

TEMPERATURE EVOLUTION OF THE OPTICAL ABSORPTION EDGE IN (*n*-PROPYLAMMONIUM) TETRACHLOROCADMATE CRYSTALS

YU.M. KORCHAK, M.V. PARTYKA^{1,2}, V.B. KAPUSTIANYK^{1,2},
D.V. RYBAKOV

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Ivan Franko Lviv National University, Faculty of Electronics
(107, Gen. Tarnavskiyi Str., Lviv 79017, Ukraine; e-mail: yurakorchak@yahoo.co.uk),

¹Ivan Franko Lviv National University, Faculty of Physics
(50, Dragomanov Str., Lviv 79005, Ukraine; e-mail: kapustianykh@yahoo.co.uk),

²Ivan Franko Lviv National University,
Scientific-Technical and Educational Center of Low Temperature Studies
(50, Dragomanov Str., Lviv 79005, Ukraine)

The temperature evolution of the absorption spectra in *n*-propylammonium tetrachlorocadmate (NH₃C₃H₇)₂CdCl₄ crystals has been studied in the energy range of 1.8–4.1 eV. In all low-temperature phases except the incommensurate one, the absorption edge is found to follow the empiric Urbach rule. The analysis of temperature dependences of the Urbach rule parameters confirmed the occurrence of phase transitions at $T_{i2} = 180$ K, $T_{c2} = 156$ K, and $T_{c3} = 106$ K. The thermo-optical memory (TOM) effect has been found in the low-temperature incommensurate phase of this crystal.

sinusoidal modulation, because an anomalous change in the temperature dependence of $\delta(\Delta n_c)$ is observed here at $T^* = 448$ K [5], and the temperature interval where this phase exists is limited by the temperatures T_i and T_c , at which the phase transitions of the second kind occur. An anomalous variation of this dependence was also observed at $T_c = 374$ K. The temperature of the other phase transition, T_i , was not achieved owing to the turbidity of the sample at its heating.

Compounds described by the formula (NH₃C_mH_{2m+1})₂MeCl₄, where Me = Mn²⁺, Cd²⁺, Fe²⁺ or Cu²⁺, crystallize as layered structures of the perovskite type [1–3]: they consist of almost isolated layers of MeCl₆ octahedra with mutual angles separated by organic cations. Voids between octahedra are occupied with NH₃ groups of alkylammonium cation, which form strong hydrogen bonds, N–H···Cl, with octahedra. The layers are superimposed and coupled by van der Waals forces; the latter act between methyl end groups. The crystal structure is orthorhombic at room temperature.

On the basis of the results of X-ray diffraction studies, it was established that, in the high-temperature incommensurate phase, long molecular axes of propylammonium groups are inclined with respect to the normals to perovskite planes. The inclination angles of organic layers, the positions of metal-halogen octahedra, and the distances between layers are modulated. The wavelength of the interlayer-distance modulation is 40 Å, and its amplitude is 0.3–0.4 Å [6, 7]. The modulation amplitude, measured by the angle of inclination of propylammonium groups, grows to the maximum near the γ -phase midpoint. At the same time, it diminishes to zero in the vicinity of T_i and T_c . Such a behavior differs from that inherent to ordinary incommensurate phases, where the order parameter grows monotonously with a temperature reduction over the whole phase volume.

Propylammonium tetrachlorocadmate crystals, (NH₃C₃H₇)₂CdCl₄ (*n*-PA-CdCl₄), demonstrate a complicated sequence of phase transitions, the characteristic feature of which is the presence of two rather unusual incommensurate phases γ and ε [4, 5]. It should be noted that, in those crystals, the upper incommensurate phase, γ , lies between two phases β and δ with identical groups of rhombic symmetry C_{mca} . Not only all the properties inherent to incommensurate phases are characteristic of it, but also some other features, which allows one to classify it as a “re-entrant” phase. In particular, it can be considered as a combination of two incommensurate phases with

In works [8–10], three low-temperature phase transitions were observed at $T_{i2} = 180$ K, $T_{c2} = 158$ K, and $T_{c3} = 110$ K from the phase δ to the phases ε , ζ , and η , respectively. However, other authors [11] reported somewhat different values for the phase transition temperatures: $T_{i2} = 178.7$ K, $T_{c2} = 156.8$ K, and $T_{c3} = 105.5$ K. The low-temperature incommensurate phase ε , according to the conclusions of work [11], lies

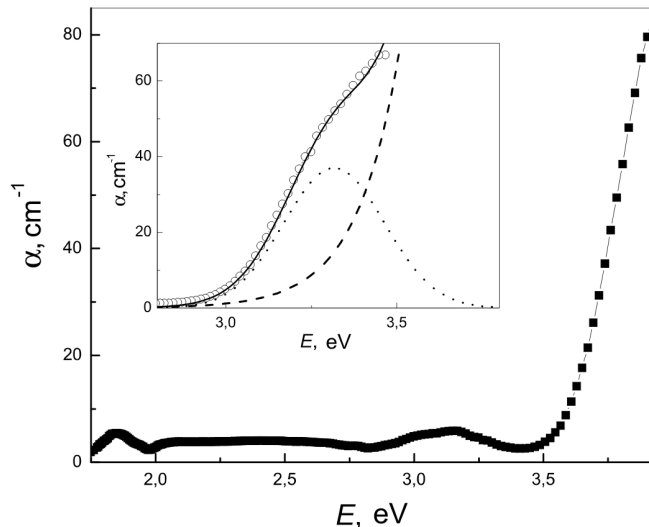


Fig. 1. Absorption spectrum of $(\text{NH}_3\text{C}_3\text{H}_7)_2\text{CdCl}_4$ crystal at room temperature (nonpolarized light). (inset) Points denote the optical absorption edge at a temperature of 158 K, the solid curve is a sum of the Gaussian (dotted curve) and exponential (dashed curve) approximation dependences

between the phases δ and ζ with rhombic symmetries $A\text{bma}$ and $P\text{bca}$, respectively. The symmetry of phase ε is described by superspatial group $P_{s11}^{A\text{bma}}$, and the modulation vector can be written as $\mathbf{q}=0.418 \mathbf{b}^*$.

To elucidate the nature of the low-temperature incommensurate phase in more details and to determine the phase transition temperatures more exactly, we studied the temperature evolution of the optical absorption edge (OAE) and the manifestations of TOM effect in propylammonium tetrachlorocadmte crystals, $n\text{-PA-CdCl}_4$. Crystals for researches were grown up from aqueous solutions of $\text{NH}_3(\text{C}_3\text{H}_7)\text{Cl}$ and CdCl_2 salts taken in the stoichiometric ratio, by the technique of slow evaporation at room temperature. Specimens for absorption spectrum measurements were cut out in the form of plates 0.2–0.4 mm in thickness and polished.

The temperature dependences of both polarized and nonpolarized absorption spectra in the ultraviolet and visible spectral ranges (300 – 700 nm) were studied on a ZMR-3 mirror monochromator (Russia). The absorption coefficient was calculated following the standard two-thickness method [12]. The relative measurement accuracy for this parameter was about 1%, the determination error of photon energy did not exceed 0.0005 eV. Temperature measurements were carried out making use of a liquid nitrogen cryostat and a “Utrex” regulation system (Special Design Bureau at the Institute of Physics of the NAS of Ukraine).

The accuracy of the temperature measurement and the stabilization was ± 0.1 K. The rate of temperature variation in the course of TOM effect investigation was 0.6 K/min.

The temperature evolution of the absorption spectra of propylammonium tetrachlorocadmte crystals was studied in the range 80–250 K, which spans the range of existence of the incommensurate phase ε . Our research of the corresponding absorption spectra at two directions of light polarization – along the crystallographic axes a and b – testified that dichroism was not considerable. The maximal shift of the OAE at the variation of the polarization direction did not exceed 1 – 2 nm, which agrees with the structure features of layered crystals concerned. Since the polarization of light in a plane perpendicular to the c -axis – simultaneously, it was a cleavage plane – did not influence the shape of spectra substantially, further researches were carried out using nonpolarized light. The direction of its propagation was parallel to the c -axis.

In Fig. 1, the absorption spectrum of an $n\text{-PA-CdCl}_4$ crystal recorded at room temperature is shown. A weak absorption band with the Gaussian shape is observed in the vicinity of a photon energy of 3.2 eV, and the OAE was found to be in the interval from 3.5 to 4 eV. On the basis of a comparative analysis carried out for the spectra obtained and the corresponding data for related crystals, we can draw a conclusion that the 3.2-eV band can originate from the presence of a noncontrollable copper impurity; in particular, it can correspond to the levels of excitons localized at impurity-induced defects [13].

Starting from the energy of 3.5 eV, a drastic growth of the absorption coefficient is observed (Fig. 1), which – according to the data of works [3,13] – can be regarded as a low-energy “tail” of a powerful band associated with an autolocalized exciton. If the temperature goes down to 80 K, the OAE of the exciton band becomes shifted toward lower energies and overlaps with the impurity absorption band (see the inset in Fig. 1). Making use of the “Origin 7.0” software package and applying approximation methods, we resolved the impurity band and the OAE of the exciton band, the latter is described by the Urbach exponential dependence of the absorption coefficient on the photon energy [13]. The inset in Fig. 1 demonstrates that the sum of the Gaussian-like and exponential contributions (the solid curve) coincides well with the experimental dependence. A similar situation is inherent to all low-temperature spectra of the crystal.

It is worth paying attention to rather a high intensity of the obtained Gaussian-like band in those spectra (the

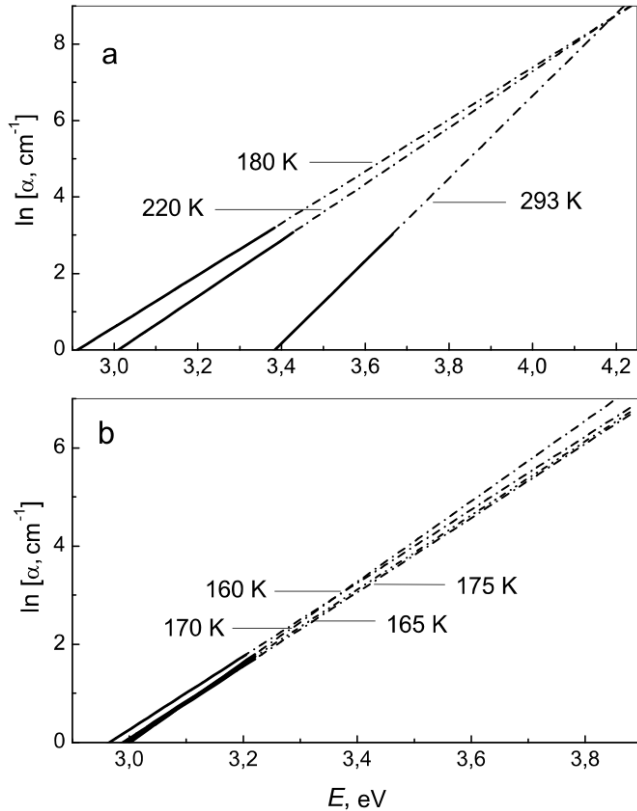


Fig. 2. Dependences of $\ln \alpha$ on the photon energy at various temperatures within the phase intervals for (a) the δ -phase ($T > 180$ K) and (b) the incommensurate ε -phase (158 K $< T < 180$ K)

inset in Fig. 1). Since the impurity concentration is not high, provided that high-purity grade salts have been used to grow up crystals, the oscillator strength of the corresponding band cannot be considerable as well. It is an extra evidence that the given band is really formed by excitons localized at defects induced by an uncontrollable impurity.

The analysis of the temperature evolution of OAE showed that, in all crystal phases except the incommensurate one, it is described by the empiric Urbach rule [14]:

$$\alpha = \alpha_0 \exp \frac{\sigma(T)}{kT} (h\nu - E_0), \quad (1)$$

where α_0 and E_0 are constants, $\sigma(T)$ is a parameter that characterizes the expansion of the absorption band edge, and k is the Boltzmann constant. In most cases, the empiric dependence (1) is associated with the electron-phonon or exciton-phonon interaction [14]. If so, the

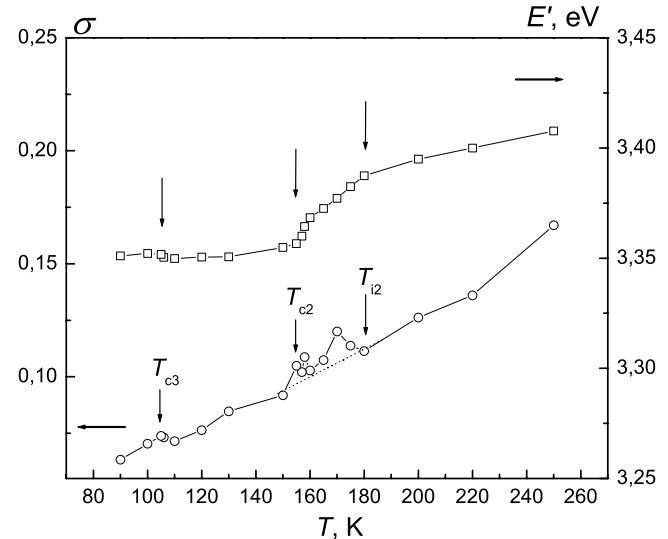


Fig. 3. Temperature dependences of the parameters σ and E' ($\ln \alpha = 3$ cm $^{-1}$)

parameter $\sigma(T)$ can be written in the form

$$\sigma(T) = \sigma_0 \frac{2kT}{h\nu_0} \ln \frac{h\nu_0}{2kT}, \quad (2)$$

where σ_0 is the exciton-phonon interaction constant, and $h\nu_0$ is the effective energy of optical phonons interacting with photons.

In agreement with relation (1), the dependences $\ln \alpha = f(h\nu)$ obtained in the phase δ at various temperatures converge at a point with coordinates ($\alpha_0 = 5.8 \times 10^3$ cm $^{-1}$, $E_0 = 4.19$ eV) (Fig. 2,a). A similar situation is also observed in the phases ζ ($\alpha_0 = 91.14$ cm $^{-1}$, $E_0 = 3.54$ eV) and η ($\alpha_0 = 3.4 \times 10^3$ cm $^{-1}$, $E_0 = 3.98$ eV). The phase ε , for which the straight lines $\ln \alpha = f(h\nu)$ do not converge, can be considered as an exception (Fig. 2,b). The violation of the Urbach rule is a characteristic feature of incommensurate phases [13].

In Fig. 3, the temperature dependences of the parameter σ , which was calculated from the slope of straight lines $\ln \alpha(h\nu)$ [13], are depicted. The value of this parameter increases in all low-temperature phases, including the incommensurate one, as the temperature grows. At the same time, the temperature dependence of the parameter σ turns out nonlinear in the phase ε , which is also a characteristic attribute of incommensurate phases. Anomalies, which correspond to phase transitions, are observed in this dependence at $T_{i2} = 180$ K, $T_{c2} = 156$ K, and $T_{c3} = 106$ K. The temperature dependence of the $\sigma(T)$ -increase in the incommensurate phase ε reflects the behavior of the crystal order parameter.

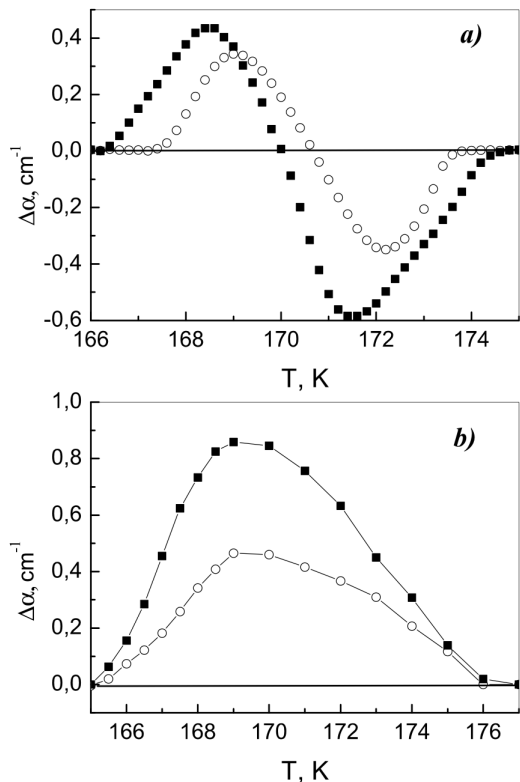


Fig. 4. Temperature dependences of the optical absorption coefficient at $\lambda = 320$ nm ($E = 3.88$ eV) measured in the heating (a) and cooling (b) modes after holding the n -PA-CdCl₄ specimen for 11 (○) and 36 h (■), at $T = 170$ K in the incommensurate phase. The quantity $\Delta\alpha$ corresponds to the deviation of the actual coefficient value from the equilibrium one measured when the specimen was kept in the commensurate phase

If one plots the isoabsorption dependence $E'(T)$ for a definite value of the absorption coefficient ($\ln \alpha = 3 \text{ cm}^{-1}$) in the band edge range (Fig. 3), it will approximately correspond to the temperature variations in the spectral position of the edge of the exciton band in n -PA-CdCl₄ crystals. As the temperature decreases, the curve $E'(T)$ changes its character at $T_{i2} = 180$ K, $T_{c2} = 156$ K, and $T_{c3} = 106$ K, which confirms the occurrence of phase transitions at these temperatures.

Knowing the data on the temperature dependence of the parameter σ and using formula (2), one can calculate the electron-phonon interaction constant σ_0 , as well as the effective energy $h\nu_0$ of phonons that participate in the formation of the OAE. The description of the calculation technique is given in work [15]. In the course of calculations, it is expedient to express the effective energy of phonons as the frequency ν_0 , in order to be able

to analyze the probable correlations with vibrational spectroscopy data.

As a result of calculations, we obtained the following values: $\nu_0 = 313 \text{ cm}^{-1}$ and $\sigma_0 = 0.151$ for the δ -phase, $\nu_0 = 177 \text{ cm}^{-1}$ and $\sigma_0 = 0.094$ for the ζ -phase, and $\nu_0 = 134 \text{ cm}^{-1}$ and $\sigma_0 = 0.076$ for the η -phase. Such values of the parameter σ_0 in these cases correspond to the medium strength of the electron-phonon interaction [16], which is inherent to an OAE formed with the participation of self-localized excitons [13]. In the case of incommensurate ε -phase, the calculation of parameters ν_0 and σ_0 is impossible, because the empirical Urbach rule is violated. On the basis of the precise analysis of the temperature evolution of OAE, the information about both the order parameter variation and the behavior of the incommensurability wave vector \mathbf{q} can be obtained. One more variant of manifestations of the TOM effect testifies to that.

Figure 4 illustrates the temperature variation of the absorption coefficient of n -PA-CdCl₄ crystal, which was measured in the incommensurate phase and at the constant wavelength $\lambda = 320$ nm in the OAE range. One can see that the temperature stabilization at $T = 170$ K in the incommensurate phase ε was accompanied by the appearance of a characteristic S-like deviation $\Delta\alpha$ of the absorption coefficient (Fig. 4,a), measured at the repeated passage of this temperature in the heating mode, from the value previously measured on the annealed specimen. As is seen from Fig. 4, the amplitude and the shape of $\Delta\alpha$ -anomaly essentially depend on the stabilization time. If the specimen underwent cooling once more, the anomaly acquired a bell-like shape due to the partial annealing of the crystal (Fig. 4,b).

The considered features in the behavior of the absorption spectra can be explained in the framework of the model, where incommensurate structures, on the one hand, and defects and impurities, on the other hand, interact. The holding of the crystal at a temperature of 170 K is accompanied by the formation of a periodic structure composed of defects which can remain stable during some time. If the stabilization point is passed again, the parameter of incommensurability δ becomes localized at this point. The annealing of the specimen in the initial phase is accompanied by the weakening and, ultimately, the disappearance of the TOM effect owing to the thermal diffusion and the relaxation of a defect wave to the uniform distribution. On the basis of a rather simple model [17], the conclusion can be made that the TOM anomaly has to increase, if either the concentration of defects or the number of nonequilibrium electrons formed at the optical excitation increases.

In the optical range, one should expect, therefore, an enhancement of the TOM effect in comparison with low-frequency dielectric measurements. In the range of the maximal optical absorption, the effect must be especially pronounced, which is generally confirmed by the presented experimental results.

To summarize, we can draw a conclusion that self-localized excitons in n -PA-CdCl₄ crystals participate in the formation of the OAE in the near ultra-violet spectral range. If the temperature reduces to 80 K, the edge of the exciton band shifts toward lower energies. The analysis of the temperature evolution of the OAE has shown that it can be described by the empirical Urbach rule. The analysis of the temperature dependences of the parameters σ and E' confirmed the occurrence of phase transitions at the temperatures $T_{i2} = 180$ K, $T_{c2} = 156$ K, and $T_{c3} = 106$ K. The violation of the Urbach rule and the manifestation of the TOM effect confirm the presence of the incommensurate modulation in the ε -phase of n -PA-CdCl₄ crystals.

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ТЕМПЕРАТУРНА ЕВОЛЮЦІЯ КРАЮ ОПТИЧНОГО ПОГЛИНАННЯ КРИСТАЛІВ n -ПРОПЛАМІН ТЕТРАХЛОРКАДМАТУ

Ю.М. Корчак, М.В. Партижа, В.Б. Капустяник,
Д.В. Рибаків

Р е з ю м е

Проведено дослідження температурної еволюції спектрів поглинання кристалів n -пропіламін тетрахлоркадмату $(\text{NH}_3\text{C}_3\text{H}_7)_2\text{CdCl}_4$ в діапазоні енергій 1,8–4,1 еВ. Встановлено, що край поглинання в усіх низькотемпературних фазах кристала, за винятком несумірної, описується емпіричним правилом Урбаха. Аналіз температурних залежностей параметрів правила Урбаха підтвердив наявність фазових переходів при $T_{i2} = 180$ К, $T_{c2} = 156$ К, і $T_{c3} = 106$ К. Виявлено ефект термооптичної пам'яті у низькотемпературній несумірній фазі даного кристала.