

Absorption spectra of layered ZnI_2 and K_2ZnI_4 compounds intercalated with CO_2

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The absorption spectra of thin films of ZnI_2 and K_2ZnI_4 layered compounds intercalated with CO_2 molecules have been investigated in temperature interval from 90 to 240 K. It is found that the intercalation results in high-frequency shift of exciton bands and their broadening. Considering the structure of ZnI_2 and K_2ZnI_4 crystal lattices, the most probable positions of CO_2 molecules in spacings between layers of compounds have been established. It is shown that, in K_2ZnI_4 compound, unlike ZnI_2 , there are two position types of intercalant molecules with molecular axes of different orientation relative to the compound crystallographic axes.

Исследованы спектры поглощения тонких пленок слоистых соединений ZnI_2 и K_2ZnI_4 , интеркалированных молекулами CO_2 , в температурном интервале от 90 до 240 К. Обнаружено, что интеркаляция приводит к высокочастотному смещению экситонных полос и их расширению. Путем рассмотрения структур кристаллических решеток ZnI_2 и K_2ZnI_4 определены наиболее вероятные положения молекул CO_2 в межслоевых промежутках соединений. Показано, что, в отличие от ZnI_2 , в K_2ZnI_4 существуют два типа положений интеркалированных молекул с различными ориентациями молекулярных осей относительно кристаллографических осей соединения.

According to [1], ZnI_2 is crystallized in two structural types. The first one is 2H structure of CdI_2 polytype (the space group D_{3d}^3) with $a = 0.425$ nm, $c = 0.654$ nm, and $z = 1$. The second type is that of CdCl_2 with $a = 0.425$ nm, $c = 2.15$ nm, and $z = 3$ (the space group D_{3d}^3) [1, 2]. At low temperatures, K_2ZnI_4 has a monoclinic lattice (Sr_2GeS_4 structure type, the space group $P 2_1/m$) with parameters $a = 0.7745$ nm, $b = 0.8121$ nm, $c = 0.9665$ nm, $\beta = 108.28^\circ$, $z = 2$ [3]. The structure elements of the K_2ZnI_4 crystal lattice are slightly distorted ZnI_4 tetrahedrons separated by K^+ ions [3, 4].

It is well known that layered compounds tend to be intercalated with various molecules. The intercalants penetrate between layers and form various chemical bonds between

those. The intercalants may substantially affect electron and optical properties of layered crystals [5, 6]. We have studied in experiment the temperature dependence of UV spectra for ZnI_2 [7] and K_2ZnI_4 [8] and have found that, when heating thin films of these compounds in a cryostat containing a coal absorbent, starting from 90 K, their absorption spectra change essentially at temperatures slightly exceeding 195 K. The temperature 195 K is just the sublimation temperature of CO_2 . This evidences the intercalation of the compounds with CO_2 molecules. The intercalant may be removed by heating films up to room temperature, but their spectrum is restored at subsequent cooling films down to liquid nitrogen temperature.

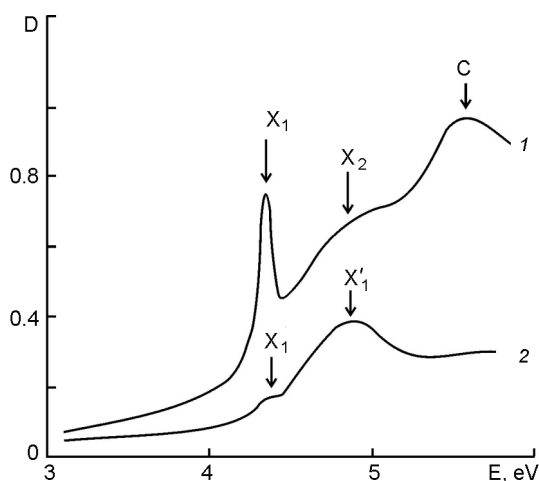


Fig. 1. Absorption spectrum of a thin ZnI_2 film at $T = 90$ K: prior to (1) and after (2) the intercalation with CO_2 molecules.

In this work, studied is the transformation of spectrum of the above-mentioned compounds as a result of intercalation with CO_2 molecules. The shift of absorption bands is interpreted. The implantation models of intercalant molecules into ZnI_2 and K_2ZnI_4 crystal lattices are proposed and discussed.

Thin ZnI_2 films were prepared by vacuum deposition of ZnI_2 powder on quartz substrates heated up to 80°C . To obtain thin K_2ZnI_4 films, we synthesized the compound by fusing chemically pure KI and ZnI_2 powders in vacuum at specified molar concentrations. The alloy was deposited on heated quartz substrates, and the film was annealed at 100°C for one hour.

Both the compounds are hygroscopic. Therefore, when being exposed to air at room temperature, they gain strong light scattering due to moisture absorption. In order to prevent such a scattering, the heated samples were transferred to a vacuum cryostat supplied with a coal adsorptive pump, and fastened on a copper holder preheated up to 70°C . The samples remained transparent after air evacuation from the cryostat and filling of liquid nitrogen. The transparent films can be stored in vacuum for a long time.

The phase composition of K_2ZnI_4 films was checked by absorption spectra [8]. Those were measured using an SF-46 spectrophotometer in the 2 to 6 eV range and at temperatures of 90 to 240 K. Use of adsorption pump allows to carry out measurements during one hour at 90 K without any additional pumping-out. Higher temperatures

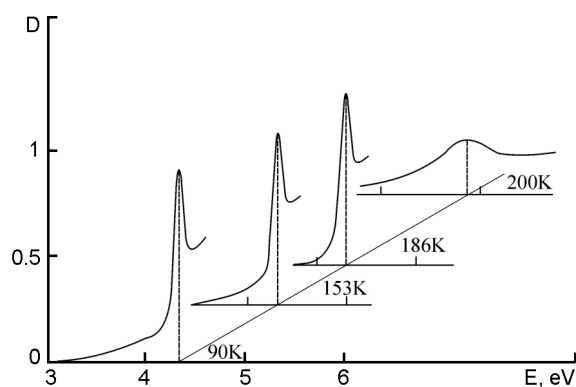


Fig. 2. Long-wave exciton absorption band in ZnI_2 at different temperatures within the 90–200 K interval. The spectra were obtained under heating of the sample. Film thickness 85 nm.

were kept stable (± 2 K) during 20 min. That is enough to measure the spectrum in the region of exciton bands. Temperature measurements were carried out under cooling samples starting from room temperature or 240 K and under heating starting from 90 K.

The long-wave X_1 (4.33 eV) and X_2 (4.87 eV) exciton bands are observed in absorption spectrum of thin ZnI_2 film (Fig. 1). These bands are associated with direct allowed transitions from the valence band formed by $5p$ states of I and $3d$ states of Zn to the conduction band. Spectral interval between X_1 and X_2 bands $E_{X_2} - E_{X_1} = 0.54$ eV is defined by spin-orbit splitting of upper valence band of ZnI_2 . The C band is of low sensitivity to thermal changes and corresponds to optical transitions between the valence band center and that of conduction band [7].

Result of ZnI_2 spectrum measurements is similar to data from [7]. However, it should be noted that the exciton band position at 90 K differs significantly (by 0.155 eV) from 4.48 eV stated in [7]. This distinction seems to be determined by tendency of ZnI_2 crystallization in two modifications mentioned above: CdI_2 type and CdCl_2 type [1, 2]. However, a special research of preparation conditions and X-ray structure analysis are required to determine what is the structure corresponding to the spectrum. It is important that both the structures belong to layered dielectrics.

Temperature increasing to $T \approx 195$ K, X_1 long-wave exciton band is shifted linearly to long-wave spectral region with $dE/dT = -7.4 \cdot 10^{-4}$ eV/K. At the same time, it is

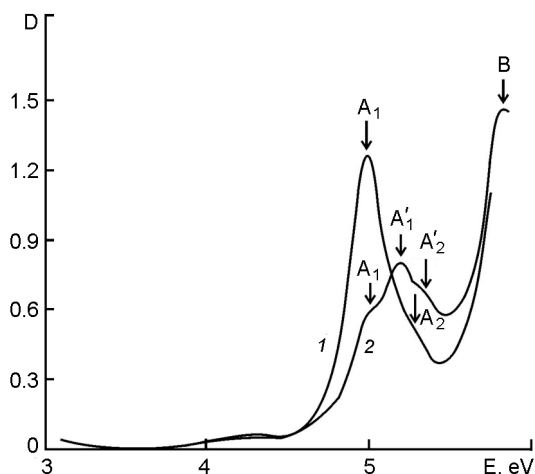


Fig. 3. Absorption spectrum of a K_2ZnI_4 thin film at $T = 90$ K, prior to (1) and after (2) the intercalation with CO_2 molecules.

weakened slightly due to exciton-phonon interaction (EPI), see Fig. 2. At temperatures close to 195 K and somewhat higher, a considerable short-wave shift and weakening of long-wave exciton band are observed. The subsequent cooling of the sample does not result in restoration of initial absorption spectrum (Fig. 1). The long-wave X_1' band gets narrowed and shifts to high-frequency spectral region due to EPI. At long-wave slope of X_1' band (4.86 eV), a weak X_1 band becomes apparent at 4.33 eV. Its position coincides with X_1 band position in the initial spectrum. No such spectrum changes take place at cooling from 290 K to 90 K. In the latter case, the long-wave exciton X_1 band shifts linearly to high-frequency spectral region with $dE/dT = -7.4 \cdot 10^{-4}$ eV/K in the whole temperature interval.

Since the spectrum changes occur at $T \sim 195$ K, we suppose that these changes are associated with intercalation of a layered dielectric with CO_2 molecules, as the CO_2 evaporation temperature is equal to 194.5 K. A rapid release of CO_2 occurs when the coal pump temperature reaches $T \sim 195$ K. Some of these CO_2 molecules were intercalated in ZnI_2 film resulting in the observed high-frequency shift of X_1 band by 0.54 eV. It is accompanied by the band widening. A similar high-frequency shift of exciton band was observed in layered dielectric PbI_2 intercalated with pyridine molecules [9]. The existence of weak X_1 band evidences an incomplete intercalation of ZnI_2 film.

Similar results are obtained for ferroelastic K_2ZnI_4 . According to [10, 11], phase

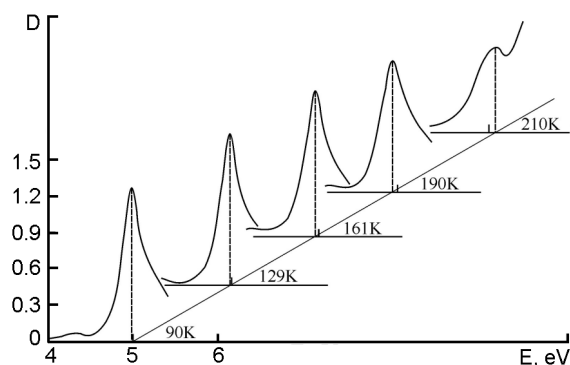


Fig. 4. Long-wave exciton absorption band in K_2ZnI_4 at different temperatures within the 90–210 K interval. The spectra were obtained under heating of the sample. Film thickness 210 nm.

change to ferroelastic phase occurs at 270 K and 190 K. However, when cooling samples, we had not observed any special features at temperatures near 195 K. At 90 K, the absorption spectrum of K_2ZnI_4 films contains a rather narrow exciton band A_1 with maximum at 4.97 eV and half-width of about 0.25 eV, a weak A_2 band (2s exciton) at 5.25 eV and B band at 5.7 eV (Fig. 3). It has been established [8] that exciton excitations in K_2ZnI_4 are localized in ZnI_4^{2-} structural elements of the compound lattice. At such localization, the upper part of valence band in K_2ZnI_4 (just as in ZnI_2) is formed by $5p$ states of I and $3d$ states of Zn while the conduction band is formed by $4s$ states of Zn. The spectral interval between A and B bands is defined by spin-orbit splitting of upper valence band in K_2ZnI_4 .

The sample heating at a temperature close to 195 K results in an abrupt weakening of A_1 band as well as for ZnI_2 (Fig. 4). The subsequent cooling down to 90 K results in a spectrum where initial A_1 band is attenuated essentially, but there are new absorption bands peaked at 5.195 eV (A_1' band) and 5.45 eV (A_2' band). All these facts evidence the K_2ZnI_4 intercalation with CO_2 molecules instead of the phase transfer mentioned in [10, 11].

The intercalation with CO_2 molecules results in a shift of A_1 band to higher frequencies, as well as in ZnI_2 : $E_{A_1'} - E_{A_1} = 0.23$ eV and $E_{A_2'} - E_{A_1} = 0.48$ eV. The band shift must be caused by distortion of ZnI_4^{2-} tetrahedrons due to insertion of CO_2 molecules into interlaminar spacings. Appearance of two bands with different shifts re-

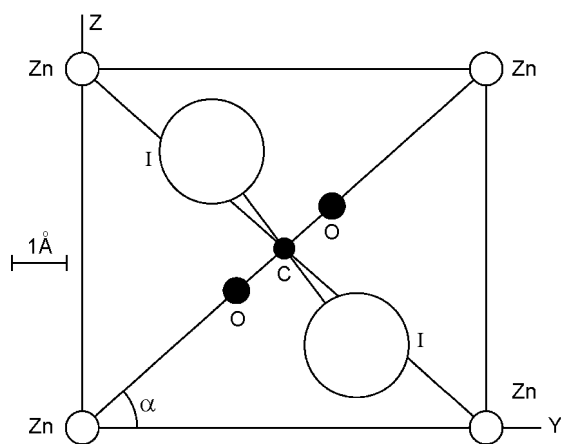


Fig. 5. Projections of ZnI_2 unit cell onto ZY plane where $Z \parallel C$ and axis Y is parallel to the rhombus long axis with $d_{(\text{Zn-Zn})} = \sqrt{3}a$.

veals the existence of two intercalation types in this compound.

The arrangement of CO_2 molecules in crystal lattices of two compounds is of interest. Linear heteropolar CO_2 molecule has a certain part of ionicity in the overall ion-covalent bond. According to Pauling [12], the share of ionicity f is defined by electronegativity difference between oxygen ($x_{\text{O}} = 3.5$) and carbon ($x_{\text{C}} = 2.5$) and equals (in %):

$$f = 100 \{1 - \exp[-0.5(x_{\text{O}} - x_{\text{C}})^2]\}.$$

Thus, $f \approx 40\%$. This specifies an effective negative charge on oxygen atom and a positive one on carbon atom. The intense absorption band of CO_2 gas in infrared region also evidences the considerable ionicity of CO_2 . This band is associated with asymmetrical valence vibrations of the molecule. It is natural to assume that at insertion of that molecule into interlaminal spacings of the ionic crystal, the axis of linear molecule is oriented along the line passing through centers of positively charged ions, and carbon ion is situated on the line connecting negatively charged ions of the crystal.

As ZnI_2 has a CdI_2 type crystal lattice with hexagonal unit cell, each Zn^{2+} ion is surrounded by six I^- ions. Using parameters $a = 0.425$ nm, $c = 0.654$ nm and $d_{\text{Zn-I}} = 0.290$ nm and for the cell, we have calculated coordinates of nonequivalent atoms I in the cell, and have determined that I atoms are situated in ZY plane where $Z \parallel C$ and axis Y is parallel to the long axis of a rhombus with $d_{\text{Zn-Zn}} = \sqrt{3}a$ (Fig. 5). It follows from the Figure that the minimum potential energy of Coulomb bond between

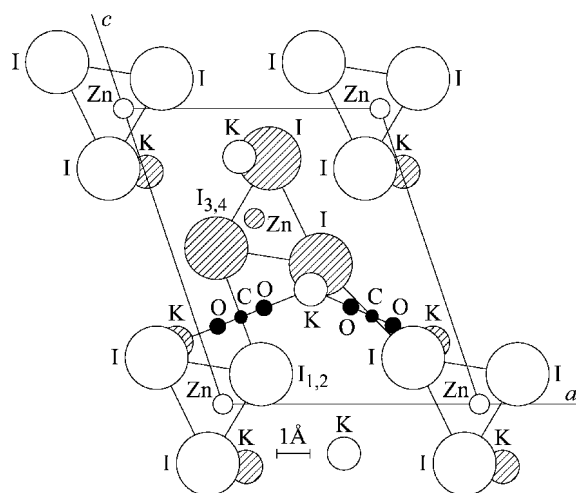


Fig. 6. A projection of K_2ZnI_4 unit cell onto the ac plane. The figure scale is indicated to find the atomic coordinates in the a,c plane.

CO_2 molecule with $d = 0.233$ nm and surrounding Zn^{2+} and I^- ions is attained at C atom coordinates of $(\sqrt{3}/2)a$ and $c/2$, the molecule axis being situated in the ZY plane at angle α to axis Y , $\alpha = \arctg(c/\sqrt{3}a)$.

There are three such planes at hexagonal symmetry of ZnI_2 . The planes are oriented at angle $\pi/3$ to each other. In a perfect crystal, CO_2 molecules may penetrate along three directions at equal probabilities. But in real crystal and in thin films, a competition between directions of molecule penetration appears due to defects. This results in disordering of crystals and broadening of shifted X_1' bands in ZnI_2 .

The consideration of CO_2 molecules insertion into K_2ZnI_4 lattice is more difficult because of presence of two K_2ZnI_4 molecules in a unit cell and existence of K^+ ions between the layers formed by ZnI_4^{2-} tetrahedrons. To find coordinates of I and K ions, we have used parameters of the monoclinic lattice cell $a = 0.7745$ nm, $b = 0.8121$ nm, $c = 0.9665$ nm, $\beta = 108.28^\circ$. The arrangement of I and K atoms is unknown, but to determine their coordinates, it is possible to use relative coordinates of Rb and I in a Rb_2CoI_4 crystal with crystalline structure similar to that of K_2ZnI_4 and similar unit cell parameters [13]. When calculating the coordinates, coincidence of relative coordinates in Rb_2CoI_4 and K_2ZnI_4 was supposed, taking into account difference of parameters of their cells. In Fig. 6, the projections of atoms in K_2ZnI_4 cell on the (010) plane of the lattice are shown with the atomic coordinates calculated by the mentioned proce-

ture. Zn atoms are placed in apexes of the unit cell. The second atom Zn is located under the plane (a,c) at coordinates 0.282, 0.406 and 0.59 nm. The shaded I atoms are also under the plane (a,c) spaced by $b/2 = 0.406$ nm. But pairs of atoms $l_{1,2}$ and $l_{3,4}$ (in the projection, they are imposed) have the following coordinates on **b** axis: -0.203, 0.203 and 0.203, 0.609 nm accordingly. The shaded K atoms have the coordinates along **b** axis equal to $b/2$. Coordinates of all the atoms in the plane (a,c) see in Fig. 6.

The plane (a,b)' separating the upper and lower layers in K_2ZnI_4 is located along a normal to the plane (a,b) at a distance of $D = 0.275$ nm. It is natural to assume that intercalated CO_2 molecules are built into interlaminar spacings of K_2ZnI_4 in such a way that C atoms are in the plane (a,b)' opposite to I^- ions, and CO_2 molecule axes are oriented along the lines connecting the proximate positively charged K^+ ions. In Fig. 6, projections of atomic coordinates in CO_2 molecules on the plane (a,c) are shown. It is seen from the Figure that two types of intercalation are possible. In the left part of Fig. 6, it is seen that the ion C^+ is attracted by 4 ions I^- : l_1, l_3 and l_2, l_4 due to Coulomb forces, but the right ion C^+ is attracted by two ions I^- . Distinction in lengths of projections on the (a,c) plane of right-hand and left-hand molecules is defined by distinction in d_{K-K} for the right and left K^+ ion pairs.

In the spectrum of intercalated K_2ZnI_4 , existence of two absorption bands shifted as compared to A_1 band is associated with two described types of CO_2 insertion into interlaminar spacing. Presumably, the more intense A_1' band at 5.2 eV is caused by the molecules interacting with 4 I^- ions while the less intense A_2' one at 5.45 eV is defined by molecules CO_2 interacting with two I^- ions.

The smaller frequency shift of A_1' band seems to be caused by larger interval d_{K-K} between K^+ ions in the left pair in comparison with that in the right pair, that is seen directly from Fig. 6. The diminution of d_{K-K} in the right pair promotes a greater deformation of the lattice in K_2ZnI_4 at CO_2 mole-

cule implantation and a greater frequency shift of A_2' band.

Thus, consideration of absorption spectra for thin ZnI_2 and K_2ZnI_4 films in temperature interval $90 K \leq T \leq 240 K$ reveals that spectral changes at $T \geq 195 K$ are caused by intercalation of CO_2 molecules into the films. The intercalation is promoted by layered structure of the compounds and weak Van der Waals bonds between layers. We have calculated coordinates of CO_2 molecule built in lattices of ZnI_2 and K_2ZnI_4 . In ZnI_2 unit cell, a CO_2 molecule may occupy three equivalent positions. The intercalation results in a strong attenuation of basic X_1 exciton band in ZnI_2 and appearance of an intense high-frequency X_1' band. In the more complex K_2ZnI_4 unit cell, CO_2 molecule can occupy two nonequivalent positions that is evidenced in absorption spectrum by appearance of high-frequency A_1' and A_2' bands. Thus, intercalation in both compounds results in high-frequency shift of exciton bands.

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Спектри поглинання шаруватих сполук ZnI_2 та K_2ZnI_4 , інтеркальованих CO_2

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Досліджено спектри поглинання тонких плівок шаруватих сполук ZnI_2 та K_2ZnI_4 , інтеркальованих молекулами CO_2 , у температурному інтервалі від 90 до 240 К. Виявлено, що інтеркаляція спричиняє високочастотний зсув екситонних смуг та їх розширення. Шляхом розгляду структур кристалічних ґраток ZnI_2 та K_2ZnI_4 визначено найімовірніші положення молекул CO_2 у міжшарових проміжках сполук. Показано, що, на відміну від ZnI_2 , в K_2ZnI_4 існують два типи положень інтеркальованих молекул з різними орієнтаціями молекулярних осей відносно кристалографічних осей сполуки.