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Landau theory on the structural phase transitions in ferroelectric materials

Phenomenological theory of phase transitions (the Landau theory) successfully explained many different kinds of structural phase transitions, e.g., proper and improper ferroelectric ones, phase transitions through the incommensurate phase of two types, complicated sequences of phase transitions including the incommensurate phase (the Devil's staircase).

We apply a phenomenological approach in order to explain the temperature-pressure, T-P, phase diagrams of the crystals from the rich family of $\{N(\text{CH}_3)_4\}_2\text{MX}_4$ compounds (TMAX-M, where X is halogen and M is divalent metal, respectively). These crystals were investigated experimentally by Japanese scientists (see, e.g. the review by Gesi: *Ferroelectrics* **66** (1986) 269). We suppose that all phases observed in experiment are determined by the single soft branch of the vibration spectrum of the crystals. We suppose also that this branch has two minima in some range of parameters. Due to this a triple point of the new

type exists on the T-P phase diagram of TMA-family crystals (this point was predicted theoretically by Aslanyan and Levanyuk: *Fiz. Tverd. Tela (Leningrad)* **20** (1978) 804). We use two different phenomenological descriptions of incommensurate phase transitions to obtain thermodynamic potentials for all phases observed on the experimental T-P phase diagram. Equating these potentials to each other, we obtain expressions for boundaries between different phases. We plot the phase diagram on the plane of the two small coefficients of the potentials which dependences on T and P can be essential. Assuming that these coefficients depend linearly on T and P, we then plot the theoretical T-P phase diagram. So deriving we obtain the T-P diagram for the TMAB-Zn crystal in sufficiently good agreement with the experimental T-P diagrams (paper 1).

The T-P phase diagram for the TMAI-Zn obtained experimentally by Gesi (*J. Phys. Soc. Jpn.* **58** (1989) 1532) has specific features. There is no incommensurate phase on it, and there is a triple point between the initial C phase (of the symmetry group D_{2h}^{16}), and the commensurate phases, C_0 , with $q=0$ and $C_{1/2}$ with $q=1/2$ (q is a dimensionless wavevector). This point of such kind is met at the first time. We suppose that these features can be explained if the C-C^{1/2} phase transition is of first order. We calculated and plot the theoretical T-P diagram for this crystal and obtain a fairly well agreement with the experimental T-P diagram (paper 2).

In the well-known paper by Iizumi et al. (*Phys. Rev.* **B15** (1977) 4392), the experimental dependence of acoustic branch of vibration spectrum of K_2SeO_4 on wavevector is presented.

At different temperatures T near the temperature $T=T_c$ of the phase transition into the incommensurate phase, we apply a phenomenological approach to calculate this dispersion. We use the simple thermodynamic potential including two variables, which interact via the Lifshitz-type invariant. Taking the values of some coefficients from experiment and giving to some other coefficients definite values we calculate and plot the dispersion of the acoustic branch, which is a comparatively good agreement with experiment (paper 3).

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