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Influence of alkaline metal to phase transitions in ferroelastics M_2CdI_4 (M = K, Rb, Cs)

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The absorption spectrum of thin films Cs_2CdI_4 was studied in energy interval 3.6–5.1 eV and temperatures 90–410 K at their heating and cooling. The regularities are ascertained in behaviour of the thin films of isostructural compounds M_2CdI_4 (M = K, Rb, Cs). With an increase of ion radius of alkali metal the temperatures of phase transitions are lowed, the value of temperature hysteresis in spectral position and halfwidth of exciton bands is decreased, and the temperature wash-out of phase transitions is increased. We supposed that these effects are connected with increase of squeezing of structural elements CdI_4^{2-} in crystal lattices of compounds as a result of increase of alkali metal ion radius.

Исследован спектр поглощения тонких пленок Cs_2CdI_4 в интервале энергий 3,6–5,1 эВ и температур 90–410 К при нагревании и охлаждении. Установлены закономерности в характере поведения тонких пленок изоструктурных соединений M_2CdI_4 (M = K, Rb, Cs) вблизи температур фазовых переходов. С ростом ионного радиуса щелочного металла снижаются температуры фазовых переходов, уменьшается величина температурного гистерезиса в спектральном положении и полуширине экситонных полос и увеличивается размытие фазовых переходов по температуре. Мы предположили, что эти эффекты связаны с увеличением сжатия структурных элементов CdI_4^{2-} в кристаллической решетке соединений, в результате роста радиуса щелочного металла.

The compounds M_2CdI_4 (M = K, Rb, Cs) of β-K_2SO_4 type orthorhombic structure are ferroelastics with incommensurate phase [1–5]. As the temperature is lowed they have the following sequence of phase transitions: paraphase $\leftrightarrow$ incommensurate phase at T_{c1}, incommensurate phase $\leftrightarrow$ first ferroelastic phase (monoclinic phase) at T_{c2} and first $\leftrightarrow$ second ferroelastic phase at T_{c3} [1–5]. Anomalously great hysteresis (AGH) of different physical quantities: of dielectric permeability [6], of birefringence [7], of piezo-optical coefficients [8], etc., are observed in the crystals with incommensurate phase near to the transition incommensurate — ferroelastic phase. The temperature dependences of long-wavelength excitonic band parameters of compounds K_2CdI_4 [9] and Rb_2CdI_4 [10] in the incommensurate phase have AGH. (AGH is revealed in the temperature dependences of long wavelength excitonic band parameters of compounds K_2CdI_4 [9] and Rb_2CdI_4 [10] in the incommensurate phase). In this paper we investigate absorption spectra of thin films of Cs_2CdI_4 in the region of long-wavelength excitonic band on heating and on cooling of sample in order to study of hysteresise effects. The temperature dependences of long-wavelength excitonic band parameters were compared in the range of compounds M_2CdI_4 (M = K, Rb, Cs) in order to ascertain regularities of phase transitions in the isomorphous range of compounds.

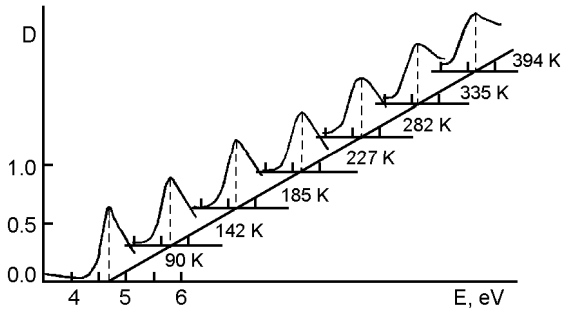

Fig. 1. Long-wavelength exciton absorption band of в Cs_2CdI_4 at various temperatures. The spectra are obtained at heating a sample. Thickness of a film is 145 nm.

The thin films of Cs_2CdI_4 with the thickness ~100 nm were prepared by vacuum evaporation of a mixture of the pure CsI and CdI_2 powders of specified composition onto quartz substrates heated to 100°C by a method [4, 5]. The film thickness was determined by a method of lines of the equal chromatic order. The absorption spectra were measured on an SF-46 spectrophotometer within an energy interval of 3.6–5.1 eV and temperature interval 90–410 K, which includes temperatures of phase transitions. The spectra were investigated in the interval 90–293 K in a vacuum cryostat and at higher temperatures in an ordinary thermostat. The each given temperature of the sample was maintained in the course of a 20 min. The long-wavelength excitonic band parameters (spectral position E_m, halfwidth Γ and ε_{2m}) were found following the technique [11].

The absorption spectrums of Cs_2CdI_4 exhibits in the interval 3.6–5.1 eV strong A_0 at 4.65 eV (90 K) and faint A_1 at 4.89 eV (90 K) exitonic bands (Fig. 1). The A_0 and A_1 bands shift with increasing temperature to longer wavelengths, broaden and weaken because of the exciton-phonon coupling (Fig. 1). The A_0 band parameters (position E_m, halfwidth Γ and ε_{2m}) were found in 21 points of temperature on heating and cooling of the sample. The temperature dependences of A_0 excitonic band position $E_m(T)$ and halfwidth $\Gamma(T)$ in Cs_2CdI_4 (Fig. 2), which has been studied on heating and on cooling of a sample, are different because of effects of thermal memory. The A_0 band in Cs_2CdI_4 is shifted with increasing of temperature to a longer wavelengths with $dE_m/dT \approx -3.1 \cdot 10^{-4}$ eV/K, the temperature induced shift was slowed down near the temperature of phase transition T_{c3} II → I ferroelastic phase, at $T \approx 200$ K the kink is observed on the $E_m(T)$ curves, in the region of I ferroelastic phase one has $dE_m/dT \approx -5.75 \cdot 10^{-4}$ eV/K. The curve $E_m(T)$ is gently sloping near the temperature of phase transition incommensurate → paraphase $T_{c1} \approx 335$ K. The linearly shift with $dE_m/dT \approx -7.3 \cdot 10^{-4}$ eV/K was observed in the paraphrase ($T > 335$ K). The coefficients dE_m/dT are typical, for ionic crystals, the temperature induced shift of the exciton band is determined primarily by the exciton-phonon coupling.

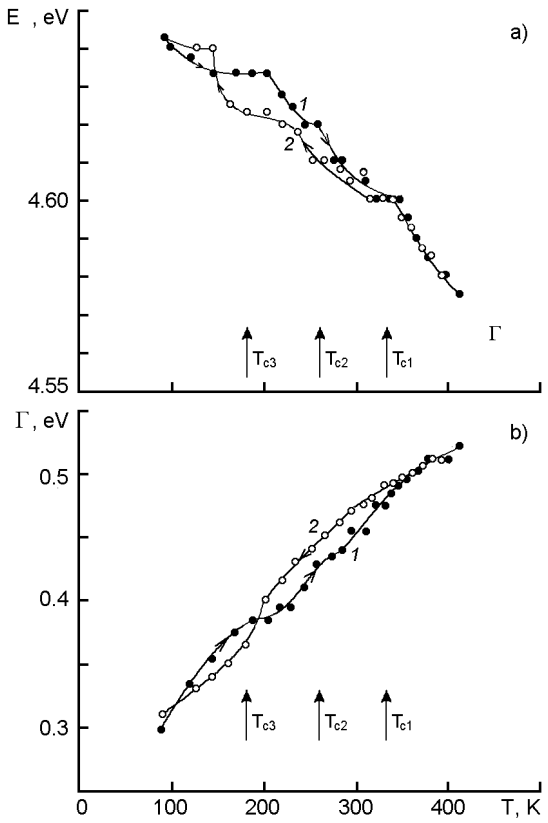

Fig. 2. Temperature dependences of a position $E_m(T)$ (a) and halfwidth $\Gamma(T)$ (b) of A_0 band in Cs_2CdI_4, obtained at heating (*1*) and cooling (*2*) of the sample.

The direct and return dependences $E_m(T)$ coincide in the paraphase, the small difference of $E_m^{\uparrow}(T)$ and $E_m^{\downarrow}(T)$ in the incommensurate phase (260 K < T < 335 K) at the high T increases near $T_{c2} \approx 260$ K, considerable uprise $E_m^{\downarrow}(T)$, which is observed in the interval 269–230 K, indicate to the first-order phase transition. The bigger ascent $E_m^{\downarrow}(T)$ is observed in an interval of temperatures 180–144 K and corresponding to phase transition I → II ferroelastic phase. The peculiarities of in dependence

$\Gamma(T)$ near to temperatures of phase transitions (Fig. 2b) also are observed. It is necessary to note, that phase transitions in Cs_2CdI_4 phase changes at T_{c2} and T_{c3} are strongly washed out on temperature — because of strong thermal inertia of the samples. The temperatures of phase transitions T_{c2} and T_{c3} on heating and cooling considerablement differ ($T_{c3}^{\uparrow}$200 K, $T_{c3}^{\downarrow}$145 K; $T_{c2}^{\uparrow}$260 K, $T_{c2}^{\downarrow}$232 K) (Fig. 2).

Thus phase transitions in thin film Cs_2CdI_4 are exhibited as kinks and jumps in temperature dependences $E_m(T)$ and $\Gamma(T)$, are strongly washed out on temperature, the quantity of a thermal hysteresis $E_m(T)$ and $\Gamma(T)$ is insignificant, it is essential smaller than in isostructural compounds K_2CdI_4 [9] and Rb_2CdI_4 [10]. In the region of incommensurate phase ($T_{c2} < T < T_{c1}$) the direct and return dependences $E_m(T)$ and $\Gamma(T)$ near T_{c1} almost coincide, the maximal difference is observed near T_{c2}. Such temperature dependences of physical quantities is characteristic for incommensurate phase and is determined by origin of solitons near T_{c1} and their pinning on the defects of a lattice near T_{c2} [1,2]. The Table contain the temperatures of phase transitions (mean value T_{ci}, which are received on heating and cooling of the sample) and position of long-wavelength excitonic band A_0 in isostructural compounds M_2CdI_4 (M = K, Rb, Cs) [9, 10]. The given values T_{ci} are conformed well with results [4–5]. The Table shows that the temperatures of phase transitions are reduced in a series M_2CdI_4, the absorption edge shift to high frequencies. Besides, the quantity of a thermal hysteresis $E_m(T)$ and $\Gamma(T)$ also decreases in a series M_2CdI_4, and the wash-out of phase transitions on temperature, on the contrary, is increased (see dependences $E_m(T)$ and $\Gamma(T)$ K_2CdI_4 [9], Rb_2CdI_4 [9]).

Examine a structure of a crystal lattice of explored samples for an explanation of observed regularity. The structural element of a lattice M_2CdI_4 are the tetrahedrons CdI_4^{2-}, which are surround by alkali metal ions M = K, Rb, Cs, they form a hendecagon [1, 2]. The arrangement of atoms in a unit cell of β-K_2SO_4 type crystals is shown in Fig. 3. Unfortunately there is not the image of a unit cell in work on examination of crystalline structure Cs_2CdI_4, therefore we give a unit cell of isostructural compound Cs_2BeCl_4 in a Fig. 3 [13]. From a Fig. 3 it is seen, that the divalent ions are found at centre of tetrahedrons from negative halide ions. The monovalent alkali metal ions form hendecagon in the second coordination sphere with respect to the divalent ion. On can also see the almost layered arrangement of tetrahedrons, the layers lying are perpendicular to the **a** axis. The similar arrangement of ions is observed in a unit cell of M_2CdI_4 crystals of β-K_2SO_4 type. In Cs_2CdI_4 the distance d_{Cs-I} = 3.825–4.499 Å is considerably larger then d_{Cd-I} = 2.76–2.91 Å [2].

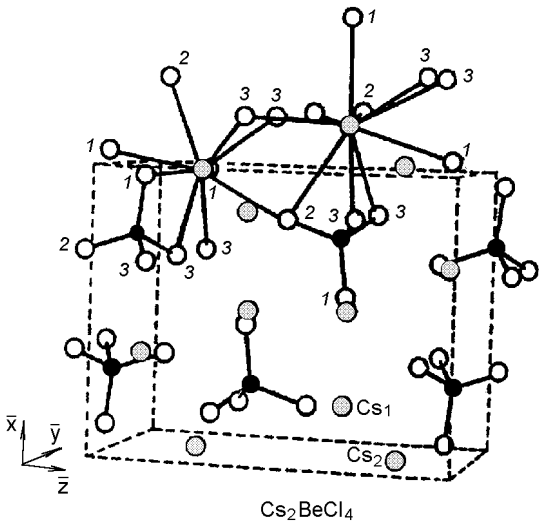

Fig. 3. A crystal lattice of a β-K_2SO_4 structural type (Cs_2BeCl_4 [13]).

The alkali metal ionic radius increases in a series M_2CdI_4 (Table). If a lattice constants M_2CdI_4 and volume of a unit cell [1, 2, 5] are similar parameters, increase of ionic radius r_i of alkali metal gives in increase of internal stresses in a crystal, equivalent multifold squeezing of tetrahedrons CdI_4^{2-}, that confirm examinations of absorption spectra M_2CdI_4 [4, 5, 9]. It is known, that the hydrostatic pressure of thin films CdI_2 gives in a short-wave shift of an absorption edge [15].

Table. Position A_0 band and temperature of phase transitions in M_2CdI_4 (M = K, Rb, Cs).

Compounds	E_m, eV	T_{c1}, K	T_{c2}, K	T_{c3}, K	r_i, pm [17]
K_2CdI_4 [9]	4.612	400	320	220	133 (K^+)
Rb_2CdI_4 [10]	4.63	380	290	210	148 (Rb^+)
Cs_2CdI_4	4.65	332	260	180	169 (Cs^+)

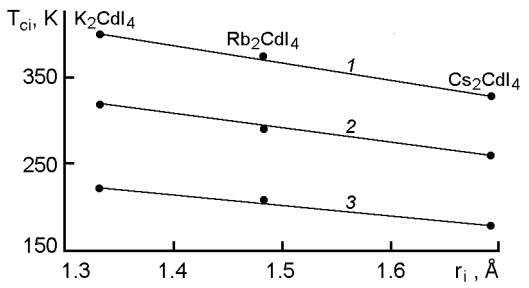

Fig. 4. Temperatures of phase transitions T_{ci} in M_2CdI_4 (M = K, Rb, Cs) versus ion radii of alkali metal: *1*—T_{c1}, *2* — T_{c2}, *3*— T_{c3}.

As in thin films M_2CdI_4 excitonic excitations are localized in CdI_4^{2-} tetrahedrons [4, 5], with increase of ionic radius r_i in a series M_2CdI_4 the absorption edge should be shifted in short-wavelength region, that proves to be true by experimental data — in a series M_2CdI_4 long-wavelength band A_0 has small short-wave shift (position A_0 band are given in (Table).

On the other hand it is known, that the mechanical stress in isostructural a crystal Rb_2ZnCl_4 gives in decrease of temperature of phase transitions, brings to diminution of quantity of a temperature hysteresis of dielectric permittivity and to wash-out of phase transitions on temperature [16, 17]. Similar changes we observe in series of compounds M_2CdI_4 in behaviour of ferroelastics films with increase of alkali metal ionic radius r_i near to temperatures of phase transitions: a decrease of temperatures of phase transitions, diminution of a temperature hysteresis and diffusion of phase transitions on a temperature. The linear relation is observed between temperatures of phase transitions T_i and quantity of ionic radius r_i in a series M_2CdI_4 (Fig. 4).

Thus, we ascertained, that the dependences $E_m(T)$ and $\Gamma(T)$ in thin films Cs_2CdI_4 are typical for ferroelastics with a incommensurate phase, quantity of a thermal hysteresis of parameters excitonic bands in Cs_2CdI_4 is least with an increase of ion radius in series of compounds M_2CdI_4 (M = K, Rb, Cs), and diffusion of phase transitions on temperature is greatest. The decrease of temperatures of phase transitions, diminution of quantity of a temperature hysteresis of excitonic band parameters and wash-out of transitions on temperature are observed in series of compounds M_2CdI_4 with increase of alkali metal ionic radius r_i. That, apparently, is concerned with magnification of internal stresses in films because of squeezing tetrahedrons CdI_4^{2+} with r_i increase.

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Вплив лужного металу на фазові переходи у сегнетоеластиках M_2CdI_4 (M = K, Rb, Cs)

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Досліджено спектр поглинання тонких плівок Cs_2Cd_4 в інтервалі енергій 3,6–5,1 еВ і температур 90–410 К при нагріванні й охолодженні. Установлено закономірності у характері поведінки тонких плівок ізоструктурних сполук $M_2Cd_4I_4$ (M = K, Rb, Cs) біля температур фазових переходів. Із зростанням іонного радіуса лужного металу знижуються температури фазових переходів, зменшується величина температурного гістерезису у спектральному положенні і напівширині екситонних смуг і збільшується розмиття фазових переходів за температурою. Ми припустили, що ці ефекти зв'язані зі збільшенням стиску структурних елементів Cd_4^{2-} у кристалічних гратах сполук внаслідок зростання радіуса лужного металу.