

BIREFRINGENT AND DIELECTRIC PROPERTIES OF $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ CRYSTALS IN PARENT PHASE

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Temperature dependences of birefringence and dielectric permittivity of $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ crystals in the parent phase have been studied. A supposition was made that the nonlinear character of those two dependences is caused by the presence of local spatial regions, where the motions of tetrahedral groups ZnCl_4^{2+} are correlated.

order of 1 K. The temperature interval, where nonlinear temperature dependences of physical quantities are observed, is by an order of magnitude wider ($\Delta T \approx 10 \div 40$ K). In order to determine the interval, where the temperature dependences of birefringence $\delta(\Delta n)$ and dielectric permittivity ϵ'_a of $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ crystals in the parent phase are nonlinear, and to elucidate the reasons of such a nonlinearity, we carried out the researches of the quantities concerned in a wide temperature range.

$[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ crystals are model objects, when studying the properties of incommensurate phases. They are characterized by a complicated sequence of phase transitions [8,9].

1. Introduction

According to the results of works [1–4], the temperature behavior of physical parameters in the parent phase of crystals belonging to A_2BX_4 group is nonlinear in the vicinity $\Delta T = T^* - T_i \approx 20$ K of the phase transition to the incommensurate phase (here, T^* is the temperature of a deviation from linearity of the temperature behavior of physical parameters, and T_i is the phase transition temperature), being governed by fluctuation processes. In the three-dimensional Heisenberg model, the critical indices for a two-component order parameter have to depend substantially on the spatial dimension. This statement is based upon the idea of phase transition universality, in the sense that critical indices do not depend on the intensity of interaction in the system and the details of its microscopic structure, being more likely determined by the number of order parameter components and the spatial dimension. In particular, it should be noted that the critical indices are different from the Landau ones ($\gamma = 1, \alpha = 0, \beta = \frac{1}{2}, \nu = \frac{1}{2}$) [5] in a real space with the dimension $d = 3$ and equal to them in a space with $d = 4$. For instance, the observed nonlinear behavior of the widths of Mn^{2+} resonance lines in the EPR spectra of Rb_2ZnCl_4 crystals in their parent phase [1] was associated with rotation angle fluctuations of tetrahedral complexes ZnCl_4 .

According to the results of classical works [6,7], the temperature interval around the phase transition point, where the order parameter fluctuates, should be of the

2. Experimental Technique

Crystals were grown up from an aqueous solution of $[\text{N}(\text{CH}_3)_4]\text{Cl}$ and ZnCl_2 salts, taken in the stoichiometric ratio, at room temperature. Temperature researches of $\delta(\Delta n)$ and ϵ'_a were carried on using the same crystal specimen in order to provide the same concentration of noncontrolled impurities and defects. The birefringence was studied by the Senarmont method with light beam modulation [10]. The temperature was measured with an accuracy of ± 0.01 K [10]; a UTREKS K24 BER system and a P3003 voltage comparator were used for this purpose. Dielectric measurements were carried on making use of plane-parallel rectangular-shaped specimens and with the help of an automated installation. Measurements of the real part of dielectric permittivity ϵ' and the tangent of dielectric losses $\tan \delta$ were carried out following a conventional method for condenser capacity measurements. A Hioki 3535 multifrequency LCR-meter was used for this purpose. Measurements were carried out at low frequencies and at a small amplitude of the measuring alternating voltage $U = 0.5$ V.

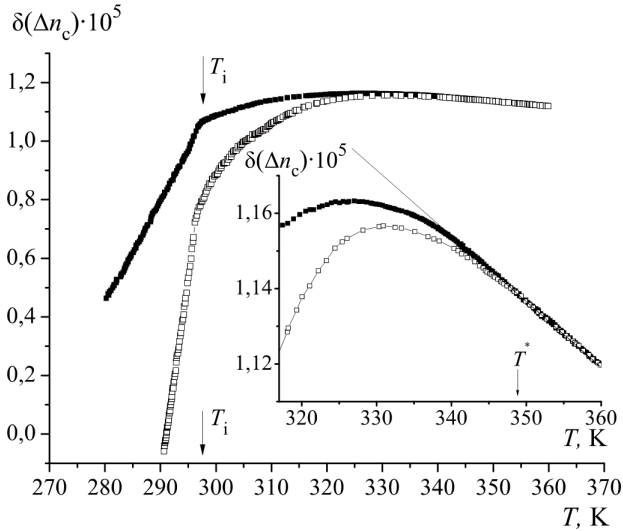


Fig. 1. Temperature dependences of the birefringence $\delta(\Delta n_c)$ for an as-cut specimen of the $[N(CH_3)_4]_2ZnCl_4$ crystal (\square) and a specimen annealed at 370 K for 1.5 h (\blacksquare). (inset) The temperature dependence of $\delta(\Delta n_c)$ in the vicinity of T^* (scaled-up)

Temperature researches of dielectric properties were fulfilled making use of a liquid nitrogen cryostat with a UNIPAN 680 thermoregulating system. The temperature of the crystal was measured with the help of a copper–constantan thermocouple to within the accuracy of about 0.01 K.

3. Experimental Results and Their Discussion

In Fig. 1, the temperature dependences of $\delta(\Delta n_c)$ for an as-cut specimen of $[N(CH_3)_4]_2ZnCl_4$ crystal and a specimen annealed at 370 K for 2 h are depicted. The dependences obtained demonstrate a deviation from the linear temperature behavior ($\propto T$) in the vicinity of $T^* \approx 350$ K for the as-cut specimen and $T^* \approx 350$ K for the annealed one. The further cooling of the specimen gives rise to that the nonlinearity in the temperature behavior of $\delta(\Delta n_c)$ increases until the temperature of phase transition into the incommensurate phase, $T_i = 296.7$ K, is attained. The annealing of the specimen at 370 K brought about a reduction of the rate of nonlinear variation of $\delta(\Delta n_c)$ with the temperature.

The temperature dependences of the dielectric permittivity ϵ'_a for an as-cut specimen of the crystal under investigation and a specimen annealed at 370 K are exhibited in Fig. 2. Here, deviations from linear temperature dependences are observed at the same

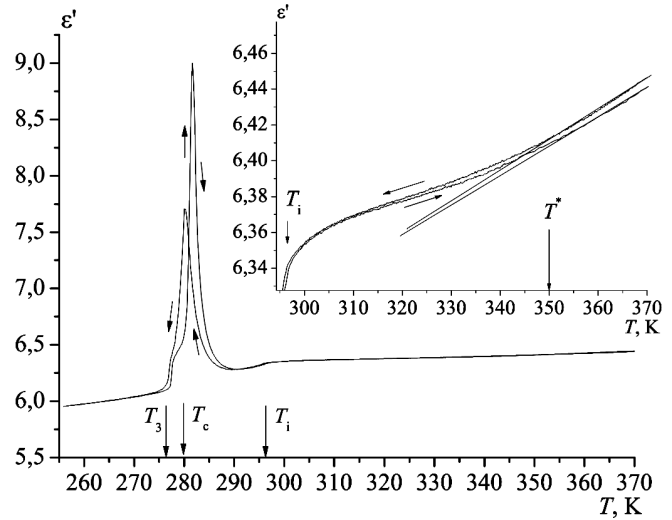


Fig. 2. Temperature dependences of ϵ'_a for an as-cut specimen of the $[N(CH_3)_4]_2ZnCl_4$ crystal (heating up) and a specimen annealed at 370 K for 2 h (cooling down). (inset) The same dependences in the vicinity of T^* (scaled-up)

temperatures ($T^* \approx 350$ K) as it was for the birefringence. Such a nonlinear behavior holds true until the temperature of transition into incommensurate phase is attained. The nonlinear temperature dependences of both $\delta(\Delta n_c)$ and ϵ'_a can originate due to two reasons: fluctuation processes and/or the appearance of a new phase state of the crystal.

The phase transition from the parent to the incommensurate phase is a continuous phase transition of the second kind. A spontaneous gain in the incommensurate phase is $\delta_s(\Delta n) \sim |\tau|^{2\beta}$, where $\tau = (T_i - T)/T_i$ [3]. This relationship is valid only in the classical region $\rho \sim \rho_0(T_i - T)^{2\beta}$ [9, 11]. To describe fluctuation processes, an expression for the thermo-optical coefficient $\xi = d(\Delta n)/dT$ is written down [3, 11]. Correction terms for fluctuations are introduced above and below T_i ; in the range above T_i , they are associated with the fluctuation of the local order parameter [3].

Though this approach describes the nonlinear temperature dependences of the physical parameters $\delta(\Delta n)$, ϵ'_a , and C_p qualitatively, a quantitative comparison is difficult to be made, because the nonlinearity is observed in a wide temperature interval [11]. Holding a crystal at a constant temperature within this interval is not accompanied by variations of $\delta(\Delta n_c)$ in time [12], which evidences for the structure stability in this range. A defect-density wave, which has been preliminarily recorded in the incommensurate phase,

remains stable within certain temperature and certain temporal intervals [13].

The existence of a new phase state in the temperature interval from T^* to T_i is testified to by data on diffusion scattering in the parent phase [14]. A considerable anisotropic scattering was observed in the parent phase around the position 20ξ , at the place of a future reflection satellite in the incommensurate phase [8]. Neutron inelastic scattering experiments [14] demonstrated that the intensity of quasielastic scattering in the parent phase strongly grows as the temperature decreases to the phase transition point T_i .

X-ray diffraction researches testify that ZnCl_4^{2+} -tetrahedra are almost regular in the parent phase, while tetramethylammonium (TMA) ions $[\text{N}(\text{CH}_3)_4]$ are deformed, the deformation of TMA-2 being stronger than that of TMA-1 [8]. Two states of tetrahedral groups ZnCl_4 and TMA-1 in the parent phase are coupled to each other: the angles of their rotation around the axes that pass through the centers of their masses and are oriented almost along the pseudo-hexagonal c -axis, are correlated. For TMA-2, the c -axis is almost parallel to the b -one. In work [8], it was supposed that rotations of all tetrahedral groups are already correlated even in the parent phase. This assumption was based on the magnitude of the root-mean-square rotation amplitude of TMA ions of both kinds and their large anisotropy. It is not true if going farther away from T_i , and the rotations of neighbor ZnCl_4^{2+} groups can be considered independent to a large extent. Hence, in the temperature range $T^* \div T_i$, there exist local spatial regions, where the motions of tetrahedral groups are correlated, and these regions may probably be responsible for the nonlinear temperature dependences of birefringence and dielectric permittivity. In particular, there emerges a deformation in those local regions, which is the origin of the temperature nonlinearity of $\delta(\Delta n_c)$. The deformation of tetrahedral groups depends on defects and impurities, as well as on their spatial distribution [17]. This is confirmed by a reduction of the T^* -value for the annealed specimen, because mobile impurities of the "strong pinning" type [15]—according to the results of work [16]—stimulate the variation of the activation energy of hydrogen in TMA ions, inducing their different deformations.

Hence, $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ crystals are in a new phase state in the temperature range $T^* \div T_i$. This state is characterized by the existence of local regions, where the motions of tetrahedral groups are correlated.

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ДВОЗАЛОМЛЮЮЧІ І ДІЕЛЕКТРИЧНІ ВЛАСТИВОСТІ КРИСТАЛІВ $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ У ВИХІДНІЙ ФАЗІ

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Резюме

Наведено температурні залежності двозаломлення та діелектричної проникності кристалів $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ у вихідній фазі. Зроблено припущення, що нелінійна з температурою поведінка двозаломлення та діелектричної проникності кристала $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ зумовлена існуванням локальних просторових областей скорельованого руху тетраедричних груп ZnCl_4^{2+} .