I_2)\exp i(n_1\vartheta_1+n_2\vartheta_2)+\text{c.c.}$$

If the values of I_1 and I_2 are close respectively to I_{1r} and I_{2r}, then a resonance arises in the system, and, according to the condition (2.3), we can retain on the right-hand side of each of the expressions (2.5) only the term from the sum with $n_1=n_{1r}$ and $n_2=-n_{2r}$. Furthermore, let us neglect in the expressions for $\dot\vartheta_1$ and $\dot\vartheta_2$ the terms of the order of ε; this will be justified below. After this, the system (2.5) in the vicinity of the resonance goes over into the following:

$$\dot I_1=2\varepsilon n_{1r}V\sin\psi,$$
$$\dot I_2=-2\varepsilon n_{2r}V\sin\psi,\tag{2.6}$$
$$\psi\equiv\frac{d}{dt}(n_{1r}\vartheta_1-n_{2r}\vartheta_2)=n_{1r}\omega_1(I_1)-n_{2r}\omega_2(I_2),$$
$$V\equiv V_{n_{1r},-n_{2r}}(I_{1r},I_{2r}).$$

From the first two equations we find the relation

$$n_{2r}I_1+n_{1r}I_2=\text{const}.\tag{2.7}$$

Let us multiply the first equation in (2.6) by ω_1, the second by ω_2, and add:

$$\omega_1(I_1)\dot I_1+\omega_2(I_2)\dot I_2-2\varepsilon V\sin\psi\cdot\dot\psi=0.$$

As a result, we find the integral of the motion:

$$\int_{I_{1r}}^{I_1}\omega_1(I_1)\,dI_1+\int_{I_{2r}}^{I_2}\omega_2(I_2)\,dI_2+2\varepsilon V\cos\psi=\text{const}.\tag{2.8}$$

Expanding ω_1 and ω_2 in the vicinity of the resonance values of I_{1r} and I_{2r}:

$$\omega_i(I_i)=\omega_i(I_{ir})+\frac{d\omega_i(I_{ir})}{dI_i}(I_i-I_{ir}),\quad i=1,2,$$

and taking (2.7) into account, we obtain from (2.8) the effective Hamiltonian in the form

$$H_r=H_1(I_{1r})+H_2(I_{2r})+\frac{1}{2}\frac{d\omega_1(I_{1r})}{dI_1}(I_1-I_{1r})^2+\frac{1}{2}\frac{d\omega_2(I_{2r})}{dI_2}(I_2-I_{2r})^2+2\varepsilon V\cos\psi. \tag{2.9}$$

The expression (2.9) describes coupled oscillations of two degrees of freedom in the vicinity of the resonance (2.3)

From (2.9) we estimate the maximum change in the action in the vicinity of the resonance ($i=1,2$):

$$\delta I_i=\max(I_i-I_{ir})=\left[4\varepsilon V\Big/\frac{d\omega_i(I_{ir})}{dI_i}\right]^{1/2}, \tag{2.10}$$

and the maximum frequency change:

$$\delta\omega_i=\frac{d\omega_i(I_{ir})}{dI_i}\delta I_i=\left[4\varepsilon V\frac{d\omega_i(I_{ir})}{dI_i}\right]^{1/2}. \tag{2.11}$$

In the equation for $\dot{\psi}$ in (2.6) we neglected the terms of order εV. The condition under which this is valid is obtained from the inequality $\delta\omega\gg\varepsilon V$, or with allowance for (2.11):

$$(\alpha/\varepsilon)^{1/2}\gg1; \tag{2.12}$$

here we have introduced the dimensionless nonlinearity parameter $\alpha\equiv(d\omega/dI)(I/\omega)$. The inequality (2.12) is decisive for what follows, and expresses the condition for "capture" of the system into resonance. As can be seen from (2.12), the nonlinear resonance can also arise in the case of weak anharmonicity ($\alpha\ll1$) provided the mode-coupling constant ε is sufficiently small.

The obtained expression (2.9) allows us to write down the effective Hamiltonian (1.1), (1.2) describing the strong (resonance) coupling of the l- and c-vibrations. For this purpose, let us set in (2.9)

$$H=H_c=\omega_cI_c,\quad d\omega_1/dI_1=0,\quad H_2=\sum_{j=1}^{N}H_j(I_{jr}).$$

Comparing (2.9) and (1.1), (1.2), we arrive at the expression

$$\mathscr{H}=\omega_cI_c+\sum_{j=1}^{N}H_j(I_{jr})+\frac{1}{2}\sum_{j=1}^{N}\frac{d\omega_j(I_{jr})}{dI_j}(I_j-I_{jr})^2+2\frac{\varepsilon}{\sqrt{N}}\sum_{j=1}^{N}V(I_{jr},I_c)\cos\psi_j, \tag{2.13}$$

where the factor $N^{-1/2}$ has been introduced into the interaction term for correct normalization and the phase ψ_j takes into account the position (r_j) of the vibrating atomic group and is equal to

$$\psi_j=n\vartheta_j-n_c\vartheta_c-\mathbf{k}\mathbf{r}_j. \tag{2.14}$$

In (2.14) n and n_c are a pair of whole numbers determining the resonance:

$$\dot{\psi}_j=n\omega_j-n_c\omega_c\approx0; \tag{2.15}$$

k is the wave number of the collective mode. Since all the groups will henceforth be assumed to be identical, the index j on ω_j in (2.15) and on I_{jr} in (2.13) will be dropped. The Hamiltonian (2.13) with allowance for the remarks made above assumes the following final form:

$$\mathscr{H}=\omega_cI_c+\sum_{j=1}^{N}H_j(I_r)+\frac{1}{2}\sum_{j=1}^{N}\frac{d\omega(I_j)}{dI_j}\bigg|_{I_j=I_r}(I_j-I_r)^2+2\varepsilon N^{-1/2}V(I_r,I_c)\sum_{j=1}^{N}\cos\psi_j. \tag{2.16}$$

A characteristic feature of the obtained Hamiltonian is the presence of the phases ψ_j, which describes the coupled l- and c-vibrations, ψ_j being, according to (2.15), an approximate motion integral that assumes random values for different lattice sites j. The presence of the factor $\sum\cos\psi_j$ in the interaction term of the effective Hamiltonian of the lattice expresses not only a formal, but also a fundamental difference between the approach being developed here and theories of the displacive or order-disorder type. If the spread in the phase ψ_j from site to site is "sufficiently random," then $\sum\cos\psi_j\sim0$, and the coupling between the l- and c-vibrations effectively disappears. On the other hand, as will be seen below, $\sum_j\cos\psi_j\neq0$ at $T<T_c$, which indicates, on the one hand, the formation of a bound l–c state and, on the other, the coherence of the phases ψ_j.[1)]

§3. THE CONDITIONS FOR A PHASE TRANSITION

The thermodynamic properties of the system (2.16) are determined with the aid of the statistical sum

$$Z=\int d\Gamma\exp(-\beta\mathscr{H}), \tag{3.1}$$

where $\beta=1/T$ and $d\Gamma$ is an element of phase volume. We can write

$$d\Gamma=d\Gamma_c\prod_{j=1}^{N}d\Gamma_j. \tag{3.2}$$

Here $d\Gamma_c$ is an element of volume of the collective degree of freedom, while $d\Gamma_j$ is the element of volume of the j-th atom. Using the definition of ψ, we have

$$d\Gamma_c=dI_cd\vartheta_c,\quad d\Gamma_j=dI_jd\vartheta_j=n^{-1}dP_jd\psi_j,\quad P_j=I_j-I_r. \tag{3.3}$$

Substituting (3.2) and (3.3) into (3.1), we obtain

$$\begin{aligned}Z&=\text{const}\cdot\int_0^\infty dI_c\exp(-\beta\omega_cI_c)\prod_{j=1}^{N}\int dP_j\int d\psi_j\cdot\\&\quad\times\exp\{-{}^1\!/\!_2\beta\omega'P_j^2-2\beta\varepsilon N^{-1/2}V(I_r,I_c)\cos\psi_j\}\\&=\text{const}\cdot\int_0^\infty dI_c\exp(-\beta\omega_cI_c)Q^N(I_c)\\&=\text{const}\cdot\int_0 dI_c\exp N\{-\beta\omega_cI_c/N+\ln Q(I_c)\},\end{aligned} \tag{3.4}$$

where $\omega' = d\omega(I_j)/dI_j|_{I_j=I_r}$ and

$$Q(I_c)=\int dP\int d\psi \exp\{-{}^1/_2\beta\omega' P^2-2\beta\varepsilon N^{-1/2}V(I_r, I_c)\cos\psi\}. \tag{3.5}$$

In the first order in the vibration amplitudes, the interaction has a dipolar character, and the matrix element can be represented in the form

$$V(I_r, I_c)=g(I_r)I_c^{1/2}, \tag{3.6}$$

in which g is some constant.

For $N\to\infty$, we have from (3.4)–(3.6):

$$\begin{gathered} Z\infty\max\exp N\{-\beta\omega_c y_0+\ln Q(y_0)\}, \\ Q(y)=\int dP\int d\psi\exp\{-{}^1/_2\beta\omega' P^2-2\beta\varepsilon g y^{1/2}\cos\psi\}, \\ y=I_c/N. \end{gathered} \tag{3.7}$$

The extremum value, y_0, of the action of the field of the collective mode in the volume of one unit cell of the lattice is determined from the condition

$$\beta\omega_c=\frac{1}{Q(y_0)}\frac{dQ(y_0)}{dy_0}, \tag{3.8}$$

if Eq. (3.8) has a solution $y_0>0$. In the opposite case $y_0=0$.

To estimate the quantity Q, we must accurately determine the limits of the integrations over P and ψ. Since the expression (2.16) for $\mathscr{H}$ has meaning only for particles captured into resonance with the field of the collective mode, the domain of integration over I_j lies, for each j, in the vicinity of I_r with the interval (2.10). The region of variation of the quantities P and ψ is determined from the Hamiltonian (2.9).

The computation of Q gets, however, significantly simplified at sufficiently low T if the condition

$$\beta\omega' I_r^2\gg 1 \tag{3.9}$$

is fulfilled. In this case in $Q(y)$ stands a sharp function under the integral sign and

$$\begin{aligned} Q(y) &\infty \text{const}\cdot\int_{-\pi}^{\pi} d\psi\exp(-2\beta\varepsilon g y^{1/2}\cos\psi) \\ &=\text{const}\cdot I_0(2\beta\varepsilon g y^{1/2}), \end{aligned} \tag{3.10}$$

where I_0 is the Bessel function of imaginary argument. The substitution of (3.10) into (3.8) leads to the equation

$$\frac{\omega_c y_0^{1/2}}{\varepsilon g}=\frac{I_1(2\beta\varepsilon g y_0^{1/2})}{I_0(2\beta\varepsilon g y_0^{1/2})}, \tag{3.11}$$

which is an analog of the Curie-Weiss equation. The solution to (3.11) for $y_0=y_0(T)$ is shown in Fig. 4. The critical temperature T_c is determined from (3.11) for $y_0\to 0$:

$$T_c=\varepsilon^2 g^2/\omega_c=(\varepsilon V)^2/\omega_c I_c. \tag{3.12}$$

Similarly, the magnitude of the gap can be found:

$$y_0(T=0)=\varepsilon^2 g^2/\omega_c^2. \tag{3.13}$$

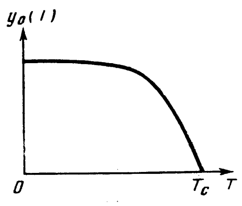

FIG. 4.

The obtained phase transition is analogous to the phase transition into a spontaneous coherent state considered in[9]. At $T<T_c$ the interaction between the collectivized mode and the localized vibrations of the groups leads to the formation of a bound state. The motion of the individual groups participating in the l-mode becomes physically ordered, i.e., becomes coherent. The onset of long-range order manifests itself in this property. Above T_c the temperature fluctuations destroy the bound state, and the existence of a finite density (y_0/h) of bound phonons of the collective mode becomes energetically disadvantageous. The term describing the interaction of the field of the collective mode with the l-mode effectively vanishes at $T>T_c$. Indeed, it follows from (2.16) that the quantity $\sum_{j=1}^N \cos\psi_j$ is of the order of $N^{1/2}$ at $T>T_c$, since it is a sum of a large number of random numbers. On the other hand, at $T<T_c$ the correlation between the phases implies that

$$\sum_{j=1}^{N}\cos\psi_j\sim N.$$

It should be noted that the appearance below T_c of a coherence state of the orientational vibrations of the atomic groups is a universal property (of the system), presupposing only anharmonicity of the potential and not depending on its concrete form. Different shapes of the potential curve for the orientational vibrations can lead to additional classification of the type of phase transition (of the displacive type, order–disorder type, etc.). If we exclude the phonon part from the interaction term in the Hamiltonian (2.16), then we can obtain direct interaction between the groups executing orientational vibrations in various unit cells. The constant of such an interaction is easy to compute, and is of the order of

$$J_{ll}\infty\varepsilon^2 V^2/\omega_c I_c. \tag{3.14}$$

Comparison of (3.14) with (3.12) leads to the natural result $J_{ll}\sim T_c$, and reveals the physical meaning of the expression for T_c.

If, for example, the characteristic potential in which the orientational vibrations are executed is a double-minimum potential, then we can make the problem less exact in the following manner. Let us average the Hamiltonian over the fast orientational vibrations of the atomic groups and introduce in place of their trajectories a spin variable characterizing only the position of the atomic group in one or the other minimum of the potential. In this case the interaction between the atomic groups in neighboring cells of the lattice has an exchange character with the coupling constant J_{ll}, and we arrive at a conventional model of the order–disorder type. The above-developed approach does not include the described rough approximation, and allows us, as will be seen below, to obtain new information about the state of the lattice when the phase transition occurs.

§4. STRUCTURAL CHANGES OCCURRING IN THE PHASE TRANSITION

In this section we consider two questions: the question of the appearance of a mean molecular displacement field at $T<T_c$ and that of the determination of the correlation function of the positions of the atomic groups executing orientational vibrations.

Let us introduce the complex amplitude, ξ, of the field of the collective mode:

$$I_c=\xi\xi^*,\quad \xi=I_c^{1/2}e^{i\vartheta}. \tag{4.1}$$

Substituting (4.1) into (2.16), and taking into account (3.6), we can derive the following equation of motion for ξ:

$$\begin{gathered}\dot{\xi}=i\frac{\partial\mathscr{H}}{\partial\xi^*}=i\omega\xi+\frac{2ig}{\sqrt{N}}\sum_{i=1}^{N}e^{i\varphi_i},\\ \varphi_i=\psi_i+\vartheta=n\vartheta_i-\mathbf{kr}_i.\end{gathered} \tag{4.2}$$

From (4.2) follows the condition for equilibrium:

$$\frac{\xi}{\sqrt{N}}=-\frac{2\varepsilon g}{\omega N}\sum_{i=1}^{N}e^{i\varphi_i}. \tag{4.3}$$

The right-hand side in (4.3) is a self-averaging quantity, i.e., for $N\to\infty$,

$$\lim_{N\to\infty}(\xi/N^{1/2})=-(2\varepsilon g/\omega)\langle e^{i\varphi_i}\rangle. \tag{4.4}$$

The basic assertion consists in the following:

$$\langle e^{i\varphi_i}\rangle\neq 0,\quad T<T_c;\quad \langle e^{i\varphi_i}\rangle=0,\quad T>T_c \tag{4.5}$$

and is deduced at once from the fact that

$$\lim_{N\to\infty}(\xi\xi^*/N)=y_0(T).$$

It also follows from (4.5) that

$$\langle e^{in\vartheta_i}\rangle\neq 0,\quad T<T_c. \tag{4.6}$$

Now let x_i be the displacement of the i-th atom. Let us write

$$x_i=\sum_m C_m(I_i)e^{im\vartheta_i}. \tag{4.7}$$

At $T>T_c$ the phases ϑ_i are distributed randomly, and $\langle x_i\rangle=0$. However, at $T<T_c$, on account of (4.6), $\langle x\rangle\neq 0$, i.e., a mean displacement field exists. The phase of the field gets frozen in and is indeterminate. Therefore,

$$\lim_{N\to\infty}(\xi/N^{1/2})\leqslant y_0^{1/2}.$$

For a more complete characteristic of the displacement field of the atoms, let us compute the correlation function

$$R_m=\langle x_ix_{i+m}\rangle=\lim_{N\to\infty}\frac{1}{N}\left\langle\sum_{i=1}^{N}x_ix_{i+m}\right\rangle. \tag{4.8}$$

Let us, for simplicity, restrict ourselves to the case of resonance of the first order ($n=1$) and of weak anharmonicity of the orientational vibrations. The latter means that we can retain in (4.7) only the term with $m=1$, $C_1=C$. It follows from (4.7) and (4.8) that

$$\begin{aligned}R_m&=\langle C(I_i)C^*(I_{i+m})\cos(\vartheta_i-\vartheta_{i+m})\\ &\approx|C(I_r)|^2\langle\cos(\psi_i-\psi_{i+m}-\mathbf{k}\Delta_m\mathbf{r})\rangle\\ &=|C(I_r)|^2\langle\cos\psi_i\rangle\langle\cos\psi_{i+m}\rangle\cos(\mathbf{k}\Delta_m\mathbf{r})\\ &=|C(I_r)|^2(\langle\cos\psi\rangle)^2\cos(\mathbf{k}\Delta_m\mathbf{r}),\end{aligned} \tag{4.9}$$

where $\Delta_m\mathbf{r}=\mathbf{r}_{i+m}-\mathbf{r}_i$, and we have taken the properties of the Hamiltonian (2.16) into account. In deriving (4.9), we used the inequality (3.9), and the quantity $C(I)$ can be taken out from under the averaging sign at the point $I=I_r$. From (3.4), (3.5), and (2.7) we find

$$\langle\cos\psi\rangle=\frac{\partial\ln Z}{\partial(2\beta\varepsilon g\sqrt{y_0})}=\frac{I_1(2\beta\varepsilon g\sqrt{y_0})}{I_0(2\beta\varepsilon g\sqrt{y_0})}. \tag{4.10}$$

Let us transform (4.10) with the aid of (2.11) and substitute it into (4.9):

$$R_m=|C(I_r)|^2\frac{y_0(T)}{y_0(0)}\cos(\mathbf{k}\Delta_m\mathbf{r}). \tag{4.11}$$

As can be seen from (4.11), the correlation function R_m is proportional to the order parameter $y_0(T)$ and vanishes identically at $T>T_c$. At $T<T_c$ there appears in (4.11) in the general case a superstructure having a characteristic period equal to the period of the collective mode. For the group of crystals under consideration an x-ray structural analysis does not reveal a superlattice. This means that the dominant contribution to the critical interaction is made by phonons with a very long wavelength, and the factor $\cos(\mathbf{k}\Delta_m\mathbf{r})$ in (4.11) can be omitted. If we take the higher-order terms in the expansion (4.7) into account, then the corresponding corrections to R_m can easily be found and are expressible in terms of $\langle\cos^m\psi\rangle$.

As has already been noted, the anomalous properties are possessed by only those degrees of freedom that have been "captured" into nonlinear resonance. In particular, the number of anomalous c-mode phonons is small. These are the phonons whose action lies in the interval $I\pm\delta I$, where δI is found from (2.10). The situation below T_c is similar to the coexistence of the normal and superfluid components in a quantum liquid. The smallness of the number of anomalous phonons leads to a situation in which, for example, the widths of the c-mode lines below and above T_c differ little from each other. This is in agreement with experiment (see Fig. 2). On the other hand, the anomalous effects at $T<T_c$ should manifest themselves strongly in the properties of the l-vibrations, since coherent motions and displacements occur only below T_c. In particular, in light scattering by the l-vibrations the intensity of the light should fall sharply at $T>T_c$ because of the straggling of the phases of the scattering atomic groups. At the same time there occurs a sharp broadening of the scattered line, which has been observed in experiments.[2]

CONCLUSION

The model developed in the present paper describes phase transitions due to the ordering of large structural elements of the lattice. There exists a semiphenomenological approach in which one or another law of interaction between, and a coupling constant for, the cell elements undergoing the ordering are assumed. We can, however, say *a priori* that the appearance of an ordered state is connected with the formation of a bound state of certain types of motion of the lattice. We considered one of the possible cases: the formation of a bound state as a result of the capture of vibrations into a nonlinear resonance. Crucial for the capture is the condition (2.12), which expresses the weakness of the coupling in comparison with the anharmonicity. The performed analysis, which partially takes the lattice dynamics into account, allows us to obtain additional information about critical phenomena and to carry out a comparison with a wider class of experimental data. Among these should be information about the coherent properties of the vibrations of characteristic atomic groups and spectral line widths and intensities and their temperature dependences. On the other hand, the dynamical character of the analysis leaves untouched a number of questions about the structure of the lattice, questions which are purely symmetry-related in character. For this reason, in the present paper the specific type of transition (displacive or order–disorder) is not ascertained, and only its more general and more universal property—spontaneous coherence below T_c, the appearance of which is characteristic of diverse resonance processes[9]—is established.

Although the approach to ferroelectric phase transitions that has been developed in the present paper pertains to a definite class of crystals, it is, nevertheless, clear that it is based on ideas of sufficiently general character, the realization of which may, in the general case, prove to be not so simple a problem. In this connection, it is useful to note some general consequences of the performed analysis:

1) The more exact allowance for the dynamics of the atomic groups in the effective Hamiltonian introduces into the theory detailed characteristics of the localized potential for the atomic groups, characteristics on which depend T_c, the mean polarization, etc. This may allow us to express a number of phenomenological parameters in terms of the constants of the potential.

2) The coherence properties of the trajectories of the various atomic groups determine the various characteristics of photon or phonon scattering by the lattice. These results cannot be obtained in the approximation in which the orbits of the atomic groups are replaced by the equilibrium positions of the groups.

3) The correct analysis of the dynamical susceptibility near the phase transition point is, apparently, impossible in principle without the correct allowance for the dynamics of the atomic groups in the lattice. The model Hamiltonian obtained in the paper can be used for such an analysis.

4) Finally, we can, in the framework of the model developed, compare in a satisfactory way the obtained theoretical results with the experimental RS data for the group of crystals of the TGS type.

1) It should be noted that, as a rule, the phase, ψ_j, of the bound state is ignored in papers on the microscopic models for ferroelectricity. It may be inferred, however, that the temporal dynamics of the phases ψ_j has a strong influence on the spectral properties of the system.

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