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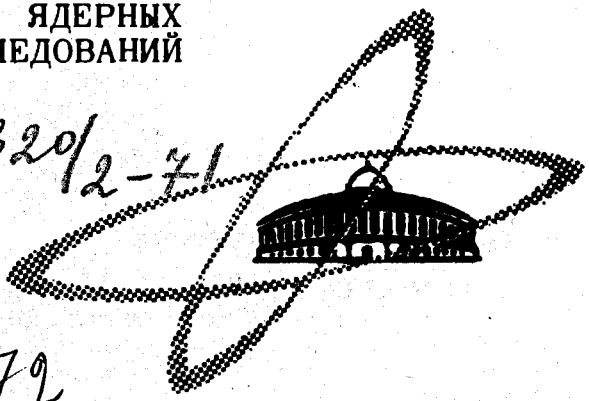

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THERMODYNAMICS OF STRONGLY ANHARMONIC CRYSTALS.

I. Self-Consistent Theory of Anharmonic Crystals at Fixed Pressure

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1. Introduction

Recently a self-consistent (S.C.) theory of strongly anharmonic crystals has been developed which allows to take into account in the lower order perturbation theory all the higher order anharmonic terms in a S.C. manner (see/1-3/ and the references cited in/3/). The properties of the three-dimensional lattice, namely the face-centred cubic (f.c.c.) one with the nearest neighbour central force interaction were considered in paper/4/ in the case of a small pressure. The properties of this lattice for the case of arbitrary external pressure were investigated in/5/ in the pseudoharmonic approximation.

In the present paper we take into account the damping of the S.C. phonons and consider the properties of the f.c.c. lattice with the nearest neighbour central force interaction in the case of the arbitrary external pressure.

In Section 2 we obtain a S.C. system of equations for the determination of the physical properties of the crystal at fixed pressure.

2. S.C. System of Equations for Strongly Anharmonic Crystal at Fixed Pressure

We consider a f.c.c. lattice consisting of N identical atoms of mass M. Applying the method, which was formulated in/3/, a S.C. system of equations for the investigation of the f.c.c. lattice with the nearest neighbour central force interaction was obtained in/4/.

The one-phonon Green's function was obtained in the following form:

$$G_k(\omega) = \ll A_k | A_k^+ \gg_\omega = \frac{2\omega_k}{\omega^2 - \omega_k^2 - 2\omega_k \Pi_k(\omega)} \quad . \tag{1.1}$$

The frequencies ω_k ($k = \{\vec{k}, j\}$) in equation (1.1) are determined in the pseudoharmonic approximation according to/3/ by the equation

$$\omega_k^2 = \frac{f(\theta, \ell)}{f} \omega_{0k} \quad , \tag{1.2}$$

where ω_{0k} is the harmonic frequency corresponding to the strength constant f.

The renormalized phonon frequencies ϵ_k and phonon widths Γ_k are determined approximately in the form

$$\epsilon_k \approx \omega_k + \mathrm{Re}\,\Pi_k(\epsilon_k) \; ; \; \Gamma_k = -\mathrm{Im}\,\Pi_k(\omega + i\delta) \; . \tag{1.3}$$

The self-energy operator in the effective cubic approximation takes the form:

$$\Pi_k(\omega) = \sum_{p,p'} |\tilde{V}_3(-k, p, p')|^2 \left\{ \frac{(n_p + n_{p'} + 1)(\omega_p + \omega_{p'})}{\omega^2 - (\omega_p + \omega_{p'})^2} - \right. \tag{1.4}$$

$$\left. - \frac{(n_p - n_{p'})(\omega_p - \omega_{p'})}{\omega^2 - (\omega_p - \omega_{p'})^2} \right\} ,$$

where $n_p = [\exp(\omega_p / \theta) - 1]^{-1}$.

For the central pair force model the function $|\tilde{V}_3|^2$ reads:

$$|\tilde{V}_3(-k,p,p')|^2 = \frac{\Delta(\vec{p}+\vec{p}'-\vec{k})}{4M^3 N \omega_k \omega_p \omega_{p'}} g^2(\theta,\ell) F^2(-k,p,p'), \qquad (1.5)$$

where $F(k_1,k_2,k_3)$ is a dimensionless sum over the lattice points which is given in/4/.

The pseudoharmonic $f(\theta,\ell)$ and the effective cubic $g(\theta,\ell)$ strength constants in equations (1.2) and (1.5) are determined in the S.C. manner

$$f(\theta,\ell) = \tilde{\phi}''(\ell), \quad g(\theta,\ell) = \tilde{\phi}'''(\ell), \qquad (1.6)$$

where $\tilde{\phi}(\ell)$ is the S.C. potential which is given in certain approximation/4/ by the equation

$$\tilde{\phi}(\ell) \approx \sum_{n=0}^{\infty} \frac{1}{n!} \left[\frac{1}{2} \overline{u^2(\ell)}\right]^n \phi^{(2n)}(\ell), \qquad (1.7)$$

$\overline{u^2(\ell)}$ is the mean square relative displacement of neighbouring atoms. It can be written using the Green's function (1.1) in the form:

$$\overline{u^2(\ell)} = \frac{1}{ZN f(\theta,\ell)} \sum_k \omega_k \frac{1}{\pi} \int_0^{\infty} d\omega \coth \frac{\omega}{2\theta} [-\mathrm{Im}\, G_k(\omega + i\delta)], \qquad (1.8)$$

where Z is the number of the nearest neighbours (for f.c.c. lattice $Z = 12$.).

In addition to the temperature $\theta = kT$ the properties of the lattice are determined also by the volume V of the crystal or by the external pressure P. According to/3,4/ these parameters satisfy the following equation

$$P = -\frac{Z\ell}{6v} \tilde{\phi}'(\ell) = -\frac{2\sqrt{2}}{\ell^2} \tilde{\phi}'(\ell), \qquad (1.9)$$

where $v = (V/N) = \ell^3/\sqrt{2}$, ℓ is the equilibrium separation of neighbouring atoms.

The thermal properties of the anharmonic crystal are determined by the internal energy E and free energy F which according to/1,3,4/ we write in the following form:

$$E = \langle H \rangle = \frac{NZ}{2} \{ \tilde{\phi}(\ell) + \frac{1}{2} f(\theta, \ell) \overline{u^2(\ell)} \} + 5 \tilde{F}_3(\theta) \tag{1.10}$$

$$F = F_0 + \frac{NZ}{2} \{ \tilde{\phi}(\ell) - \frac{1}{2} f(\theta, \ell) \overline{u^2(\ell)} \} + \tilde{F}_3(\theta), \tag{1.11}$$

where

$$F_0 = \theta \sum_k \ln \{ 2 \sinh \omega_k / 2\theta \} \tag{1.12}$$

and the effective cubic anharmonic contribution to the free energy reads

$$\tilde{F}_3(\theta) = -\frac{1}{6} \sum_{k,p,p'} |\tilde{V}_3(k,p,p')|^2 \{ \frac{n_k(1+n_p+n_{p'}) - n_p n_{p'}}{\omega_p + \omega_{p'} - \omega_k} + \frac{(1+n_p)(1+n_{p'})(1+n_k) - n_p n_{p'} n_k}{\omega_p + \omega_{p'} + \omega_k} \} . \tag{1.13}$$

Therefore both the dynamical (1.3) and thermodynamical (1.10) and (1.11) properties of the anharmonic crystal are determined by the S.C. system of equations (1.1)-(1.9). To solve them we should introduce the interatomic pair potential $\phi(R)$ in the equation (1.7), which as in/4/ is taken as the model Morse potential; then for equation (1.7) we get:

$$\tilde{\phi}(\ell) = \epsilon\{ e^{-2a(\ell - r_0)} e^{2y} - 2e^{-a(\ell - r_0)} e^{y/2} \}, \qquad (1.14)$$

where ϵ is the depth of the Morse potential and r_0 is the average distance between neighbouring atoms in the harmonic approximation. The strength constant in the harmonic approximation is given by $f = \phi''(r_0) = 2\epsilon a^2$. $y = (f/2\epsilon)\overline{u^2(\ell)} = a^2 r_0^2 (\overline{u^2}(\ell)/r_0^2)$ is the dimensionless mean square relative displacement of neighbouring atoms. We note here after/1/ that the deviation of a Lennard-Jones (12-6) interatomic potential from the Morse potential with $ar_0 = 6$ in the domain of the thermal expansion of the lattice is rather small. Therefore we shall take further $ar_0 = 6$.

Let us consider the case in which the external pressure is fixed $P = \text{const}$., but contrary to/4/ we do not suppose that P is small. The equilibrium lattice constant depends on the temperature of the crystal if we keep the external pressure fixed. The equlibrium separation of neighbouring atoms ℓ can be written as follows

$$\ell(\theta) = \ell_0 + \delta\ell = r_0 \{1 + \frac{1}{4} y + \frac{\delta\ell}{r_0}\}, \qquad (1.15)$$

where ℓ_0 is the equilibrium separation at $P = 0$ which can be determined using equations (1.9) and (1.14). It is convenient to introduce the reduced pressure $P^* = P(\sigma^3/\epsilon)$, where $\sigma^6 = r_0^6/2$ is the parameter of the Lennard-Jones (12-6) interatomic potential. Then equation (1.9), taking into account (1.14) and (1.15), reads

$$P^* = \frac{24}{(\ell/r_0)^2} e^{-y} e^{-6\frac{\delta\ell}{r_0}} \{ e^{-6\frac{\delta\ell}{r_0}} - 1 \}. \qquad (1.16)$$

Using equations (1.14), (1.15) and (1.16) the dimensionless pseudoharmonic strength constant α according to (1.6) can be written as follows

$$a^2 = \frac{f(\theta,\ell)}{f} = \frac{P^*}{12}\left(\frac{\ell}{r_0}\right)^2 + \frac{e^{-y}}{2}(1+\gamma) \qquad (1.17)$$

where

$$\gamma = \left\{1 + \frac{P^*}{6}\left(\frac{\ell}{r_0}\right)^2 e^{y}\right\}^{1/2} . \qquad (1.18)$$

Solving the last equation for y we get

$$y = \ln \frac{a^2 - \frac{P^*}{24}\left(\frac{\ell}{r_0}\right)^2}{\left[a^2 - \frac{P^*}{12}\left(\frac{\ell}{r}\right)^2\right]^2} . \qquad (1.19)$$

Consequently, the expressions for the S.C. potential (1.14), the equlibrium separation of neighbouring atoms (1.15) and the effective cubic strength constant (1.6) can be written as follows

$$\tilde{\phi}(\ell) = -\epsilon\left\{a^2 - \frac{P^*}{8}\left(\frac{\ell}{r_0}\right)^2\right\} =$$

$$= -\epsilon\left\{\frac{e^{-y}}{2}(1+\gamma) - \frac{P^*}{24}\left(\frac{\ell}{r_0}\right)^2\right\} \qquad (1.20)$$

$$\frac{\ell}{r_0} = 1 + \frac{1}{12}\ln \frac{a^2 - \frac{P^*}{24}\left(\frac{\ell}{r_0}\right)^2}{\left[a^2 - \frac{P^*}{12}\left(\frac{\ell}{r_0}\right)^2\right]^4} =$$

$$= 1 + \frac{1}{4}y - \frac{1}{6}\ln\frac{1+\gamma}{2} \qquad (1.21)$$

$$\frac{g(\theta,\ell)}{g} = \left\{a^2 - \frac{P^*}{36}\left(\frac{\ell}{r_0}\right)^2\right\} = \frac{P^*}{18}\left(\frac{\ell}{r_0}\right)^2 + \frac{e^{-y}}{2}\{1+\gamma\}, \qquad (1.22)$$

where $g \approx \phi'''(r_0) = -6\epsilon a^3$.

Evaluation of the ω-integral in expression (1.8) in the case of finite phonon widths is not so easy as it was in the pseudoharmonic approximation/5/ and should be done numerically. But we can obtain an approximate expression for (1.8) if we take into account the explicit form of the self-energy operator (1.4) in the high and low temperature limits. The results of these calculations will be given in following papers.

References

1. Ph.F. Choquard. The Anharmonic Crystal. W.A. Benjamin Inc. New-York/Amsterdam, 1967.
2. N.M. Plakida and T. Siklós. Acta Phys.Hung., 25, 17 (1968).
3. N.M. Plakida and T. Siklós. phys.stat.sol., 33, 103 (1969).
4. N.M. Plakida and T. Siklós. phys.stat.sol., 39, 171 (1970).
5. T. Siklós. Acta. Phys.Hung., 30, No. 2 (1971); JINR, E4-5390, Dubna, 1970.

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