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Phase Transition of Perovskite-Type Ferroelectrics*

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Using the Hartree and time-dependent Hartree approximations, static and dynamic properties of a model for a perovskite-type ferroelectric near its transition temperature are calculated. In this model only one ion per unit cell is treated dynamically. The influence of the rigid frame of the other ions is idealized by an essentially anharmonic single-particle potential. The ions in different cells interact via the dipole-dipole force plus a repulsive force of shorter range. This model gives a phase transition of second order. The temperature dependence of the "soft" modes, of the Debye-Waller factor, of the displacement correlation functions, and of the specific heat is calculated, and the connection with static properties, such as the Curie constants, is established. The critical transverse modes are split in the presence of the spontaneous or an externally induced polarization. Finally, the model and the results are discussed.

I. INTRODUCTION

THERE are mainly two different approaches for a microscopic description of the strongly temperature-dependent properties near the critical temperature of a displacement-type ferroelectric like $BaTiO_3$.

In the first one, based on the work of Devonshire,[1] an essentially anharmonic potential well for the motion of the Ti ion is assumed. By calculating the free energy, equilibrium quantities such as the static dielectric constant and the spontaneous polarization are expressed in terms of the potential parameters. In the second one, following Anderson and Cochran,[2] the connection of the phase transition with an instability of the lattice is pointed out. It is assumed that the coupling parameters are temperature-dependent, leading at a finite temperature to a vanishing transverse-optical frequency in the harmonic approximation, which is still taken to be valid. Then the consequences of this "soft mode" on other quantities near T_c are considered.

A microscopic theory of the phase transition, of course, should describe the static as well as the dynamic properties in a unified and consistent way. It should especially show how the temperature dependence occurs as a result of the anharmonic terms in the temperature-independent Hamiltonian. The calculation of lattice vibrations in the presence of essential anharmonicities is difficult, and the harmonic approximation is, perhaps, not the appropriate starting point.[3]

We have investigated a very simple—in fact an oversimplified—model which allows in the molecular-field approximation a unified quantum-mechanical description of a ferroelectric phase transition of second order. In the present paper we report the results.

In Sec. II we give the formulation of the model: one dynamical ion per unit cell, in the rigid frame of the other ions, which acts as an anharmonic potential. The interaction is taken to be quadratic in the displacements. Section III contains the calculation of equilibrium properties in Hartree approximation. The spontaneous polarization, the static dielectric constant, and the specific heat are primarily considered. This section does not give any essentially new results. It is only a slight modification of Slater's calculation, so as to include quantum effects. In Sec. IV we consider response functions of this model on both sides of the transition temperature. They are used to give expressions for the displacement correlation function, the Debye-Waller factor, and the singularity of the specific heat. All explicit calculations are performed for the high-temperature side of the phase transition. Section V contains a critical discussion of the model and the results.

II. FORMULATION OF THE MODEL

The most simple crystals showing ferroelectricity, for example, $BaTiO_3$, have the perovskite structure. In the nonpolar phase the Ba^{2+} ions form a simple cubic lattice having the O^{2-} ions at the centers of its faces and the Ti^{4+} ions at the centers of its cubes. Thus every lattice site is a center of reflection symmetry.

At about 120°C a phase transition into a ferroelectric state occurs: The Ti ion moves out of the center of the cell parallel to one of the edges of the cube. This change in position of the Ti ion with respect to the Ba frame is accompanied by a sudden tetragonal deformation of the entire lattice, thus leading to a phase transition of first order. Similar transitions occur in other perovskites.[4]

In our calculations we shall neglect the deformation of the cell and all electronic polarizations of the ions. In fact, we shall treat only one ion (Ti) per cell dynamically in the rigid frame of the others. The effective interaction between these ions is taken to be the usual dipole-dipole force and an additional harmonic two-body interaction of shorter range. We neglect the coupling of the charged particles with the photons.

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[1] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); J. C. Slater, Phys. Rev. **78**, 748 (1950).

[2] P. W. Anderson, Phys. Rev. **78**, 341 (1950); W. Cochran, Phys. Rev. Letters **3**, 412 (1959); Advan. Phys. **10**, 401 (1961).

[3] B. D. Silverman, Phys. Rev. **135**, A1596 (1964). R. A. Cowley, Phil. Mag. **11**, 112 (1965).

[4] For a review of ferroelectrics see F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

The Hamiltonian of the system is thus

$$H=\sum_i \left[-(h^2/2m)\nabla_i^2+W(\mathbf{X}_i)\right] +\tfrac{1}{2}\sum_{i\neq j} V_{ij}(\mathbf{X}_i,\mathbf{X}_j), \qquad (2.1)$$

where $\mathbf{X}_i$ describes the position of the dynamical ion with respect to the center of the ith cell, m is its mass, and $W(\mathbf{X}_i)$ is the single-particle potential acting on the ion. It is produced by the interaction with those ions which constitute the rigid frame. So it contains the repulsive short-range forces between the nearest neighbors and is therefore essentially anharmonic. The interaction between the dynamical ions is assumed to be a quadratic form of the displacement components:

$$V_{ij}=\sum_{r,s=1}^{3} T_{rs}(\mathbf{R}_{ij})X_{ir}X_{js}, \quad i\neq j \qquad (2.2)$$

with $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$, where $\mathbf{R}_i$ is the position of the center of the ith cell. The interaction tensor consists of two parts:

$$\mathsf{T}=\mathsf{T}^0+\mathsf{T}^1,$$

where T^0 describes the dipole-dipole interaction

$$T_{rs}^0(\mathbf{R}_{ij})=\frac{e^2}{|\mathbf{R}_{ij}|^3}\left(\delta_{rs}-\frac{R_{ij}^r R_{ij}^s}{|\mathbf{R}_{ij}|^2}\right). \qquad (2.3)$$

(δ_{rs} is the Kronecker delta function and e is the effective charge of the ion.) The residual effective short-range interactions between the dynamical ions are contained in T^1. We assume that these forces are invariant with respect to translations of the sublattice. Because of the periodicity of the whole lattice it is convenient to use instead of T its Fourier transform

$$F_{rs}(\mathbf{K})=\frac{v}{e^2}\sum_m e^{-i\mathbf{K}\cdot\mathbf{R}_m}T_{rs}(\mathbf{R}_m) \qquad (2.4)$$

(v is the volume of the unit cell). The Fourier transform F^0 of T^0 is nonanalytic at $k=0$,[5] whereas the corresponding F^1 vanishes at $\mathbf{K}=0$ as a consequence of the assumed invariance of this part under translations of the sublattice, which means

$$V^{(1)}=\frac{N}{2}\sum_i\sum_{rs} T_{rs}^1(\mathbf{R}_i)X_{ir}X_{is}=0$$

whenever the displacements X_{ir} are independent of the cell number i. Therefore we obtain

$$F_{rs}^1(0)=\frac{v}{e^2}\sum_m T_{rs}^1(\mathbf{R}_m)=0.$$

The two-body forces contained in T^1 do not change their contribution to the total energy of the crystal as long as the sublattice of the dynamical ions remains undistorted, no matter whether the crystal is in a nonpolar or a ferroelectric state. They are, however, important for stabilizing the cubic sublattice, and therefore for the question of whether antiferroelectricity or an even more complicated lattice structure occurs.

III. HARTREE APPROXIMATION FOR EQUILIBRIUM PROPERTIES

A. Hartree Equations

For the calculation of the equilibrium properties we use the Hartree approximation for the density matrix, i.e.,

$$P(\mathbf{X}_1\cdots\mathbf{X}_N;\mathbf{X}_1'\cdots\mathbf{X}_N')=\prod_{i=1}^{N}\rho_i(\mathbf{X}_i,\mathbf{X}_i'), \qquad (3.1)$$

where ρ_i is the single-particle density matrix of the ith ion and is normalized to

$$\mathrm{Tr}\rho_i=1. \qquad (3.2)$$

From the equation of motion

$$[H,P]=0,$$

we get the Hartree equations

$$[H_i,\rho_i]=0, \qquad (3.3)$$

with

$$H_i=-(h^2/2m)\Delta_i+W(\mathbf{X}_i)+V_i(\rho),$$
$$V_i(\rho)=\sum_{j\neq i}\int d^3X_j\,\rho_j(\mathbf{X}_j,\mathbf{X}_j)V_{ij}(\mathbf{X}_i,\mathbf{X}_j). \qquad (3.4)$$

As is well known, the solution of Eq. (3.3) with the least free energy has the form

$$\rho_i=e^{-\beta H_i}/\mathrm{Tr}(e^{-\beta H_i}), \qquad (3.5)$$

with

$$\beta=(k_BT)^{-1}$$

(k_B = Boltzmann's constant, T = temperature). Equation (3.3) has always solutions, where ρ_i is independent of i. We assume that the equilibrium state has this form and therefore drop the index i wherever it is convenient. In this case the Hartree potential corresponds to the local field of a simple cubic lattice of dipoles with the moment $v\mathbf{P}$ and is thus given by

$$V(\mathbf{X})=-e^*\mathbf{P}\cdot\mathbf{X}, \quad e^*=4\pi e/3. \qquad (3.6)$$

The polarization $\mathbf{P}$ is defined as

$$\mathbf{P}=(e/v)\,\mathrm{Tr}(\rho\mathbf{X}). \qquad (3.7)$$

Thus the equation for the self-consistent determination of $\mathbf{P}$ can be written

$$\mathbf{P}=\frac{e}{v}\frac{\mathrm{Tr}\{\mathbf{X}\exp[-\beta(H_0-e^*\mathbf{P}\cdot\mathbf{X})]\}}{\mathrm{Tr}\{\exp[-\beta(H_0-e^*\mathbf{P}\cdot\mathbf{X})]\}}. \qquad (3.8)$$

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[5] M. H. Cohen and F. Keffer, Phys. Rev. 99, 1128 (1955).

This equation always has the trivial solution $\mathbf{P}=0$, which describes the nonpolar state. It is easy to include an external electric field $\mathbf{E}$ in the Hamiltonian. Then we have to replace H_0 by $H_0-e\mathbf{E}\cdot\mathbf{X}$, making the equation of self-consistency

$$\mathbf{P}=-\frac{1}{v}\frac{\partial}{\partial\mathbf{E}}Z, \tag{3.9}$$

with

$$Z=(1/\beta)\ln\{\mathrm{Tr}\exp[-\beta(H_0-e(\mathbf{E}+\tfrac{4}{3}\pi\mathbf{P})\cdot\mathbf{X})]\}. \tag{3.10}$$

In order to determine the temperature at which a phase transition into a ferroelectric state may occur, we consider the response of the system to a small macroscopic electric field $\mathbf{E}$.

B. Dielectric Constant

The dielectric tensor ϵ is defined by

$$\mathbf{P}'=(1/4\pi)(\epsilon-1)\mathbf{E}, \tag{3.11}$$

where $\mathbf{P}'$ is the change of the polarization induced by the field $\mathbf{E}$. We determine $\mathbf{P}'$ by the change ρ' of the density matrix

$$\mathbf{P}'=(e/v)\,\mathrm{Tr}(\rho'\mathbf{X}).$$

Taking

$$\delta H=-e\mathbf{X}\cdot\mathbf{E}$$

into account, we get from Eq. (3.3) the linearized equation

$$[H,\rho']-e^*[\mathbf{P}\cdot\mathbf{X},\rho]=e[\mathbf{X}\cdot\mathbf{E},\rho]. \tag{3.12}$$

For a field $\mathbf{E}$ parallel to an axis of the tensor of polarizability for the unit cell,

$$\alpha_{rs}=\frac{e^2}{v}\sum_{\alpha\beta}\frac{f_\beta-f_\alpha}{E_\alpha-E_\beta}X_{\alpha\beta}{}^rX_{\beta\alpha}{}^s. \tag{3.13}$$

The solution of Eq. (3.9) is

$$P_r'=\frac{\alpha_r(T)}{1-(4\pi/3)\alpha_r(T)}E^r. \tag{3.14}$$

In (3.13) E_α and f_α are the eigenvalues of H and ρ, respectively, and $X_{\alpha\beta}{}^r$ is the matrix element of X^r between the corresponding states. α_r is the eigenvalue of α for the r direction. Comparing Eq. (3.14) and Eq. (3.11) we get the usual Lorentz-Lorenz formula for the eigenvalues of the dielectric tensor:

$$\epsilon_r=\frac{1+(8\pi/3)\alpha_r(T)}{1-(4\pi/3)\alpha_r(T)}. \tag{3.15}$$

Because of the cubic symmetry of the perovskites in the nonpolar phase, all α_r are equal:

$$\alpha_r=\alpha.$$

At the critical temperature T_c, defined by

$$1-(4\pi/3)\alpha(T_c)=0, \tag{3.16}$$

the dielectric constant has a pole, indicating an instability of this phase. In the vicinity of T_c the dielectric constants are described by a Curie-Weiss law:

$$\begin{aligned}\epsilon(T)&=C/(T-T_c), \quad T>T_c\\ \epsilon_r(T)&=C_r/(T_c-T), \quad T<T_c\end{aligned} \tag{3.17}$$

with the Curie constants

$$\begin{aligned}C&=-(9/4\pi)(d\alpha/dT)_{T_c}{}^{-1},\\ C_r&=(9/4\pi)(d\alpha_r/dT)_{T_c}{}^{-1}.\end{aligned} \tag{3.18}$$

The calculation of the static properties is thus reduced to a single-particle problem, namely, the solution of Eq. (3.12) and the subsequent determination of the tensor of polarizability for the unit cell. These problems are already treated by Slater and Triebwasser for classical models and partly by Barrett for a quantum system.[6]

To get an explicit expression for $\mathbf{P}(T)$ and $\alpha(T)$ we use the single-particle Hamiltonian

$$\begin{aligned}H_0&=H_{00}+H_1,\\ H_{00}&=-\hbar^2/(2m)\nabla^2+(\tfrac{1}{2}m\epsilon^2)\mathbf{X}^2.\end{aligned} \tag{3.19}$$

H_1 is the essential anharmonic term

$$\begin{aligned}&=b_1(X_1{}^4+X_2{}^4+X_3{}^4)\\ &\quad+2b_2(X_1{}^2X_2{}^2+X_1{}^2X_3{}^2+X_2{}^2X_3{}^2),\end{aligned} \tag{3.20}$$

which will be treated as a perturbation. In calculating Z of Eq. (3.10) as a function of

$$\mathbf{E}'=\mathbf{E}+(4\pi/3)\mathbf{P}, \tag{3.21}$$

we transform to coordinates

$$\mathbf{X}'=\mathbf{X}-(e/m\epsilon^2)\mathbf{E}'.$$

Then we obtain up to first order in H_1

$$\begin{aligned}Z(\mathbf{E}')&=Z_0(\mathbf{E}')-\mathrm{Tr}(\exp[-\beta H_{00}(\mathbf{X}')]H_1(\mathbf{X})),\\ &=Z(0)+[\tfrac{1}{2}v\alpha_0-2(v^2/e^2)\alpha_0{}^2(3b_1+2b_2)\langle X_1{}^2\rangle_0]E'^2\\ &\quad-(v^4/e^4)\alpha_0{}^4[b_1(E_1'^4+E_2'^4+E_3'^4)\\ &\quad+2b_2(E_1'^2E_2'^2+E_1'^2E_3'^2+E_2'^2E_3'^2)],\end{aligned} \tag{3.22}$$

where α_0 is the temperature-independent polarizability of the harmonic oscillator of Eq. (3.19).

$$\alpha_0=e^2/vm\epsilon^2 \tag{3.23}$$

and

$$\langle X_1{}^2\rangle_0=\hbar/(2m\epsilon)\coth\tfrac{1}{2}\beta\hbar\epsilon \tag{3.24}$$

is the mean-square displacement of a harmonic oscillator. In first-order perturbation theory it is only in this

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[6] J. C. Slater, Ref. 1; S. Triebwasser, J. Phys. Chem. Solids **3**, 53 (1957); J. H. Barrett, Phys. Rev. **86**, 118 (1952). See also: V. K. Kozlovskii, Zh. Eksperim. i Teor. Fiz. **30**, 766 (1956) [English transl.: Soviet Phys.—JETP **3**, 601 (1956)]; Fiz. Tver. Tela **2**, 1733 (1960) [English transl.: Soviet Phys.—Solid State **2**, 1566 (1961)].

quantity that a quantitative difference between the classical and the quantum systems appears in the calculation of the static properties. Apart from that, the basic equations, (3.9) and (3.22) are exactly the same as in the classical case. For $T<T_c$ we get three solutions for the spontaneous polarization in the absence of an external field—in the directions (1,0,0), (1,1,0), and (1,1,1). If $b_2>b_1$, the solution with the highest spontaneous polarization at a given temperature, and therefore—as we shall see—the stable one, is the first one, which is observed, for example, in $BaTiO_3$. Using Eqs. (3.22) and (3.9) we obtain the polarization

$$\mathbf{P}^2(T)=(3/4\pi)^2(e^4/4v^3\alpha_0{}^4b_1)[\alpha-3/(4\pi)], \tag{3.25}$$

where α is the polarizability of the unpolarized unit cell:

$$\alpha(T)=\alpha_0-4(v/e^2)\alpha_0{}^2(3b_1+2b_2)\langle X_1{}^2\rangle_0. \tag{3.26}$$

From Eqs. (3.22), (3.10), (3.9) and the definition

$$\alpha_r=\frac{\partial P_r}{\partial E_r}\bigg|_{E=0},$$

we get the polarizability for $T<T_c$, where the unit cell is polarized.

$$\begin{aligned}\alpha_{\parallel}&=-2\alpha+9/(4\pi),\\ \alpha_{\perp}&=-[(b_2-b_1)/b_1]\alpha+3b_2/(4\pi b_1).\end{aligned} \tag{3.27}$$

(The subscripts $\parallel$ and $\perp$ denote the directions parallel and perpendicular, respectively, to the spontaneous polarization.) The Curie constants of Eq. (3.18) have, then, the values

$$\begin{aligned}C&=\frac{m^2\epsilon^3k_BT_c{}^2}{(1+2b_2/3b_1)\hbar^2b_1}\sinh^2\!\left(\frac{\hbar\epsilon}{2k_BT_c}\right),\\ C_{\parallel}&=\tfrac{1}{2}C,\\ C_{\perp}&=[b_1/(b_2-b_1)]C.\end{aligned} \tag{3.28}$$

In the vicinity of T_c the spontaneous polarization Eq. (3.25) is

$$P_r{}^2(T)=\left(\frac{3}{4\pi}\right)^3\frac{3e^4}{4v^3\alpha_0{}^4b_1C}(T_c-T)\quad\text{for}\quad T_c>T. \tag{3.29}$$

C. Thermodynamic Quantities

In order to calculate the free energy F near the transition temperature it is convenient to introduce a coupling constant λ and to use the Hamiltonian

$$H=H_0+\lambda V, \tag{3.30}$$

which for $\lambda=1$ agrees with Eq. (2.1). The free energy is then given by

$$F(T)=F_0(T)+\int_0^1\frac{d\lambda}{\lambda}\langle V\rangle_\lambda, \tag{3.31}$$

where F_0 is the free energy of the system without interaction and, therefore, a smooth function of the temperature. The expectation value of the interaction energy is to be taken with the Hamiltonian of Eq. (3.30). Using Eq. (2.2) we get

$$\langle V\rangle_\lambda=\frac{N}{2}\sum_{rs}\sum_{m}T_{rs}(\mathbf{R}_m)\times\{\bar{X}_{mr}\bar{X}_{0s}+\langle(X_{mr}-\bar{X}_{mr})(X_{0s}-\bar{X}_{0s})\rangle_\lambda\}, \tag{3.32}$$

with

$$\bar{X}_{mr}\equiv\langle X_{mr}\rangle_\lambda.$$

In the Hartree approximation we neglect the correlation between the displacements of different particles, described by the second term in Eq. (3.32). The remaining first term is just the static energy of a lattice of dipoles. This contribution F_1 to the free energy thus vanishes beyond the critical temperature. Below T_c it is

$$F_1(T)=-\frac{N}{2}\frac{4\pi}{3}\int_{\lambda_c(T)}^1\frac{d\lambda}{\lambda}\mathbf{P}^2(\lambda,T), \tag{3.33}$$

where λ_c is the coupling constant at which the spontaneous polarization vanishes:

$$1-\lambda_c(T)(4\pi/3)\alpha(T)=0. \tag{3.34}$$

Equation (3.33) shows that the free energy and its temperature derivative are continuous at T_c. The phase transition thus is of second order. The phase with the highest spontaneous polarization gives the least free energy and therefore is the stable one. The second derivative of F_1, however, and consequently the specific heat, has a finite discontinuity at T_c. Using Eqs. (3.33) and (3.34), we get the discontinuity

$$\Delta C_v=-T_c\frac{\partial^2}{\partial T^2}F_1=Nv2\pi\frac{T_c}{C}\frac{d(P^2)}{dT}. \tag{3.35}$$

This expression agrees with the result of the phenomenological theory of ferroelectrics.[1]

IV. RPA FOR RESPONSE FUNCTIONS

A. Time-Dependent Hartree Equation and the General Solution

We now consider the reaction of the system to small external fields, described by the contribution $\hat{\mathcal{H}}(t)$ to the Hamiltonian:

$$\hat{\mathcal{H}}(t)=\sum_m\hat{H}_m(t), \tag{4.1}$$

where $\hat{H}_m$ acts only upon the mth particle. We write the density matrix

$$\rho_m(t)=\rho+\hat{\rho}_m(t). \tag{4.2}$$

Here ρ is the equilibrium density which was the subject of the last section, and $\hat{\rho}_m$ is the deviation caused by the external field. The linearized equation of motion for ρ_m is[7]

$$-i\partial_t\hat{\rho}_m=[\rho,\hat{V}_m]+[\hat{\rho}_m,H]+[\rho,\hat{H}_m]. \qquad (4.3)$$

$\hat{V}$ is the change of the Hartree potential of Eq. (3.4) due to the change of all densities $\hat{\rho}_i$. Fourier transformation of all quantities with respect to time

$$g(t)=\frac{1}{2\pi}\int d\omega\, e^{-i\omega t}g(\omega) \qquad (4.4)$$

and space

$$g_m=\frac{1}{N}\sum_{K} e^{i\mathbf{K}\cdot\mathbf{R}_m}g(\mathbf{K}) \qquad (4.5)$$

yield in the representation in which ρ and H are diagonal

$$(E_\beta-E_\alpha+\omega)\langle\alpha|\hat{\rho}(\mathbf{K},\omega)|\beta\rangle+(f_\alpha-f_\beta) \times\frac{e^2}{v}\sum F_{rs}(\mathbf{K})X_{\alpha\beta}{}^r\sum_{\gamma\delta}X_{\gamma\delta}{}^s\langle\gamma|\hat{\rho}(\mathbf{K},\omega)|\delta\rangle =(f_\beta-f_\alpha)\langle\alpha|\hat{H}(\mathbf{K},\omega)|\beta\rangle. \qquad (4.6)$$

The simple structure of the harmonic interaction makes it possible to give the general solution of Eq. (4.6):

$$\langle\alpha|\hat{\rho}(\mathbf{K},\omega)|\beta\rangle=\frac{f_\beta-f_\alpha}{E_\beta-E_\alpha+\omega}\left[\langle\alpha|\hat{H}(\mathbf{K},\omega)|\beta\rangle +\frac{e^2}{v}\sum_{rs}X_{\alpha\beta}{}^rF_{rs}{}^{(\mathbf{K})}\tilde{\mathbf{X}}_s(\mathbf{K},\omega)\right]. \qquad (4.7)$$

Here the 3-dimensional vector X is defined by

$$\tilde{\mathbf{X}}(\mathbf{K},\omega)=\sum_{\gamma r}\langle\gamma|\hat{\rho}(\mathbf{K},\omega)|\delta\rangle\mathbf{X}_{\delta\gamma} \qquad (4.8)$$

and, as is seen from Eq. (4.6), it is the solution of

$$\sum_t[\delta_{rt}+\sum_s\alpha_{rs}(\omega)F_{st}(\mathbf{K})]\tilde{X}_t(K,\omega) =\sum_{\alpha\beta}X_{\beta\alpha}{}^r\frac{f_\beta-f_\alpha}{E_\beta-E_\alpha+\omega}\langle\alpha|\hat{H}(\mathbf{K},\omega)|\beta\rangle, \qquad (4.9)$$

where we have introduced the frequency- and temperature-dependent polarizability of the unit cell

$$\alpha_{rs}(\omega)=\frac{e^2}{v}\sum\frac{f_\beta-f_\alpha}{E_\alpha-E_\beta-\omega}X_{\alpha\beta}{}^rX_{\beta\alpha}{}^s. \qquad (4.10)$$

$\alpha(0)$ coincides with the definition [Eq. (3.17)] of the static polarizability.

B. Critical Modes

From Eqs. (4.7) and (4.9) we find the secular equation for the resonant frequencies[8] $\omega(\mathbf{K})$:

$$|\delta_{rt}+\sum_s\alpha_{rs}(\omega(\mathbf{K}))F_{st}(\mathbf{K})|=0. \qquad (4.11)$$

The tensor α_{rs} is diagonal in the cubic as well as in the tetragonal phase. For long waves ($k\rightarrow 0$) the tensor F consists of a longitudinal and a transverse part:

$$F_{rs}(\mathbf{K})=f_lP_{rs}{}^l+f_tP_{rs}{}^t \qquad (4.12)$$

with

$$P_{rs}{}^l=K_rK_s/\mathbf{K}^2,\quad P_{rs}{}^t=\delta_{rs}-K_rK_s/\mathbf{K}^2, \qquad (4.13)$$

and

$$f_l=8\pi/3,\quad f_t=-4\pi/3. \qquad (4.14)$$

If $\mathbf{K}$ is parallel to one of the edges of the unit cell, the decomposition [Eq. (4.13)] of F is possible even for finite $\mathbf{K}$, with f_l and f_t now depending on $\mathbf{K}^2$. For the sake of simplicity we shall restrict the discussion to these cases. The secular equation for longitudinal and transverse waves, respectively, then reads

$$1+\alpha_r(T,\omega_r{}^2)f_l(\mathbf{K}^2)=0, \qquad (4.15)$$

$$1+\alpha_s(T,\omega_r{}^2)f_t(\mathbf{K}^2)=0, \qquad (4.16)$$

where $\mathbf{K}$ is chosen along the r axis and $r\neq s$.

Comparison of Eq. (4.16) with the critical equation [Eq. (3.16)] shows that at T_c and $\mathbf{K}=0$ the frequency of transverse waves vanishes. The temperature dependence near T_c of the critical mode at $\mathbf{K}=0$ is easily derived from Eq. (4.16):

$$\omega_s{}^2(\mathbf{K}=0)=-\frac{1}{A}\frac{\partial\alpha_s}{\partial T}\bigg|_{T_c,\omega=0}(T-T_c), \qquad (4.17)$$

where

$$A=\frac{\partial\alpha_s}{\partial(\omega^2)}\bigg|_{T_c,\omega=0}=\frac{e^2}{v}\sum_{\alpha\beta}{}'\frac{(f_\beta-f_\alpha)}{(E_\alpha-E_\beta)^3}|X_{\alpha\beta}{}^s|^2 \qquad (4.18)$$

is independent of s. Approaching T_c from higher temperatures, there is just one critical frequency. Using the expression Eq. (3.18) for the Curie constant C, its temperature dependence can be written as

$$\omega^2=9(T-T_c)/(4\pi CA),\quad T>T_c. \qquad (4.19)$$

For temperatures below T_c and for those directions of $\mathbf{K}$, which we consider here, we get two different frequencies of the critical transverse modes, according to whether the polarization of the wave is parallel ($\omega_{\parallel}$) or normal ($\omega_{\perp}$) to the spontaneous polarization. As in the nonpolar phase [Eq. (4.19)] we write the frequencies in terms of the corresponding Curie constants in the ferroelectric

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[7] The time-dependent Hartree equations were previously used in connection with lattice vibrations by W. Brenig [Z. Physik **171**, 60 (1963)] and D. R. Fredkin and N. R. Werthamer [Phys. Rev. **138**, A1527 (1965)]. For an application to a ferroelectric model see R. Brout, K. A. Muller, and H. Thomas (to be published).

[8] The eigenfrequencies of a cubic array of harmonic dipoles at $T=0$ are discussed in U. Fano, Phys. Rev. **118**, 451 (1960).

state (3.28):

$$\begin{aligned} \omega_{\shortparallel}^2&=9(T_c-T)/(4\pi C_{\shortparallel}A), \\ \omega_{\perp}^2&=9(T_c-T)/(4\pi C_{\perp}A), \end{aligned} \qquad T<T_c \qquad (4.20)$$

with the same constant A as in Eq. (4.19).

The **K** dependence of the resonance frequencies follows from the secular Eq. (4.16):

$$\omega_s^2(\mathbf{K}^2)=\omega_s^2(0)-\mathbf{K}^2\frac{df_t(0)}{dK^2} \times\alpha_s(\omega_s^2(0))\left[f_t(0)\frac{\partial\alpha_s(\omega_s^2(0))}{\partial(\omega^2)}\right]^{-1}. \qquad (4.21)$$

In the limit $T\rightarrow T_c$ the **K** dependence of all critical modes becomes the same:

$$\omega_s^2(\mathbf{K}^2)=-\mathbf{K}^2 f_t'(0)\alpha(T_c,\,\omega=0)/f_t(0)A. \qquad (4.22)$$

We consider

$$f_t'(0)=\left.\frac{df_t(\mathbf{K}^2)}{d\mathbf{K}^2}\right|_{\mathbf{K}=0}$$

as another adjustable parameter. Its actual calculation requires knowledge of the effective two-body forces, which act in addition to the Coulomb forces. In fact, the dipole-dipole forces alone would give a negative value for $f_t'(0)$, indicating that the critical mode for a dipole lattice has a finite K value. That means that a simple cubic dipole lattice shows antiferroelectricity rather than ferroelectricity no matter what the anharmonicities of the single-particle potential are.[9]

For crystals, where the anharmonicity of the single-particle potential and hence the temperature dependence of the polarizability of the unit cell are small, it seems sufficient to use for $\alpha(\omega^2)$ and its derivatives with respect to the frequency the values for the harmonic oscillator. We then obtain

$$\begin{aligned} \alpha(\omega^2)&=\alpha_0\epsilon^2/(\epsilon^2-\omega^2), \\ \partial\alpha(\omega^2)/\partial(\omega^2)&=\frac{\alpha(\omega^2)}{(\epsilon^2-\omega^2)}. \end{aligned} \qquad (4.23)$$

Putting these expressions into Eq. (4.21), we find the K dependence of the "soft mode":

$$\omega_s^2(\mathbf{K}^2)=\omega_s^2(T,\,\mathbf{K}=0) -\mathbf{K}^2(f_t'/f_t)[\epsilon^2-\omega_s^2(T,\,\mathbf{K}=0)], \qquad (4.24)$$

where the value of ω_s^2 at $\mathbf{K}=0$ is given by Eq. (4.20) with

$$A=\alpha_0/\epsilon^2.$$

So far we have only discussed the frequencies of the system without external fields. Application of an external static electric field, however, changes the resonance frequencies, since the polarizability α is changed by the induced polarization. In the secular equation, Eq. (4.16), we have to replace $\alpha(T,\omega^2)$ by $\alpha(T,\omega^2,E)$. For $\omega^2=0$ this function is easily calculated in the case of the model Hamiltonian [Eq. (3.19)] using Eqs. (3.22), (3.10), (3.9) and the definition

$$\alpha_r(E)=\partial P_r(E)/\partial E_r.$$

As an example we consider the case of a nonpolar crystal. There the external field causes a splitting of the otherwise degenerate critical mode. At a temperature where the frequency of the critical mode is low enough to justify the static approximation for the derivatives of the polarizability, we obtain from Eq. (4.16)

$$\frac{\partial(\omega_r^2)}{\partial(E^2)}=-\left(\frac{\partial\alpha_r(T,\,\omega=0,\,E)}{\partial(E^2)}\Big/\frac{\partial\alpha_r(T,\omega^2,0)}{\partial(\omega^2)}\right)_{E=\omega=0},$$

which gives, in terms of the potential parameters,

$$\begin{aligned} \left.\frac{\partial(\omega_{\shortparallel}^2)}{\partial(E^2)}\right|_{\mathbf{K},T}&=12v^3\alpha_0^4b_1/(e^4A), \\ \left.\frac{\partial(\omega_{\perp}^2)}{\partial(E^2)}\right|_{\mathbf{K},T}&=4v^3\alpha_0^4b_2/(e^4A). \end{aligned} \qquad (4.25)$$

C. Response Functions

From $\hat{\rho}(K,\omega)$ of Eq. (4.8) it is easy to obtain the usual response functions. We take the external perturbation $\hat{H}(t)$ [Eq. (4.1)] to be of the form

$$\hat{H}_m(t)=g_m(t)B_m,$$

where B_m is a single-particle operator acting on the mth particle, and g_m is a c number. Then we have

$$\langle\alpha|\hat{H}(\mathbf{K},\omega)|\beta\rangle=g(\mathbf{K},\omega)\langle\alpha|B|\beta\rangle.$$

Let A_n be any other single-particle operator and $\langle A_n\rangle_t$ its expectation value at the time t. Then the response function $\chi_{AB}{}^{nm}$ is defined by

$$\chi_{AB}{}^{nm}(t-t')=\delta\langle A_n\rangle_t/\delta g_m(t'). \qquad (4.26)$$

Using

$$\delta\langle A_n\rangle_t=\mathrm{Tr}[A\hat{\rho}_n(t)],$$

we get for the Fourier transform of χ

$$\chi_{AB}(K,\omega)=\sum_{\alpha\beta}\langle\alpha|A|\beta\rangle\frac{\delta\langle\beta|\hat{\rho}(\mathbf{K},\omega)|\alpha\rangle}{\delta g(\mathbf{K},\omega)}. \qquad (4.27)$$

The Fourier transform of the correlation function of the unperturbed system

$$\langle A_n(t)B_m(t)\rangle=\frac{1}{2\pi N}\int d\omega \times e^{-i\omega(t-t')}\sum_K e^{i\mathbf{K}\cdot(\mathbf{R}_n-\mathbf{R}_m)}\mathcal{J}_{AB}(\mathbf{K},\omega) \qquad (4.28)$$

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[9] Compare: J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

is known to be connected with the analytic continuation of the response function by[10]

$$\mathcal{G}_{AB}(K,\omega)=2i/(1-e^{-\beta\omega})\times\{\chi_{AB}(\mathbf{K},\,\omega+i\eta)-\chi_{AB}(\mathbf{K},\,\omega-i\eta)\}\,, \tag{4.29}$$

with $\eta=+0$.

1. *Displacement Correlation*

We set $A=(x^r-\bar{x}^r)$ and $B=(x^s-\bar{x}^s)$. Then

$$\chi_{rs}(\mathbf{K},\omega)=\chi_{AB}(\mathbf{K},\omega)$$

describes the change of polarization induced by an external electric field, whereas the corresponding $\mathcal{G}_{rs}(\mathbf{K},\omega)$ of Eq. (4.29) gives the frequency spectrum of the fluctuations of the spontaneous polarization with wave vector $\mathbf{K}$. From Eqs. (4.9) and (4.27) we obtain

$$\chi_{rs}(,\mathbf{K}\omega)=-(v/e^2)\{\alpha-\alpha F(F+F\alpha F)^{-1}F\alpha\}_{rs}\,, \tag{4.30}$$

where α and F are the matrices defined in Eqs. (4.10) and (4.12). In order to calculate the expression in curly brackets we have to invert the matrix $(F+F\alpha F)$. This is particularly simple if $\mathbf{K}$ has the direction of a principal axis of α, the result being

$$(F+F\alpha F)^{-1}=\frac{1}{f_l+f_l\alpha_{\shortparallel}f_l}P^l+\frac{1}{f_t+f_t\alpha_{\perp}f_t}P^t\,.$$

In the general case, below T_c the matrices F and α do not commute. For the sake of simplicity we shall, however, neglect this complication by using instead of α

$$\tilde{\alpha}=P^l\alpha P^l+P^t\alpha P^t\,, \tag{4.31}$$

which can be written as

$$\tilde{\alpha}=\tilde{\alpha}_0P^{(0)}+\tilde{\alpha}_1P^{(1)}+\tilde{\alpha}_2P^{(2)}\,.$$

Here $\tilde{\alpha}_0$ is the nontrivial eigenvalue of $P^l\alpha P^l$ and $\tilde{\alpha}_1,\tilde{\alpha}_2$ are those of $P^t\alpha P^t$, while $P^{(0)}$, $P^{(1)}$, and $P^{(2)}$ are the corresponding projection operators. Choosing the system of coordinates so that the spontaneous polarization—if any—is in the (1,0,0) direction, we give explicit expressions for these quantities in terms of $\mathbf{K}/|K|=(e_1,e_2,e_3)$:

$$P_{rs}^{(0)}=e_re_s\,,\quad \tilde{\alpha}_0=\sum_r \alpha_re_r^2\,,$$

$$\begin{aligned}P^{(1)}&=\begin{bmatrix}0&0&0\\0&e_3^2&e_2e_3\\0&e_2e_3&e_2^2\end{bmatrix}\Big/(e_2^2+e_3^2)\,,\\ \tilde{\alpha}_1&=(\alpha_2e_3^2+\alpha_3e_2^2)/(e_2^2+e_3^2)\,,\\ P^{(2)}&=1-P^{(0)}-P^{(1)}\,,\\ \tilde{\alpha}_2&=[\alpha_1(e_1^2-e_3^2)+\alpha_2e_1^2e_2^2+\alpha_3e_1^2e_3^2]/\\&\qquad[(e_2^2-e_3^2)^2+e_1^2(e_2^2+e_3^2)]\,.\end{aligned} \tag{4.32}$$

In this way we do not neglect the whole anisotropy of the polarizability but only the mixing between longitudinal and transverse waves.

Equation (4.30) now reads

$$\chi_{rs}(\mathbf{K},\omega)=-\frac{v}{e^2}\sum_{i=0}^{2}\frac{\tilde{\alpha}_i}{1+\tilde{\alpha}_if_i}P_{rs}^{(1)} \tag{4.33}$$

with $f_0=f_l$, $f_1=f_2=f_t$, and finally we get

$$\mathcal{G}_{rs}(\mathbf{K},\omega)=\frac{2\pi v}{e^2(1-e^{-\beta\omega})}\sum_{i\nu}\frac{\tilde{\alpha}_i}{\tilde{\alpha}_i'f_i\omega_{i\nu}}\times\{\delta(\omega+\omega_{i\nu})-\delta(\omega-\omega_{i\nu})\}P_{rs}^{(i)}(\mathbf{K})\,. \tag{4.34}$$

The quantities f_i are functions of $\mathbf{K}^2$, and the $\tilde{\alpha}_i$ depend on T, ω^2, and the direction of $\mathbf{K}$. In Eq. (4.34) we have used the abbreviation

$$\tilde{\alpha}_i'=[\partial/\partial(\omega^2)]\alpha_i\,.$$

The positive frequencies $\omega_{i\nu}$ depend on $\mathbf{K}$ and are the roots of

$$1+\tilde{\alpha}_i(\omega^2)f_i(\mathbf{K}^2)=0\,.$$

We have discussed them for special directions in the previous section.

Debye-Waller Factor. We now use the function $\mathcal{G}_{rs}$ [Eq. (4.34)] to calculate the temperature dependence of the Debye-Waller factor. It is usually written in the form $\exp(-2W)$. W is a function of the momentum transfer $\boldsymbol{\kappa}$ and is given by

$$W=\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle=\sum_r\kappa_r^2\langle u_r^2\rangle\,, \tag{4.35}$$

where u is the displacement of any ion:

$$u_n=x_n-\langle x_n\rangle\,.$$

The definition Eq. (4.28) of $\mathcal{G}$ together with Eq. (4.34) yields

$$\begin{aligned}\langle u_r^2\rangle&=\frac{1}{2\pi N}\int d\omega\sum_K\mathcal{G}_{rr}(\mathbf{K},\omega)\\&=-\frac{v}{Ne^2}\sum_K\sum_{i,\nu}\frac{\tilde{\alpha}_i}{\tilde{\alpha}_i'f_i\omega_{i\nu}}\coth\left(\frac{\omega_{i\nu}}{2T}\right)P_{rr}^{(1)}(\mathbf{K})\,.\end{aligned}$$

This expression is a decomposition of the mean-square displacement into the contributions of the normal modes. As we are interested only in the strongly temperature-dependent part near T_c, we pick out the contribution of the critical modes with frequencies ω_{i0}, which is

$$\delta\langle(u_r)^2\rangle=-\frac{v}{Ne^2}\sum_K\sum_{i=1}^{2}\frac{\tilde{\alpha}_i2T}{\tilde{\alpha}_i'f_i\omega_{i0}^2}\times\frac{\omega_{i0}}{2T}\coth\frac{\omega_{i0}}{2T}P_{rr}^{(i)}(\mathbf{K})\,. \tag{4.36}$$

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[10] V. L. Bonch-Bruevich and S. V. Tyablikov, *The Green's Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).

The calculation of this part still essentially involves a summation over the whole Brillouin zone, whereas we have discussed the spectrum only for small **K**. For a rough estimate of $\delta\langle u_r^2\rangle$ for $T>T_c$ we take the spectrum

$$\omega_{i0}^2=\left(\frac{3}{4\pi}\right)^2\frac{1}{A}\left(4\pi\frac{T-T_c}{C}+f_t'\mathbf{K}^2\right), \qquad (4.37)$$

which is valid for small **K** near T_c throughout the whole Brillouin zone, a volume which we will approximate by a sphere of radius $\bar{K}=(6\pi^2/v)^{1/3}$. For simplicity we furthermore replace in Eq. (4.36) the expression in curly brackets by its low-frequency limit 1. Doing the same with $\tilde{\alpha}_i$ and $\tilde{\alpha}_i'$ and neglecting the **K** dependence of f_i finally leads to the result

$$\Delta\langle u_r^2\rangle=\langle 2v^2k_BT\bar{K}/3\pi^2e^2f_t'\rangle(1-y\,\arctan y^{-1})\,, \qquad (4.38)$$

with

$$Y=\left(\frac{T-T_c}{4\pi Cf_t'\bar{K}^2}\right)^{1/2}.$$

Equation (4.38) yields at T_c a peak of finite height:

$$\Delta\langle u_r^2\rangle_{\max}=2v^2k_BT_c\bar{K}/3\pi^2e^2f_t'. \qquad (4.39)$$

Our approximations are restricted to the case that the temperature is near T_c, so we can write

$$\Delta\langle u_r^2\rangle=\Delta\langle u_r^2\rangle_{\max}(1-\tfrac{1}{2}\pi Y). \qquad (4.40)$$

We see that $\Delta\langle u_r^2\rangle$ decreases with an infinite slope as the temperature increases. According to Eq. (4.35), this gives rise to a dip in the Debye-Waller factor in the vicinity of the critical temperature. In the ferroelectric state this dip depends on whether $\boldsymbol{\kappa}$ is parallel or normal to the axis of spontaneous polarization.

Static Displacement Correlation. The essentially collective behavior of the system near the critical temperature is shown more clearly in the displacement correlation function than in the Debye-Waller factor. We consider the static correlation function, defined by

$$g_{rs}(\mathbf{R}_n)=\langle(X_n{}^r-\bar{X}_n{}^r)(X_0{}^s-\bar{X}_0{}^s)\rangle.$$

From Eq. (4.28) we find

$$g_{rs}(\mathbf{R})=\frac{1}{2\pi N}\sum_K e^{i\mathbf{K}\cdot\mathbf{R}}\int d\omega\;\mathcal{G}_{rs}(K,\omega).$$

The long-range part is mainly determined by the contributions of small **K** and ω. Thus, near T_c we only take the critical modes into account:

$$g_{rs}(R)=\frac{2}{\beta e^2(2\pi)^3}\int d^3K\,e^{i\mathbf{K}\cdot\mathbf{R}}\sum_{i=1}^{2}\frac{\tilde{\alpha}_i}{f_i\tilde{\alpha}_i\omega_{i0}^2}\times\left\{\frac{\beta\omega_{i0}}{2}\coth\frac{\beta\omega_{i0}}{2}\right\}P_{rs}{}^{(i)}(\mathbf{K}). \qquad (4.41)$$

Again we restrict the explicit calculation of g_{rs} to the case $T>T_c$ and use the spectrum given by Eq. (4.37) throughout the whole Brillouin zone. It is convenient to use coordinates where $\mathbf{R}=(R,0,0)$. Then g is diagonal:

$$g_{rs}(R)=g_r\delta_{rs}.$$

There are no correlations between different components. Because of the axial symmetry the correlations between components perpendicular to **R** are equal:

$$g_\perp=g_2=g_3.$$

The result of straightforward integration in Eq. (4.41) is

$$g_{\parallel}(R)=2\,\mathrm{const}\times\left[(1+2/K_0R)e^{-K_0R}-\frac{2}{(K_0R)^2}(1-e^{-K_0R})\right]\Big/R, \qquad (4.42)$$

with

$$\mathrm{const.}=\frac{1}{4\pi}\frac{v^2T_c}{e^2f_t'}$$

and

$$K_0=[4\pi(T-T_c)/(Cf_t')]^{1/2}.$$

The quantity K_0 vanishes at T_c and so does the expression Eq. (4.42) for the correlation function between the displacement components parallel to the distance vector R. The corresponding result for the components perpendicular to R is

$$g_\perp(R)=\mathrm{const.}\times\frac{e^{-RK_0}}{R}-\tfrac{1}{2}g_{\parallel}(R). \qquad (4.43)$$

Because of the transverse character of the critical modes, there is a strong correlation between the perpendicular components of the displacements. The range of this correlation becomes infinite at T_c.

2. *Dielectric Tensor*

The frequency- and wave-vector dependent dielectric tensor connects the change $\mathbf{P}'$ of the polarization with the change $\mathbf{E}'$ of the macroscopic electric field:

$$\mathbf{P}'(\mathbf{K},\omega)=(1/4\pi)[\epsilon(\mathbf{K},\omega)-1]\mathbf{E}'(\mathbf{K},\omega). \qquad (4.44)$$

Neglecting retardation effects the macroscopic field is given by[11]

$$\mathbf{E}'=\mathbf{E}_{\mathrm{ext}}-4\pi P^l\mathbf{P}'.$$

Using Eq. (4.9) we can write

$$\mathbf{P}'=\alpha(1+F\alpha)^{-1}\mathbf{E}_{\mathrm{ext}}.$$

So we get

$$\mathbf{P}'=\alpha[1+f_t\alpha+(f_l-f_t-4\pi)P^l\alpha]^{-1}\mathbf{E}',$$

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[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

and finally

$$\epsilon(\mathbf{K},\omega)=1+4\pi\alpha(1+f_t\alpha+\{f_l-f_t-4\pi\}P^l\alpha)^{-1}. \quad (4.45)$$

We note that the expression in curly brackets vanishes for $k=0$. Therefore the dielectric tensor does not depend on the direction in which **K** goes to the origin. In the approximation (4.31) for α it is possible to decompose ϵ into a transverse and a longitudinal part:

$$\epsilon=\epsilon^{\shortparallel}+\epsilon^{\perp},$$

$$\epsilon_{rs}{}^{\perp}=\sum_{i=1}^{2}\frac{1+(f_t+4\pi)\tilde{\alpha}_i}{1+f_t\tilde{\alpha}_i}P_{rs}{}^{(i)}, \quad (4.46)$$

$$\epsilon_{rs}{}^{\shortparallel}=\frac{1+f_l\tilde{\alpha}_0}{1+(f_l-4\pi)\tilde{\alpha}_0}P_{rs}{}^{(0)}. \quad (4.47)$$

$\epsilon_{\perp}$ has poles at the frequencies of the transverse modes and $\epsilon_{\shortparallel}$ vanishes at the frequencies of the longitudinal ones.[12] For $\mathbf{K}=0$ Eq. (4.46) reduces to the usual Lorentz-Lorenz formula.

D. Thermodynamic Quantities

In the vicinity of T_c the spectrum of the transverse collective modes is strongly temperature-dependent. The corresponding long-range correlations give a contribution to the free energy, which is contained in the second term of Eq. (3.32) and was neglected in the Hartree approximation. By means of Eqs. (2.4) and (4.28) this part can be written as

$$\langle V\rangle_{\text{RPA}}=\frac{e^2}{v}\sum_{rs}\sum_{\mathbf{K}}\int\frac{d\omega}{2\pi}\frac{i}{1-e^{-\beta\omega}}F_{rs}(\mathbf{K})$$
$$\times\{\chi_{rs}(\mathbf{K},\,\omega+i\eta)-\chi_{rs}(\mathbf{K},\,\omega-i\eta)\}. \quad (4.48)$$

Using Eq. (4.33) we obtain the corresponding part of the free energy:

$$F_2(T)=\sum_{\mathbf{K}}\int\frac{d\omega}{2\pi}\frac{i}{1-e^{-\beta\omega}}$$
$$\times\sum_{i=0}^{2}\operatorname{Tr}\int_0^1\frac{d\lambda}{\lambda}\left\{\frac{P^{(i)}}{1+\lambda f_i\tilde{\alpha}_i(\omega+i\eta)}-\frac{P^{(i)}}{1+\lambda f_i\tilde{\alpha}_i(\omega-i\eta)}\right\}.$$

We perform the λ integration with the aid of the relation

$$\delta(1+\lambda f_i\tilde{\alpha}_i(\omega^2))=[2\lambda f_i\tilde{\alpha}_i'(\omega^2)\omega]^{-1}\sum_{\nu}\delta(\omega-\omega_\nu) \quad (4.49)$$

and get

$$F_2(T)=\sum_{i=1}\sum_{\mathbf{K}}\sum_{E_\alpha>E_\beta}\int_{\omega_{i\nu}(K)}^{E_\alpha-E_\beta}d\omega\coth\left(\frac{\beta\omega}{2}\right)$$
$$\times[f_i(\mathbf{K})\tilde{\alpha}_i(\omega^2)]^{-1}\operatorname{Tr}\{P^{(i)}(\mathbf{K})\}. \quad (4.50)$$

Here $\omega_{i\nu}(\mathbf{K})$ are, as before, the resonance frequencies of the actual system, that is, for $\lambda=1$, whereas in Eq. (4.49) the eigenfrequencies ω_ν still depend on the coupling constant λ. In the form of Eq. (4.50), $F_2(T)$ no longer contains any λ-dependent quantity. The correspondence between the indices (α,β) and (ν) is, for $\lambda=0$,

$$\omega_{i\nu}=E_\alpha-E_\beta.$$

In the expression Eq. (4.50) for the contribution of the correlations to the free energy, the temperature enters through the polarizability $\tilde{\alpha}$, the resonance frequencies $\omega_{i\nu}$, and explicitly through β. Because of the critical-temperature dependence of the low-frequency spectrum, F_2 leads to a singularity in the specific heat as the critical temperature is approached from either side. Using the spectrum of Eq. (4.37) we find the singularity of $-T\partial^2F_2/\partial T^2$ on the high-temperature side of T_c:

$$\Delta\tilde{C}_v=Nk_B(2\sqrt{\pi})\left(\frac{T_c}{C}\right)^2\frac{v}{f_t{}^{3/2}}\left(\frac{C}{T-T_c}\right)^{1/2}. \quad (4.51)$$

This singularity is quite analogous to the square-root singularity in the specific heat of a ferromagnet, described in molecular-field approximation.[13]

V. DISCUSSION OF THE MODEL AND THE RESULTS

We have described a microscopic model for the phase transition of perovskite-type ferroelectrics. The Hartree approximation for the static properties is merely a quantum-mechanical derivation of some results of Devonshire and Slater for the most simple version of their model. Using the random-phase approximation we were able to express the frequencies of the "soft" transverse-optical modes, as well as displacement correlation functions, in terms of those parameters which were already used in the static theory, except for one additional parameter, which determines the dependence of the resonant frequencies on the wavelength.

This model is in several respect insufficient to give a realistic description of a ferroelectric crystal: We treat only one ion per unit cell dynamically, thereby assuming a completely clamped crystal. The model therefore shows a phase transition of second order rather than of first order, as observed, for example, in $BaTiO_3$. We neglect all electronic polarizabilities, which are known to be quantitatively important.[6]

Despite these shortcomings of the model some of its features are expected to appear also in a more sophisticated and more realistic theory:

(1) The temperature dependences of the critical modes in the nonpolar and the ferroelectric phase are strongly correlated. Their ratio is given by the ratio of the Curie constants [Eqs. (4.19) and (4.20)]. For the

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[12] V. M. Agranovich and V. L. Ginzburg, Usp. Fiz. Nauk **76**, 643 (1962) [English transl.: Soviet Phys.—Usp. **5**, 323 (1962)].

[13] R. H. Brout, *Phase Transitions* (W. A. Benjamin, Inc., New York, 1965).

ferroelectric state this means especially a splitting of the soft mode according to the ratio of the Curie constants [Eq. (4.20)], which in $BaTiO_3$ is $C_{\parallel}/C_{\perp}\approx 3$.[14] This effect has not yet been observed.

(2) The $\mathbf{K}^2$ dependence of $\omega_s{}^2$ is expected to vary only slightly with temperature [Eq. (4.24)] and to be the same for all critical modes below and above the transition point [Eq. (4.22)]. For $BaTiO_3$ the $\mathbf{K}$ dependence of the soft modes is not yet determined experimentally. For $SrTiO_3$ the spectra are measured by neutron scattering[15] for different temperatures. Using the temperature dependence of the $\mathbf{K}=0$ frequency we obtain by means of Eqs. (4.19) and (4.25), taking $\alpha_0=3/4\pi$, $\epsilon=930$ cm^{-1}. The dispersion curve for $T=90$°K together with Eq. (4.22) gives $f_t'=0.526$ Å^2. From Eq. (4.24) we then find, for 296°K and $K=0$, $d\omega_s{}^2(K^2)/dk^2=7.65\times 10^{-12}$, in good agreement with the experimental result, which is 7.75×10^{-12}.

(3) A splitting of the lowest transverse-optical mode is also expected at temperatures above T_c if an external electric field is applied [Eq. (4.25)]. This would give information about the anisotropy of the single-particle potential [the difference between b_1 and b_2 in Eq. (4.25)] in cases where only the nonpolar phase is accessable, as in $SrTiO_3$.

The result for the Debye-Waller factor is in qualitative agreement with the measurements of the Mössbauer effect[16,17] of Fe^{57} and Sn^{119} impurities in $BaTiO_3$ insofar as it gives the dip at the phase transition point which was predicted by Muzikar *et al.*[18] There are, however, two reasons why our result is not reliable. Firstly, the calculation of this quantity involves essentially the spectrum in the entire Brillouin zone. Even within this model we calculated only the long-wavelength part of the spectrum and made crude assumptions concerning the rest of it. Secondly, the Debye-Waller factor is determined by the total displacement of the particle—not only by the displacement with respect to the other ions of the same unit cell—which gives its polarization. So, for a complete calculation, we have to take the acoustic modes into account and, therefore, have to go beyond a model which keeps the centers of all units cells completely fixed.[19]

It might be of interest to compare the discontinuity of Eq. (3.35) and the singularity [Eq. (4.51)] of the specific heat at the temperature T_c. This gives an indication of the importance of the fluctuations in the polarization, which give rise to the singularity, for the thermodynamic quantities. We use for $BaTiO_3$, $T_c=390$°K, $C=1.1\times 10^5$ °K,

$$dP^2/dT=2\times 10^{-11}\ \mathrm{C^2/cm^4\,{}^\circ K},$$

and f_t' as before in the case of $SrTiO_3$. Then we find that we have to go as close as 1°C to the Curie point in order to make $\Delta\tilde{C}_v$ as large as ΔC_v. The first-order phase transition, however, has already occurred at roughly 10°C above this temperature, so that the fluctuations, in this case, actually never become important. In fact, an attempt by Brophy and Webb[20] to measure critical fluctuations of the polarization in the case of $BaTiO_3$ exhibited only thermal Barkhausen noise.

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