ON LOW-TEMPERATURE PROPERTIES OF UNIAXIAL DIELECTRICS WITH A SOFT OPTIC MODE

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1. A uniaxial dielectric with a charge separation among the constituent atoms has an optic phonon mode, which corresponds to oscillation of the dielectric polarization $P_z$ along the $z$ axis. The frequency of such a mode at small wave vectors $k$ is described by the relation

$$
\omega^2(k) = \omega^2(0) + \kappa k^2 + \frac{k^2}{k^2},
$$

(1)

where

$$
\kappa = \sum_j \frac{4\pi \kappa_j^2}{m_j \mu_0}.
$$

The coefficient $\kappa$ reflects the degree of charge separation among the constituent atoms. The parameters $\kappa_j$ and $m_j$ respectively represent the charge and the mass of the ion of kind $j$, and $\mu_0$ is the volume of the elementary cell. In typical ionic crystals, the parameter $\kappa$ (the square of the plasma frequency of ions) is of the order of the square $\omega_D^2$ of the Debye frequency. It follows from Eq. (1) that as $k \to 0$, the frequency $\omega(k)$ depends on the angle between the direction of the wave vector $k$ and $z$ axis. This reflects the long-range character of dipole–dipole interaction between polarizations at different points in space1).

2. The dipole–dipole modification of the phonon spectrum presented in Eq. (1) plays an important role if the frequency $\omega(0)$ in the centre of the Brillouin zone is especially small (soft optic mode $\omega(0) \ll \omega_D$). In such a case, anharmonicity plays an important role, which results in a temperature dependence of the frequency $\omega(0)$ of the soft mode. As was shown in Ref. [1],

$$
\omega^2(0, T) - \omega^2(0, 0) \propto \int (dk) \frac{n(k)}{\omega(k)}.
$$

(2)

$$
n(k) = \left\{ \exp \left[ \frac{\hbar \omega(k)}{T} \right] - 1 \right\}^{-1}.
$$

Calculating the integral in Eq. (2) with dispersion law (1), we obtain

$$
\omega^2(0, T) = \omega^2(0, 0) + AT^3.
$$

(3)

The parameter $\omega^2(0, 0)$ in Eq. (3) can, in principle, be negative2). This means that the crystal undergoes a displacement-type phase transition at the temperature $T_c$ that can be found from the relation

$$
\omega^2(0, T_c) = 0 = \omega^2(0, 0) + AT_c^3.
$$

At $T \leq T_c$, a spontaneous polarization $P$ along $z$ axis appears.

Thermal dependence of the frequency of the soft mode (3) results in a modification of the Curie–Weiss law for dielectric susceptibility $\chi(T)$,

$$
\chi(T) = \frac{C^3}{T^3 - T_c^3}, \quad T \geq T_c.
$$

(4)

The parameter $T_c$ can be positive or negative. If $T_c > 0$, the dielectric susceptibility $\chi(T)$ diverges at a finite temperature, indicating a transition into the

1) Strictly speaking, dispersion of the frequency $\omega(k)$ depends on the direction of the wave vector $k$. For simplicity, we neglect this anisotropy as not leading to a qualitative difference and replace the tensor $\hat{s}$ by a scalar coefficient $s$.

2) In the case where $\omega^2(0, 0) < 0$, it is assumed in Eq. (3) that $A T^3 \geq \omega^2(0)$. 

153
ferroelectric phase at \( T \leq T_c \). If \( T_c < 0 \), \( \chi(T) \) remains finite at all temperatures. The difference from the results in Ref. [1] is in appearance of a \( T^3 \) dependence in Eqs. (3) and (4).

3. As was mentioned in Ref. [1], the presence of a soft optic mode in the phonon spectrum results in a modification of the thermal expansion in the temperature range

\[
\frac{1}{\tau_1(T)} \sim T^4, \quad h\omega(0) < T < \Theta_D.
\]

Modification of this result for a uniaxial crystal goes along the same line as in the analysis of dielectric susceptibility: the thermal expansion coefficient \( \alpha(T) \) is proportional to the derivative of the number of thermally excited optic phonons with respect to the temperature, and therefore

\[
\alpha(T) \propto \left( \frac{\partial}{\partial T} \right) \rho \int (dk) \frac{n(k)}{\omega(k)} \sim T^2.
\]

4. As was shown in Ref. [2], the phase diagram in the temperature-pressure plane \((T, p)\) is determined by the number \( N(T) \) of thermally excited optic phonons at low temperatures. Since the modification of the phonon spectrum due to dipole-dipole interaction leads to a reduction in \( N(T) \), the phase diagram undergoes a change: the critical pressure \( p_c \) of the ferro-electric transition depends on the temperature \( T \) as

\[
p_c(T) - p_c(0) \propto -T^3.
\]

5. The spin-lattice relaxation rate \( 1/\tau_1(T) \) in dielectrics is determined by the spin flips due to Raman-like scattering of phonons (see, e.g., Ref. [3]). At low temperatures \( T \ll \Theta_D \), in most of dielectrics, the leading contribution arises from the Raman scattering of acoustic phonons [4]

\[
\frac{1}{\tau_1(T)} \sim T^7.
\]

Here, the high power of temperature arises from the total number of thermal phonons \( N \propto T^3 \) and the fourth power of the wave vector\(^3\). The situation changes if the dielectric has a soft optic mode\(^5\). The contribution of these phonons in cubic crystals is [5]

\[
\frac{1}{\tau_1(T)} \sim T^3, \quad h\omega(0) < T < \Theta_D.
\]

\(^3\) An acoustic displacement \( u_a \) enters any equation not itself but in the form of its gradient \( u_{a\beta} \).

\(^5\) An optic displacement \( x_{\alpha} \) itself is allowed by the symmetry to enter equations.

The situation changes once again in uniaxial crystals if the soft optic mode corresponds to oscillations of the polarization along the \( z \) axis. Due to dispersion law (1),

\[
\frac{1}{\tau_1(T)} \propto T^4, \quad h\omega(0) < T < \Theta_D.
\]

6. Finally, the crystal might belong to one of piezoelectric crystalline classes (see, e.g., [6]). In this case, even for small wave vectors, we cannot separate the optic mode corresponding to oscillations of the polarization \( P \) along the \( z \) axis and the transverse acoustic mode. The Lagrangian of coupled vibrations of the polarization \( P \) and the elastic deformations

\[
\alpha_{ij} = \frac{1}{2} \left( \frac{\partial u_{ij}}{\partial r_j} + \frac{\partial u_{ij}}{\partial r_i} \right)
\]

in the long-wavelength limit has the form

\[
\mathcal{L} = \int d\mathbf{r} \times \left\{ \frac{m}{2} \mathbf{P}^2 - \frac{m_0^2 \omega(0)^2}{2} \mathbf{P}^2 - \frac{m_0^2}{2} (\nabla \mathbf{P})^2 - \frac{b}{4} \mathbf{P}^4 + \frac{M}{2} \mathbf{u}^2 + \frac{\lambda}{2} \mathbf{u}_i^2 - \mu \mathbf{u}_{ij}^2 - d \mathbf{P} \mathbf{u}_{xy} \right\}.
\]

Here, \( m \) is the reduced mass characteristic for the mode of optic vibrations, \( M \) is the mass of all atoms in the unit cell, \( \lambda \) characterises the long-wave dispersion of optic mode, \( \lambda \) and \( \mu \) are elastic moduli, and \( d \) is the piezoelectric coefficient. Diagonalizing quadratic form (9), we obtain the following expression for the frequency \( \omega(\mathbf{k}) \) of the mode, which does not vanish as \( \mathbf{k} \to 0 \) (see Refs. [6, 7]):

\[
\omega^2 = \omega^2(0) - \frac{d}{4m\mu} + s k^2 + \frac{d}{4m\mu} \left[ \frac{k^2}{k^2 + 4} \frac{\lambda + \mu}{\lambda + 2\mu} \right].
\]

Equation (10) shows that similarly to the influence of dipole-dipole interaction, the piezoelectric coupling results in introducing, into the dependence of the optic vibration frequency, a dependence on the direction of the wave vector \( \mathbf{k} \), which does not vanish at \( \mathbf{k} \to 0 \). In the spirit of the foregoing, this leads to the temperature dependence of the frequency \( \omega^2(0) \). Calculating the an-harmonic correction, we obtain

\[
\omega^2(0, T) = \omega^2(0, 0) + A'T^4.
\]

Thermal expansion is also modified:

\[
\alpha(T) \propto T^3.
\]
Equation (6) for the critical pressure $\rho_c(T)$ of the ferroelectric transition undergoes the modification

$$\rho_c(T) - \rho_c(0) \propto -T^4,$$  \hspace{1cm} (13)

and the spin–lattice relaxation rate$^5$.

$$\frac{1}{\tau_1(T)} \propto T^5, \quad \hbar \omega(0) - \frac{d}{4m\mu} < T \ll \Theta_D.$$ \hspace{1cm} (14)

7. Cubic crystals with soft optic modes are a subject of active research for nearly 50 years. As regards to uniaxial crystals, there are very few examples of this kind. In recent experiments [8], the properties of brominated tris-sarcosine calcium chloride (TSCC) were studied. These experiments showed that TSCC has a weak charge separation, the parameter $\kappa$ in Eq. (1) is anomalously small, and therefore the effects of dipole–dipole interaction are negligible. I am grateful to S. E. Rowley and S. F. Scott for the opportunity to familiarize myself with the results of these experiments and for the instructive discussions. I hope that this paper will help to find a material in which the mentioned effects are stronger.

8. Many years ago, in 1970–72, two graduate students in Chernogolovka, late V. L. Shneerson and I, embarked on the studies of the displacement type transitions at low temperatures. This short comment is dedicated to the memory of V. L. Shneerson.

REFERENCES


$^5$ The difference between Waller’s $T^7$ and $T^9$ in Ref. [5] seems very significant, while the difference between $T^7$ and $T^5$, perhaps, is not so easy to detect.