Anomalies in the dispersion of the dielectric susceptibility of intrinsic toroics

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A soft mode will be seen in the infrared spectrum in the case of an intrinsic toroic phase transition (the order parameter of such a transition transforms in the same way as the toroidal moment). The frequency of the dielectric-loss peak has an unusual temperature dependence near the transition.

By "toroics" we mean crystals which undergo a phase transition accompanied by the appearance of a spontaneous toroidal moment. Phase transitions for which the order parameter transforms in the same way as the toroidal moment are accompanied by some interesting anomalies in physical properties (see Refs. 1 and 2 and the bibliography there). In the present letter we analyze an anomaly in the frequency dependence of the dielectric susceptibility near an intrinsic toroidal phase transition. This anomaly results from the invariants $\dot{P}_i T_i$ and $P_i \dot{T}_i$ in the thermodynamic potential of the initial phase of the crystal. These invariants relate in a linear way the oscillations of the vector electric moment P_i and the toroidal moment T_i (the dot means a derivative with respect to the time).

For simplicity, we restrict the analysis to the simple case of a single-component order parameter T. We write the thermodynamic potential Φ, the kinetic energy K, and the dissipation function R in the form

$$\Phi = \frac{\alpha}{2} T^2 + \beta T^4 + \frac{\kappa}{2} P^2 + \frac{a}{2} (T\dot{P} - P\dot{T}) - PE,$$

$$K = \frac{\mu}{2} \dot{T}^2 + \frac{m}{2} \dot{P}^2, \quad R = \frac{\nu}{2} \dot{T}^2 + \frac{r}{2} \dot{P}^2. \tag{1}$$

The symmetric combination $T\dot{P} + P\dot{T}$ is a total time derivative and makes no contribution to the Euler equations. From expressions (1) we find the dispersion law of the dielectric susceptibility $\chi = dP/dE$ for harmonic oscillations $P,T \sim \exp i\omega t$:

$$\chi(\omega) = \frac{\omega_P^2 / \kappa}{\omega_P^2 - \omega^2 + i\omega\omega_r - \dfrac{\omega^2 \delta^2}{\omega_T^2 - \omega^2 + i\omega\omega_\nu}}. \tag{2}$$

Here we have introduced the following quantities, all of which have the dimensionality of a frequency:

$$\omega_P^2 = \frac{\kappa}{m}, \quad \omega_T^2 = \frac{\alpha}{\mu}, \quad \omega_r = \frac{r}{m}, \quad \omega_\nu = \frac{\nu}{\mu}, \quad \delta^2 = \frac{a^2}{m\mu}. \tag{3}$$

In restricting the discussion to only the invariants in (1), we are actually ignoring powers of ω higher than ω^2 in the expression for $\chi(\omega)$ in (2). In the low-symmetry "toroidal" phase, the dispersion $\chi(\omega)$ is of the same nature as in the initial phase, (2); all that changes is the frequency of the soft mode: $\omega^2{}_T = -2\alpha/\mu$.

To analyze the function $\chi(\omega)$ we assume $\alpha = \alpha_T(T-\theta)$, while the other coefficients in (1) do not depend on the temperature. Here $\beta > 0$; i.e., the phase transition is of second order. We assume that the natural frequency (ω_P) of the oscillations of the polarization P is large in comparison with all the other frequencies in (3): $\omega_T, \omega_r, \omega_v$, and δ. The inequality $\omega_T^2 \ll \omega_P^2$ holds near the transition point, since $\omega_T^2 \sim |\alpha| \sim |T-\theta|$. The inequalities $\omega_r, \omega_v \ll \omega_P$ mean that the damping is comparatively weak, while $\delta^2 \ll \omega_P^2$ means that the coupling of the oscillations of P and T is weak. We do not actually need this last inequality; all it does is simplify the equations slightly without having any qualitative effect on the results.

Analysis of (2) shows that the imaginary part, $\chi''(\omega)$, a measure of the dielectric loss, has two maxima, at ω_1 and ω_2. The frequency of the upper maximum, ω_2, is approximately equal to ω_P and varies slightly with the temperature:

$$\omega_2^2 = \omega_P^2 + \delta^2 + \frac{\delta^2}{\omega_P^2}\,\omega_T^2 - \frac{1}{4}\,\omega_r^2 . \tag{4}$$

Here we have $\chi''(\omega_2) = \omega_P/\omega_r\kappa \gg 1$, so that the function $\chi(\omega)$ is a resonant function (under the condition $\omega_r \ll \omega_P$).

The behavior of the lower maximum is more complicated. At a sufficient distance from the transition point, under the condition $\omega_v \ll \omega_T$, we have

$$\omega_1^2 = \omega_T^2 - \frac{\delta^2}{\omega_P^2}\,\omega_T^2 + \frac{1}{4}\,\omega_v^2 . \tag{5}$$

Here we have $\chi''(\omega_1) = \omega_T\delta^2/\omega_v\omega_P^2\kappa$, and the functional dependence $\chi(\omega)$ is of a resonant nature if the damping is weak.

From (5) we see that as the point of the phase transition is approached along the temperature scale, the value of ω_1^2 decreases, initially linearly, and then progressively more slowly. At the value $\omega_T \sim \omega_v$ the frequency ω_1 reaches a minimum, and the functional dependence $\chi(\omega)$ acquires a relaxation nature. As we move closer to the transition point, the maximum disappears entirely if $\delta^2/8 < \omega_r\omega_v$. If $\omega_r\omega_v \ll \delta^2$, the maximum of χ'' is retained, while its frequency increases, taking on the values (for $\omega_T \ll \omega_v$).

$$\omega_1^2 = \omega_v^2 - 2\omega_T^2 . \tag{6}$$

Right at the phase-transition point, at $\omega_T = 0$, we have $\omega_1 = \omega_v$ according to (6); i.e., ω_1 does not vanish. Here we have $\chi''(\omega_1) = \delta^2/\omega_p^2\kappa$. This value, we might note, does not depend on how well the inequality $\omega_r\omega_v \ll \delta^2$ holds, so that this value is correct, in particular, at $\omega_r = 0$. The frequency ω_r has a generally weak effect on the lower maximum, while ω_v correspondingly has a generally weak effect on the upper maximum.

We conclude by emphasizing that the soft mode in the initial phase is active in the infrared absorption spectrum for an intrinsic ferroelectric phase transition. It was shown above that this comment also applies to an intrinsic toroidal phase transition; the temperature dependence of the frequency of the absorption maximum is unusual. Specifically, this frequency does not behave in a monotonic way (it goes through a minimum), and it does not vanish at the point of the second-order phase transition. We recall that for an intrinsic ferroelectric phase transition we have $\omega_1^2 = \omega_P^2 \sim T - \theta$ for $\omega_r \ll \omega_P$ and $\omega_1 = \omega_P^2/\omega_r \sim T - \theta$ at $\omega_P \ll \omega_r$. It would be interesting to see an experimental observation of the behavior found here. Some possible toroics are the nickel boracites, in particular, nickel iodide boracite.[3,4]

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