CONDENSED-MATTER
SPECTROSCOPY

Electronic Absorption Spectrum of Thin K_2ZnI_4 Films

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Abstract—The absorption spectrum of thin K_2ZnI_4 films has been investigated in the range of 3–6 eV at temperatures from 90 to 340 K. It is established that this compound belongs to direct-gap insulators; low-frequency exciton excitations are localized in the ZnI_4 lattice layers and have a quasi-two-dimensional character. The spectral analysis revealed the existence of two K_2ZnI_4 modifications, which presumably belong to the monoclinic (I) and orthorhombic (II) phases. The temperature dependences of the spectral position and halfwidth of the low-frequency exciton band in K_2ZnI_4 revealed the existence of first-order phase transitions at 215 and 225 K in the monoclinic and orthorhombic phases, respectively.

The K_2ZnI_4 compound belongs to ferroelectrics [1, 2] with a structure of the Sr_2GeS_4 type [3]. At room temperature, K_2ZnI_4 has a monoclinic lattice with two molecules per unit cell and the unit-cell parameters $a = 0.7745$ nm, $b = 0.8121$ nm, $c = 0.9665$ nm, and $\beta = 108.28°$ (space group $P\,2_1/m$) [3]. Structural elements of the lattice are slightly distorted ZnI_4 tetrahedra, separated by K^+ ions [3, 4].

With a decrease in temperature, K_2ZnI_4 undergoes phase transitions at $T_{c1} = 270$ K (from an ordered phase to a polar phase) and at $T_{c2} = 190$ K (between two polar phases). The phase transitions were revealed from the temperature dependences of the permittivity and spontaneous polarization [1, 2]. The high-temperature transition to the more ordered orthorhombic structure of the β-K_2SO_4 type, which is characteristic of many ferroelectrics of the A_2BX_4 type (A = K, Rb, Cs; B = Cd, Zn; X = Cl, Br, I), has not been found in K_2ZnI_4 [2].

Although the crystal structure and ferroelectric properties of this compound are known fairly well, the absorption spectrum and exciton states in K_2ZnI_4 have not been investigated. At the same time, phase transitions significantly affect the exciton-band parameters [5, 6]. In this paper, we report the results of studying the absorption spectrum of thin K_2ZnI_4 films in the range of 3–6 eV at temperatures of 90–390 K, including the phase-transition temperature.

EXPERIMENTAL

The K_2ZnI_4 compound was synthesized by alloying a mixture of chemically stoichiometric pure KI and ZnI_2 powders in vacuum. Thin films were prepared by thermal vacuum deposition of the alloy on a quartz substrate heated to 100°C; then, the films were annealed at the same temperature for 1 h.

K_2ZnI_4 films are hygroscopic. After exposure to air and cooling to room temperature, they exhibit strong light scattering. To avoid this, heated samples were placed in a vacuum cryostat in which copper finger was heated to 70°C. After pumping the cryostat and filling it with liquid nitrogen, the samples remain transparent. In a vacuum, films remain transparent for a long time. However, five days after, their absorption spectrum slightly changes. We will consider this phenomenon in greater detail below.

The quality and phase composition of the films were controlled from the absorption spectrum measured at $T = 90$ K. The long-wavelength exciton bands in the spectra of K_2ZnI_4 (4.95 eV), ZnI_2 (4.48 eV [5]), and KI (5.84 eV) have significantly different positions; hence, one can monitor the phase composition of the films by observing their absorption spectra. When the composition of the evaporated mixture $(KI)_{1-x}(ZnI_2)_x$ deviates from stoichiometric ($x > x^* = 0.33$), the exciton band of ZnI_2 (4.48 eV) arises in the absorption spectrum of K_2ZnI_4 in the transparency region.

The absorption spectra were measured on an SF-46 spectrophotometer in the spectral range of 2–6 eV at temperatures of 90–340 K. The temperature measurements metal the following difficulty. When a sample cooled to 90 K was heated in the cryostat to $T \geq 195$ K, the long-wavelength exciton band in K_2ZnI_4 undergoes a significant (more than 0.12 eV) blue shift and weakens. Upon subsequent sample cooling to $T = 90$ K, the blue shift of the exciton band is retained, i.e., the shift of the spectral position of exciton band at $T \geq 195$ K is
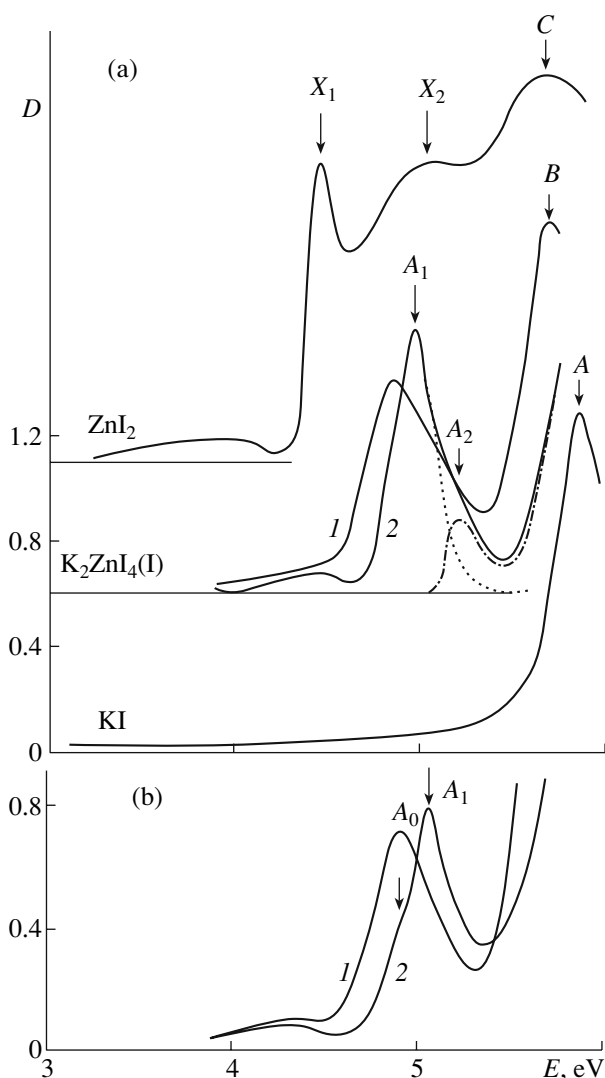
Fig. 1. Absorption spectra of (a) ZnI$_2$ at $T = 90$ K, K$_2$ZnI$_4$ (I) at $T = $ (1) 290 and (2) 90 K, and KI ($T = 90$ K) and (b) K$_2$ZnI$_4$ (II) at $T = $ (1) 290 and (2) 90 K.

not related to the phase transition. This observation is confirmed by the temperature spectral measurements upon sample cooling: there are no specific features in the temperature behavior of the spectral position of the long-wavelength exciton band near $T \approx 195$ K, which occur at phase transitions. The similar blue shift of the exciton band was observed by us previously for thin ZnI$_2$ films at the same temperature $T \geq 195$ K and only upon sample heating in a cryostat [5]. A hypothetical reason for the blue shift of the absorption edge in K$_2$ZnI$_4$ and ZnI$_2$ is the release of CO$_2$ from the carbon adsorption pump of the cryostat (the CO$_2$ sublimation temperature is 194.5 K), and the shift itself is related to the intercalation of the layered K$_2$ZnI$_4$ and ZnI$_2$ compounds by carbon dioxide molecules. To implement intercalation in layered compounds, the intercalant concentration around the sample should be fairly high.

When the cryostat is heated at $T \geq 195$ K, CO$_2$ starts to be intensively released from the carbon adsorption pump; upon cooling, vice versa, CO$_2$ is frozen out. Therefore, intercalation occurs only upon sample heating in the cryostat. After heating the intercalated films ($T \approx 340$ K) and evacuating the cryostat, the absorption spectrum of thin K$_2$ZnI$_4$ films (at $T = 90$ K) is recovered, which indicates release of CO$_2$ from the film. To avoid the influence of intercalation on the absorption spectrum of thin K$_2$ZnI$_4$ films, the temperature measurements of the sample spectra were performed upon cooling.

The parameters of long-wavelength exciton bands (position E_m; halfwidth Γ; and the imaginary part of the permittivity in the band maximum, ε_{2m}) were determined using the technique described in [6], by approximating the experimental dependence of the optical density by a mixed symmetric contour (a linear combination of Lorentzian and Gaussian profiles).

ABSORPTION SPECTRUM OF A THIN K$_2$ZnI$_4$ FILM

The structure and position of the main absorption bands in the K$_2$ZnI$_4$ spectrum are similar to those for the spectra of Rb$_2$ZnI$_4$ [7] and Cs$_2$ZnI$_4$ [6]. The absorption spectrum of a thin K$_2$ZnI$_4$ film (Fig. 1) contains a strong long-wavelength band A_1 at 4.97 eV ($T = 90$ K); the short-wavelength band B in the measured spectral region is observed only at high temperatures (5.69 eV at $T = 290$ K). After splitting off the A_1 band by a symmetric mixed contour, a weak A_2 band at 5.25 eV can be seen on the long-wavelength slope of the B band.

With an increase in temperature, the A_1 band shifts to longer wavelengths, broadens, and weakens due to the exciton–phonon interactio, which indicates the exciton origin of the A_1 band. The spectral positions and the oscillator strength ratios for the A_1 and A_2 bands indicate that these bands apparently belong to the same exciton series with the leading band A_1 (1s exciton, $n = 1$). Using the spectral positions of the A_1 and A_2 bands, we determined (within the Wannier–Mott approximation) the exciton binding energy $R_{\text{ex}} = (4/3)(E_{A2} - E_{A1}) = 0.37$ eV and the band gap $E_g = E_{A1} + R_{\text{ex}} = 5.34$ eV.

To interpret the absorption spectrum of K$_2$ZnI$_4$, it is expedient to compare it with the spectra of the initial components, i.e., ZnI$_2$ and KI. The absorption spectrum of ZnI$_2$ (Fig. 1) contains long-wavelength exciton bands X_1 (4.48 eV) and X_2 (5.02 eV), which are due to direct allowed transitions from the valence band, formed by the I 5p states and Zn 3d states, to the Zn 4s conduction band [5, 6]. The spectral range between the X_1 and X_2 bands, $\Delta E = E_{X1} - E_{X2} = 0.54$ eV, is determined by the spin–orbit (SO) splitting of the upper valence band of ZnI$_2$ [5]. In the wavelength range under

study, only the long-wavelength band A at 5.84 eV is observed in the absorption spectrum of KI.

The A_1 band in the K_2ZnI_4 spectrum occupies an intermediate position between the X_1 band of ZnI_2 and the A band of KI; however, its spectral position it closer to the X_1 band of ZnI_2 ($\Delta E = E_{A1} - E_{X1} = 0.49$ eV) than to the A band of KI ($\Delta E = E_{KI} - E_{A1} = 0.87$ eV), which suggests the localization of exciton excitations in ZnI_4^{2-} (lattice structural elements). The similar position of the long-wavelength exciton band of the Rb_2ZnI_4 (4.95 eV [7]) and Cs_2ZnI_4 (5.05 eV [6]) compounds with similar structure is in favor of such localization. When exciton excitations are localized in ZnI_4^{2-} tetrahedra, the top of the valence band in K_2ZnI_4 and ZnI_2 is apparently formed by I $5p$ and Zn $3d$ states, while the conduction band is formed by the Zn $4s$ states.

The spacing between the A_1 and B bands ($\Delta E = 0.845$ eV at $T = 290$ K) is apparently determined, as in Cs_2ZnI_4 [6] and Rb_2ZnI_4 [7], by the SO splitting of the upper valence band in K_2ZnI_4. It is known that the SO splitting for binary compounds is determined by the relation

$$\Delta_{CO} = C(\xi^{(1)}\Delta_{CO}^{(1)} + \xi^{(2)}\Delta_{CO}^{(2)}),$$

where $\Delta_{CO}^{(1, 2)}$ is the SO splitting of atoms and $\xi^{(1, 2)}$ characterizes the fraction of each atom in the SO splitting of a compound ($\xi^{(1)} + \xi^{(2)} = 1$) [8]. Generalizing the above formula to a ternary compound; assuming that $C = 1$, $\Delta_{CO}^{(1)} = \Delta_{CO}(ZnI_2) = 0.54$ eV [5], and $\Delta_{CO}^{(2)} = \Delta_{CO}(KI) = 1.38$ eV [8]; and taking Δ_{CO} to be 0.845 eV for K_2ZnI_4, we calculated $\xi^{(1)} = 0.63$ and $\xi^{(2)} = 0.37$ from the above relation. Hence, the ZnI_2 sublattice makes the main contribution to the SO splitting in K_2ZnI_4, which additionally proves the localization of exciton excitations in ZnI_4^{2-} tetrahedra.

As was mentioned above, after the long-term (more than 5 days) storage of thin K_2ZnI_4 films, their absorption spectrum slightly changes: the A_1 band shifts to shorter wavelengths and is split into weak (A_0, 4.92 eV) and strong (A_1, 5.06 eV) bands (Fig. 1b). The splitting of the A_1 band manifests itself in the absorption spectrum as an asymmetry of the long-wavelength band edge.

To interpret the absorption spectra of the as-prepared K_2ZnI_4 sample (I, Fig. 1a) and that exposed for 5 days (II, Fig. 1b), we will compare them with the spectra of related compounds: Rb_2ZnI_4 [7] and Cs_2ZnI_4 [6]. It is known that Rb_2ZnI_4, as well as K_2ZnI_4, is crystallized into a monoclinic lattice of the $SrGe_2S_4$ type at room temperature [7], while Cs_2ZnI_4, independent of the preparation method, has an orthorhombic lattice of the β-K_2SO_4 type at $T = 290$ K. Some crystals of the

same structure type A_2BX_4, depending on the growth conditions, may exist in both modifications (for example, Cs_2CdI_4 [4, 9]). However, upon heating, the Cs_2CdI_4 modification of the $SrGe_2S_4$ type undergoes a transition to β-K_2SO_4; a reverse transition occurs when Cs_2CdI_4 crystals with a structure of the β-K_2SO_4 type are exposed in a wet atmosphere [4, 9]. Note that the absorption edge of the monoclinic modification of Cs_2CdI_4 is shifted to longer wavelengths in comparison with that of the orthorhombic modification [10]. With respect to the spectral position, the A_1 band of K_2ZnI_4 (I, 4.97 eV) is closer to the A_1 band in Rb_2ZnI_4 (4.95 eV [7]), while the same band of K_2ZnI_4 (II, 5.06 eV) is closer to the A_1 band in Cs_2ZnI_4 (5.05 eV [6]). Therefore, we can suggest that the absorption spectrum of thin K_2ZnI_4 (I) films reflects the crystal structure of the $SrGe_2S_4$ type, while the K_2ZnI_4 (II) structure is of the β-K_2SO_4 type. This assumption needs structural investigation; however, such an investigation is hindered due to the high hygroscopicity of the compound studied.

TEMPERATURE DEPENDENCE OF THE PARAMETERS OF THE LONG-WAVELENGTH EXCITON BAND A_1

Within the long-wavelength exciton band (4.1–5.4 eV), the absorption spectrum of the samples was measured in the temperature range 90–340 K upon cooling. The measurements were performed on samples of both modifications: I and II. The temperature dependences of the spectral position $E_m(T)$ and halfwidth $\Gamma(T)$ of the A_1 band in both modifications are shown in Fig. 2.

It can be seen that both modifications exhibit a general tendency: with an increase in T, the A_1 band shifts to low frequencies and its halfwidth increases. The red shift of the A_1 band and the increase in $\Gamma(T)$ with an increase in T are caused by the exciton–phonon interaction.

Near the temperatures $T_{c1} \approx 215$ K for K_2ZnI_4 (I) and $T_{c1} \approx 225$ K for K_2ZnI_4 (II), there are specific features in the temperature dependences $E_m(T)$ and $\Gamma(T)$, i.e., a step high-frequency shift of $E_m(T)$ with a decrease in T, which is accompanied by an increase in the halfwidth $\Gamma(T)$. Apparently, a phase transition occurs near T_{c1}. The jumps in the dependences $E_m(T)$ and $\Gamma(T)$ near T_{c1} indicate a first-order phase transition.

Far from the phase-transition temperature T_{c1}, the dependence $E_m(T)$ is linear, the temperature-shift coefficient dE_m/dT of the A_1 band for modification I is -7.5×10^{-4} eV/K in the range $220 < T \leq 340$ K and -4.4×10^{-4} eV/K in the range $90 \leq T \leq 210$ K; for modification II, this parameter is 4.3×10^{-4} eV/K ($235 < T \leq 330$ K) and 4.6×10^{-4} eV/K ($90 \leq T \leq 218$ K). The order of magnitude of dE_m/dT is typical of ionic crystals, i.e.,
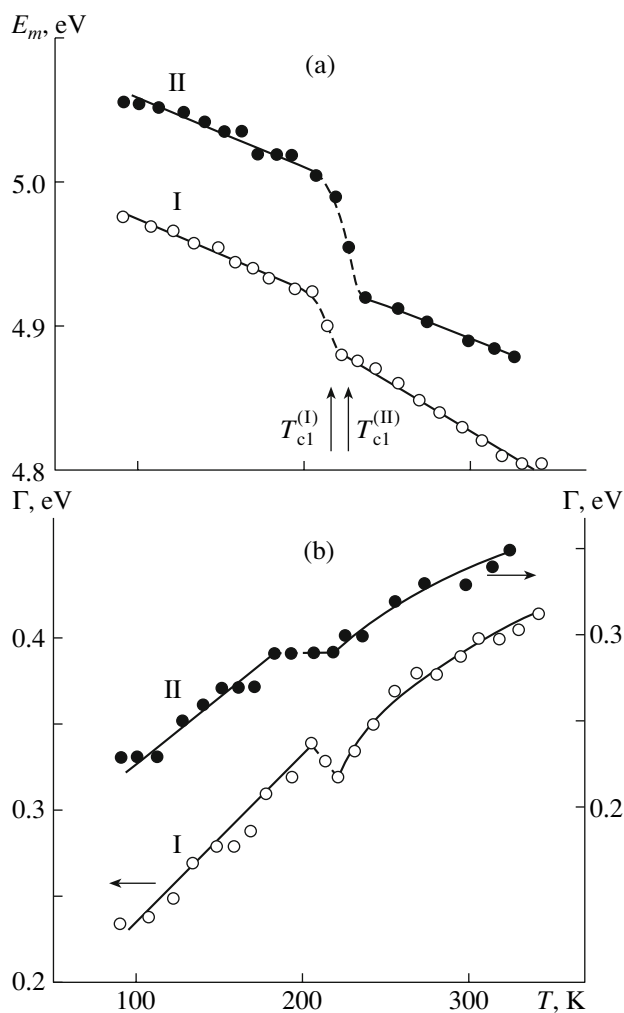
Fig. 2. Temperature dependences of the (a) spectral position $E_m(T)$ and (b) halfwidth $\Gamma(T)$ of the A_1 band in K_2ZnI_4 of modifications I and II (the dependences $\Gamma(T)$ (I) and (II) are shifted along the Γ axis).

the temperature shift of the A_1 exciton band is due to the exciton–phonon interaction.

The temperature dependence of the A_1-band halfwidth is unusual (Fig. 2b). Far from the phase-transition temperature, in the range $90 \leq T < T_{c1}$, the dependence $\Gamma(T)$ is linear and obeys the law

$$\Gamma(T) = \Gamma(0) + aT,$$

where $a = d\Gamma/dT = 9.6 \times 10^{-4}$ and 7.8×10^{-4} eV/K for I and II, respectively, and $\Gamma(0) = 0.14$ eV for I and 0.15 eV for II is the residual broadening, determined by the lattice defects.

The linear dependence $\Gamma(T)$ is indicative of a low dimension of excitons in the low-temperature K_2ZnI_4 phase. According to [11], a linear dependence $\Gamma(T)$ is characteristic of two-dimensional excitons. The conclusion about the two-dimensionality of excitons is in agreement with the structure of the K_2ZnI_4 lattice and

localization of exciton excitations in ZnI_4^{2-} tetrahedra; the latter form layers in the *ab* plane of the crystal, separated by a wide gap with $c\sin\beta = 0.918$ nm, filled with K^+ ions [3, 4]. The distance $d_{Zn–Zn} \approx 0.56$ nm between tetrahedra in a layer is much smaller than the spacing between the layers, and exciton translation over the ZnI_4^{2-} sublattice occurs within a layer; i.e., the probability of exciton jumps between layers is low.

An anomalous increase in $\Gamma(T)$ with a decrease in T is observed near the phase-transition temperature T_{c1}, which indicates additional broadening of the exciton band in the low-temperature phase. Such an anomalous increase in the exciton band halfwidth was observed in the ferroelastics M_2CdI_4 (M = K, Rb, Cs) [10, 12, 13] and Cs_2ZnI_4 [6] at phase transitions to the ferroelastic phase. Therefore, we suggest that a phase transition to the polar phase occurs in K_2ZnI_4 at T_{c1}. The increase in Γ near T_{c1} is likely due to the formation of a domain structure and twinning in the polar phase [14]. Scattering of excitons from domain walls leads to an additional exciton-band broadening in the polar phase.

Thus, we have revealed first-order phase transitions at $T_{c1} \approx 215$ K in the monoclinic modification I and $T_{c1} \approx 225$ K in the orthorhombic modification II from the temperature dependences $E_m(T)$ and $\Gamma(T)$ for the long-wavelength exciton band in a thin K_2ZnI_4 film. The value $T_{c1} \approx 215$ K for thin K_2ZnI_4 (I) films is much below than that obtained in [1, 2] for single crystals: $T_{c1} = 270$ K. Possible reasons for such a discrepancy between the values of T_{c1} for thin films and single crystals are as follows. The first reason is the high thermal inertia of thin films. Upon film cooling, the phase transition occurs at a lower temperature due to the thermal inertia. The second possible reason is the higher concentration of defects in the films in comparison with single crystals. In this case, the theory [15] predicts a decrease in the phase-transition temperature, which is confirmed experimentally [16].

In the temperature range under study, we revealed only one phase transition: the first-order transition to a polar phase at T_{c1}. The phase transition between polar phases, which was mentioned in [1, 2], was not found. It is possible that it occurs at lower temperatures ($T_{c2} < 90$ K) in thin films.

CONCLUSIONS

The electronic absorption spectrum of thin K_2ZnI_4 films has been investigated for the first time. A comparison of this spectrum with the spectra of ZnI_2, Rb_2ZnI_4, and Cs_2ZnI_4 revealed localization of low-frequency exciton excitations in ZnI_4^{2-} tetrahedra (structural elements of the K_2ZnI_4 lattice). At this localization, the interband absorption edge in K_2ZnI_4 is formed by direct allowed transitions with $E_g = 5.37$ eV. The A_1 and B

exciton bands are related to the transitions from the upper valence band, formed by I $5p$ and Zn $3d$ states to the Zn $4s$ conduction band. The spectral gap between the A_1 and B bands is determined by the SO splitting of the upper valence band $\Delta_{CO} = 0.845$ eV.

Apparently, the K_2ZnI_4 compound exists in two modifications: monoclinic (I, structure of the Sr_2GeS_4 type) and orthorhombic (II, structure of the β-K_2SO_4 type). Analysis of the temperature dependences of the spectral position and halfwidth of the A_1 band in the temperature range under study ($90 < T \le 340$ K) revealed first-order phase transitions at $T_{c1} \approx 215$ K and 225 K in the monoclinic and orthorhombic modifications of K_2ZnI_4, respectively.

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