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Characteristic Features of the Modulated Phases in $(MgGeF_6)\cdot 6H_2O$ Crystals

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The temperature dependences of the optical birefringence $\delta(\Delta n_c)$ in $(MgGeF_6)\cdot 6H_2O$ crystal have been investigated. Specific properties observed in experiment such as global hysteresis, kinetic effect, thermooptic memory effect, localization of the incommensurability wave vector on the commensurate values of higher order, sensibility to the external mechanical stress confirm the existence of the incommensurate phase in current crystals.

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1. Introduction

$(MgGeF_6)\cdot 6H_2O$ (MGFH) crystals belong to $(ABF_6)\cdot 6H_2O$ (where A = Mg, Mn, Fe, Co, Zn, Ni, Cd, and B = Ti, Si, Ge, Zr) group of crystal materials. Current crystals at lowering temperature undergo a transition from triclinic phase (space group $R\bar{3}m$) into monoclinic one (space group $P2_1/c$) [1]. The transition process is followed by the transformation of the optically uniaxial crystal into biaxial. According to [1] in MGFH crystals the second-order phase transition occurs at $T_i = 401$ K and the first-order one occurs at $T_c = 313$ K. Due to work [2] it was postulated that the incommensurate (IC) phase exists in the temperature range from T_i to T_c between high temperature and low temperature symmetric phases. Also, the authors of work [3] by EPR treatment of $(MgGeF_6)\cdot 6H_2O{:}Mn^{2+}$

crystals indicate the inhomogeneous phases existing in the temperature interval of $T_c = 311.0 \pm 0.3$ K $< T < T_i = 403 \pm 0.3$ K.

To obtain more information about the crystalline structure in temperature region $T_i \div T_c$ and to confirm the IC phase existence the experimental investigations of the birefringent and piezooptic properties of the $(MgGeF_6) \cdot 6H_2O$ crystals have been carried out in detail.

2. Experimental methods

Single crystals have been grown by the evaporation method from aqueous solutions.

The measurement of the spontaneous increment of optical birefringence with a change of temperature and applied mechanical stress were performed using Senarmont's method at the wavelength of 633 nm. Due to the employment of a magneto-optical modulator the accuracy of the $\delta(\Delta n)$ determination was 10^{-7}. The total error of piezooptic coefficient measurement, connected with inaccurate determination of sample thickness and inhomogeneity of applied mechanical stress, is near 1 to 3%. The temperature was kept and measured with an accuracy of 0.01 K.

3. Results and discussion

The temperature dependences of the birefringence $\delta(\Delta n_c)$ for MFGH obtained in heating as well as in cooling runs are plotted in Fig. 1. As one can see at $T_c^h = 327.3$ K the phase transition of the first order occurs. The temperature hysteresis of the phase transition at T_c is equal to 18.25 K at the temperature change rate $dT/dt = 1$ K/h. At heating run the phase transition is followed by a jump of $\delta(\Delta n_c)$ by 11×10^{-5} that is due to the value order which overcomes analogous birefringence change at a cooling run. Besides, the sign of $\delta(\Delta n_c)$ changes at the transition point. On the $\delta(\Delta n_c) \sim f(T)$ dependence at a cooling run at temperatures $T = 311.9$, 319.5, 330.5, 336.8, 343.5, 348.3, 354.7, 361.7, 368.4, 374.7 K the birefringence anomalies are observed. They are similar to the $\delta(\Delta n)$ anomalous changes comprised by the increase in the static defects concentration [4]. Following analytical approach [4] to explain the obtained results (Fig. 1) one can conclude the IC structure existence in the temperature range of $T_i - T_c$ in MGFH crystals. While approaching the transition point T_i the number of birefringence anomalies increases which is caused by the sample defection rise comprised with an extraction of the crystalline water from the crystal. This has not allowed us to measure $\delta(\Delta n)$ in the vicinity of T_i temperature. Thus, at a cooling run on $\delta(\Delta n_c) \sim f(T)$ dependence the characteristic changes of $\delta(\Delta n_c)$ appear (Fig. 1), and the birefringence behavior near phase transition point T_c has a characteristic shape as for virgin sample (Fig. 2).

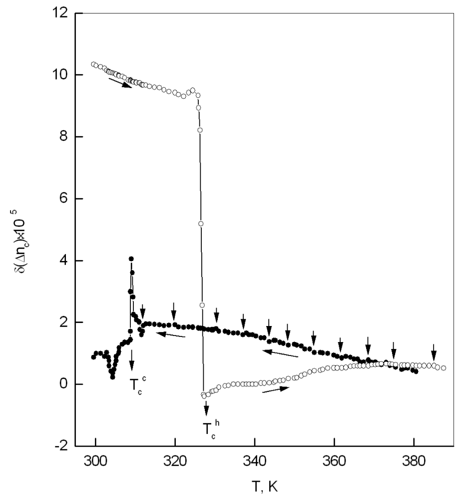

Fig. 1. Temperature dependences of optical birefringence $\delta(\Delta n_c)$ in $(MgGeF_6)\cdot 6H_2O$ crystals at a heating run (T_c^h ○) and cooling run (T_c^c ●).

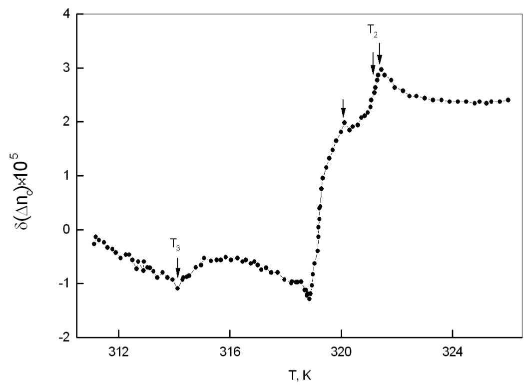

Fig. 2. Temperature behavior of optical birefringence $\delta(\Delta n_c)$ in virgin sample of $(MgGeF_6)\cdot 6H_2O$ crystals.

To clear up the nature of the considered phase the presence of the specific effects: global hysteresis, thermal cycling, kinetic effect, and thermooptic memory effect have been studied. Taking into account the data presented in Fig. 1 one may conclude that MGFH in T_i–T_c possesses a temperature global hysteresis. According to Fig. 3, passage from heating to cooling and back on the $\delta(\Delta n_c) \sim f(T)$ dependence describes a geometric figure of "parallelogram" shape with the sides laying on the correspond heating and cooling branches. To explain these results one should suppose the incommensurate structure existence in this temperature range and crossing between cooling and heating branches at a condition of constant soliton density [5]. The crystal keeping at the constant temperature $T_{st} = 324.5$ K

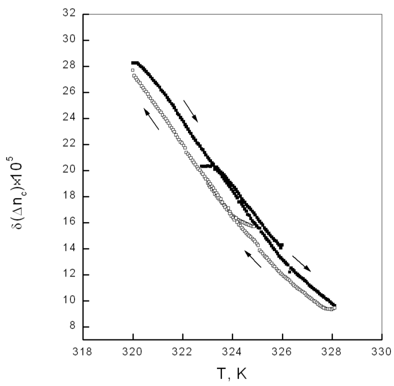

Fig. 3. Specific "parallelogram" cycle in temperature behavior of $\delta(\Delta n_c)$ in $(MgGeF_6)\cdot 6H_2O$ crystals.

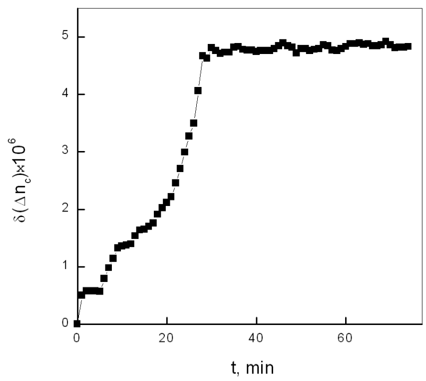

Fig. 4. Temporal dependence of optical birefringence $\delta(\Delta n_c)$ in $(MgGeF_6)\cdot 6H_2O$ crystals keeping the sample at the constant temperature $T_{st} = 324.5$ K.

gave the temporal dependence of $\delta(\Delta n_c)$ with the periodic anomalous changes (Fig. 4). Such kinetic feature shows that the soliton structure relaxes to the equilibrium state through the set of the intermediate metastable states. At a repeated passing through the temperature point of stabilization (T_{st}) in a heating run as well as in a cooling one the anomalous changes of the $\delta(\Delta n_c)$ display the thermooptic memory effect observed on the $\delta(\Delta n) \sim f(T)$ dependences (Fig. 5). The set of the observed effects indicates the IC structure existence [6]. Comparing the obtained data with the results of [3] one can conclude that below $T < 380$ K the soliton regime of modulated structure exists.

One more confirmation of the IC structure existence in $(MgGeF_6)\cdot 6H_2O$ crystals is the fact of distinguished changes of the birefringence in the vicinity of T_c. Such behavior of the $\delta(\Delta n_c)$ may be explained by existence of the commensurate long- -periodic phases (temperature regions, where incommensurability wave vector is localized on the commensurate values of a higher or-

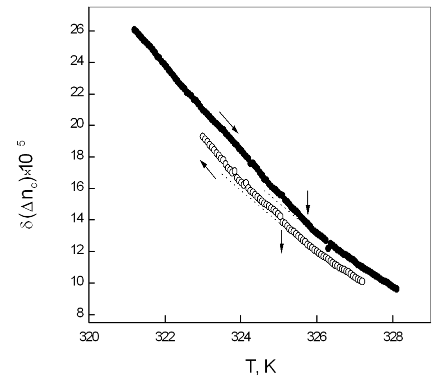

Fig. 5. Thermooptical memory effect on temperature dependence $\delta(\Delta n_c)$ in $(MgGeF_6)\cdot 6H_2O$ crystals.

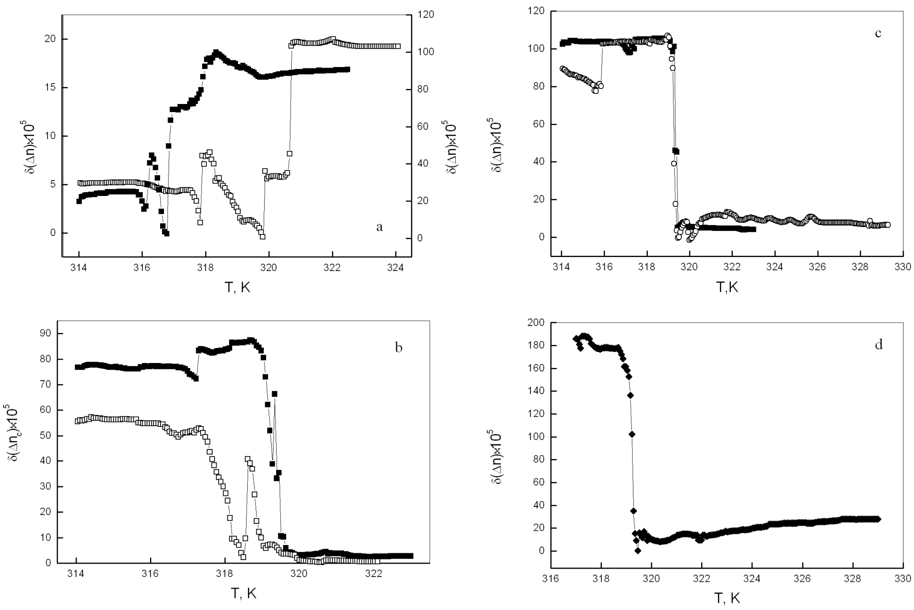

Fig. 6. Temperature dependence of $\delta(\Delta n_c)$ under influence of mechanical stress in $(MgGeF_6)\cdot 6H_2O$ crystals: (a) ■ — $\sigma_6 = 0$, □ — $\sigma_6 = 2\times 10^5$ N/m^2; (b) □ — $\sigma_6 = 4\times 10^5$ N/m^2, ■ — $\sigma_6 = 6\times 10^5$ N/m^2; (c) □ — $\sigma_6 = 8\times 10^5$ N/m^2, ■ — $\sigma_6 = 10\times 10^5$ N/m^2; (d) $\sigma_6 = 16\times 10^5$ N/m^2.

der). Hence, the phase transitions into these temperature regions correspond to the changes of $\delta(\Delta n_c)$. Due to Fig. 6 one can define the six temperatures $(T_1 = 316.1, T_2 = 316.34,\ T_3 = 317, T_4 = 318.14,\ T_5 = 318.38, T_6 = 319.82$ K) of such transitions. According to [7] under the influence of the external stresses (electric or mechanical fields) the temperature range of the metastable states existence changes, otherwise the region of commensurate phases existence changes too. To confirm the existence of such regions in the vicinity of T_c the mechanical stress was applied to the sample. At first under the σ influence the temperature region between phase transitions widens and shifts toward higher temperatures (Fig. 6a, b). At the mechanical stress intensity value $\sigma_6 = 10^6$ N/m^2 the $\delta(\Delta n_c)$ increment in the vicinity of T_c changes its sign to opposite. A further increasing of the applied stress σ_6 comprises a further widening of the commensurate regions, their shift toward higher temperatures (Fig. 6c, d) and $\delta(\Delta n_c)$ increment rise at the phase transition. Besides, the piezooptic coefficients have a characteristic anomalous behavior with temperature (Fig. 7).

The specific feature of the current crystals is the internal mechanical strains at $\sigma = 0$. They influence the incommensurability wave vector behavior. Our

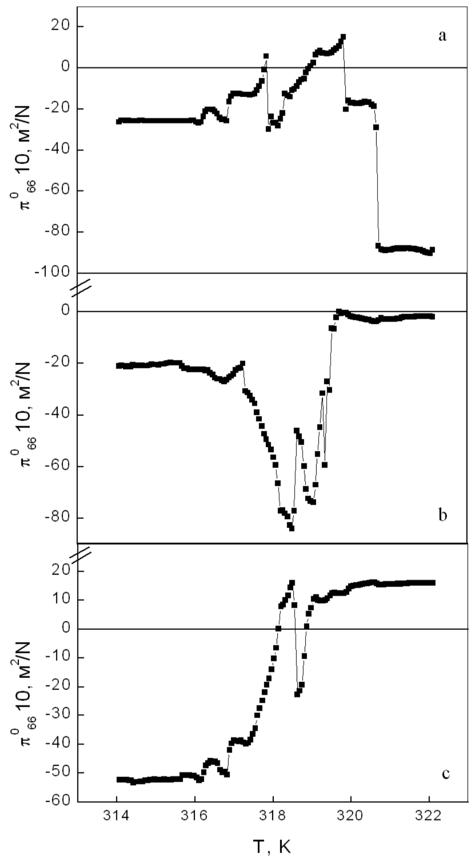

Fig. 7. Temperature dependence piezooptic coefficient π_{66}^0 in $(MgGeF_6)\cdot 6H_2O$ crystals: the difference between optical birefringence increments determined at: (a) $\sigma_6 = 0$ and $\sigma_6 = 2 \times 10^5$ N/m^2; (b) $\sigma_6 = 4 \times 10^5$ N/m^2 and $\sigma_6 = 6 \times 10^5$ N/m^2; (c) $\sigma_6 = 0$ and $\sigma_6 = 6 \times 10^5$ N/m^2.

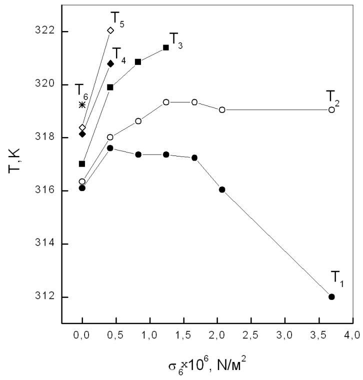

Fig. 8. Applied mechanical stress influence on the temperatures of phase transitions in $(MgGeF_6) \cdot 6H_2O$ crystals.

experimental results show that the external mechanical stress changes the soliton density and shifts the phase transitions temperatures (Fig. 8). According to the conclusions of [8] the applied mechanical stress changes the stability of the crystal in metastable state accelerating or slowing down the relaxation to the equilibrium state, as it has been observed in the experiment. Under mechanical strain influence the soliton density differs more from the equilibrium value. As a result the relaxation processes become more brightly expressed. An increasing of the sample defection in the case of the phase transition at T_{i} comprises defects "viscous interaction" with the incommensurate structure.

4. Conclusions

As one can see, the presence of the set of specific effects reflects the IC phase existence in $(MgGeF_6) \cdot 6H_2O$ crystals. The obtained experimental data on birefringent and piezooptic properties of MGFH correlate well with the results of Ref. [3].

The significant temperature hysteresis $\Delta T = 18.25$ K of the phase transition at T_{c}, in our mind, can be comprised with the crystal structure deformation caused by the crystalline water extraction from the sample.

The physical properties of the $(MgGeF_6) \cdot 6H_2O$ crystals are analogous to the ones in $(MgSiF_6) \cdot 6H_2O$ considered in [9]. The properties of both of them depend from the sample "pre-history".

It has been found that the mechanical stress causes a further widening of the temperature intervals of the IC regions existence, where the IC wave vector localizes the commensurate values of the higher order.

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