STRUCTURAL PECULIARITIES OF CADMIUM HALIDES AND THEIR MANIFESTATION IN ELECTRONIC SPECTRUM AND OPTO-LUMINESCENT STUDIES: EXPERIMENT AND THEORETICAL JUSTIFICATION

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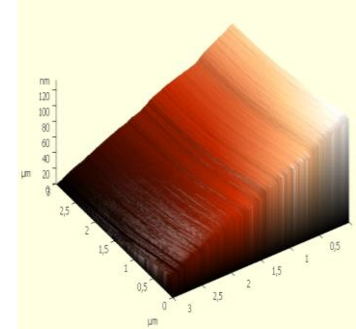
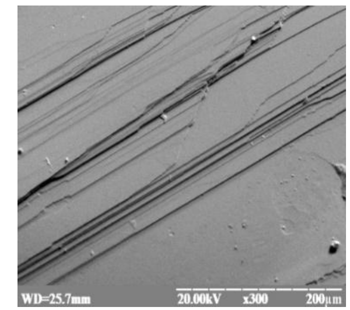
SCOPE

- **INTRODUCTION**
- **STRUCTURE OF** CdX_2
- **LUMINESCENCE PROPERTIES**
- **MODEL AND CALCULATIONS**
- **CONCLUSIONS**

Introduction

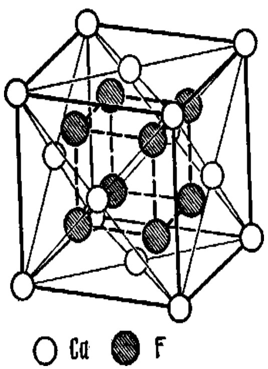
Crystals $\mathbf{CdX_2}$ (*X = F, Cl, Br, J*) are layered crystals with sandwiches of *X-Cd-X* where cation (*Cd*) occupies only half of hollows between anion layers (*X*)





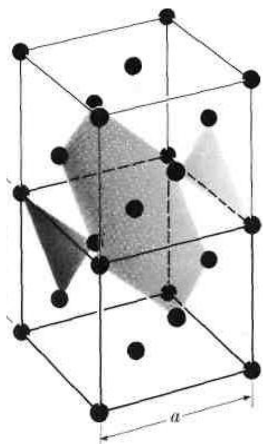
Some peculiarities:

- depending on the size of the halogen, the physical properties vary from isotropic (CdF_2) to highly anisotropic (CdI_2)
- within the structural layer, covalent bonding dominates over ionic bonding; between layers, van der Waals interactions are weak
- the band gap at room temperatures increases with decreasing halogen size from 3 eV to 6 eV
- have luminescent properties (both photoluminescence (PL) and X-ray luminescence (XRL)), especially at low temperatures (50…180 K)
- The materials are wide-band and their fundamental absorption edge shifts with decreasing temperature to the short-wavelength region, "exposing" selective absorption bands and luminescence excitation bands at T< 200 K.
- the spectral composition of the luminescent glow of all is approximately the same
- impurities can significantly increase the luminescence intensity of cadmium halides



CdF_2

$r_c/r_a \approx 0{,}74$

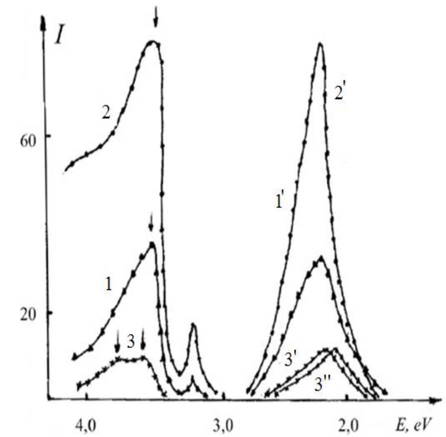


$CdBr_2$ $CdCl_2$

$r_c/r_a \approx 0{,}55$ $r_c/r_a \approx 0{,}51$

CdJ_2

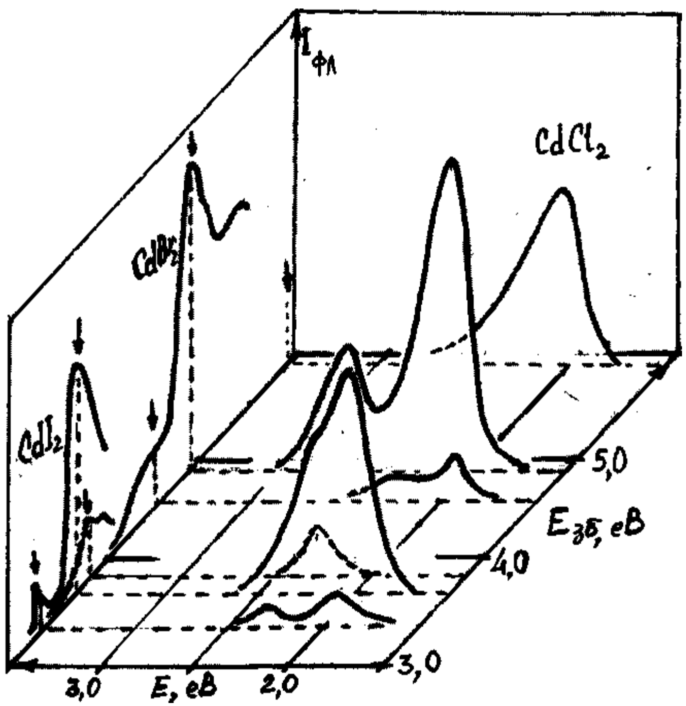
$r_c/r_a \approx 0{,}45$

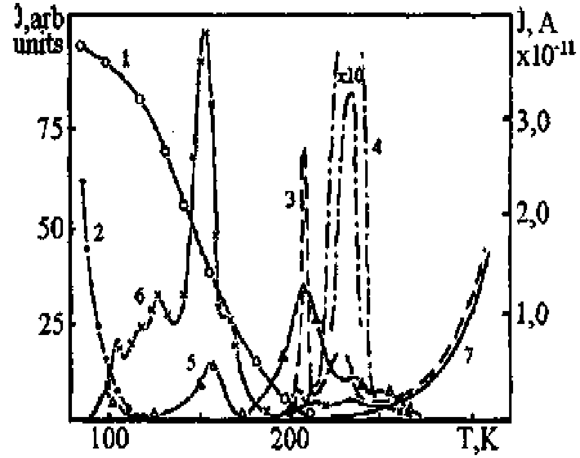


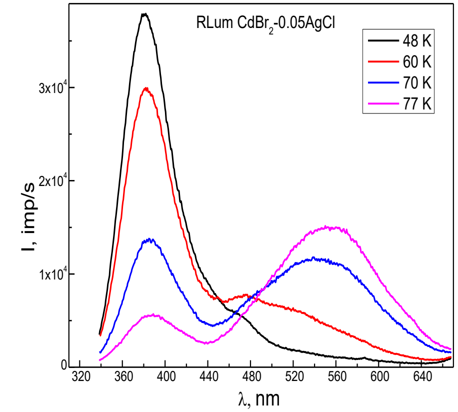
$$\left(D_s^0 - A_{Cd}^- - D_i^+\right)$$

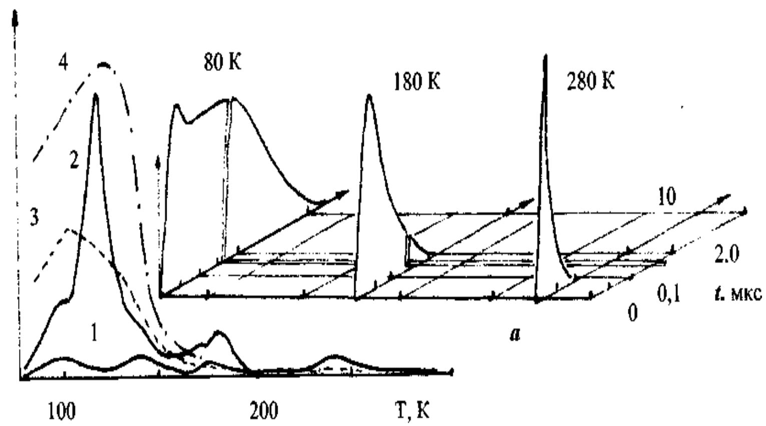
Luminescence properties

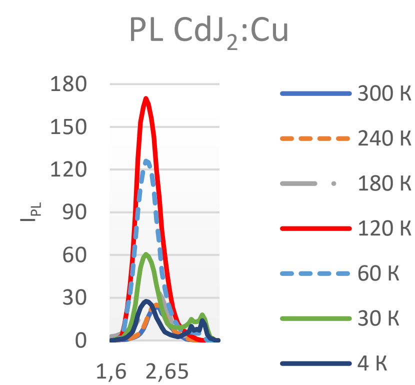
RESULTS











Taking into account the force constants of the coupling [1]

	ionic bond $(Cd-X)$	***covalent bond*** $(Cd-Cd)$, $(X-X)$	molecular bond (*interlayer*)
for $CdBr_2$ -	0,472 *mdyn/A*^{0}	~ 1,2 *mdyn /A*^{0}	0,073 *mdyn /A*^{0}
for CdJ_2 -	0,277 *mdyn /A*^{0}	~ 1,2 *mdyn /A*^{0}	0,081 *mdyn /A*^{0}

The values of cationic and anionic effective charges were estimated:

for $CdBr_2$ - $Cd^{+1,38}$, $Br^{-0,69}$; for CdJ_2 - $Cd^{+1,30}$, $J^{-0,65}$.

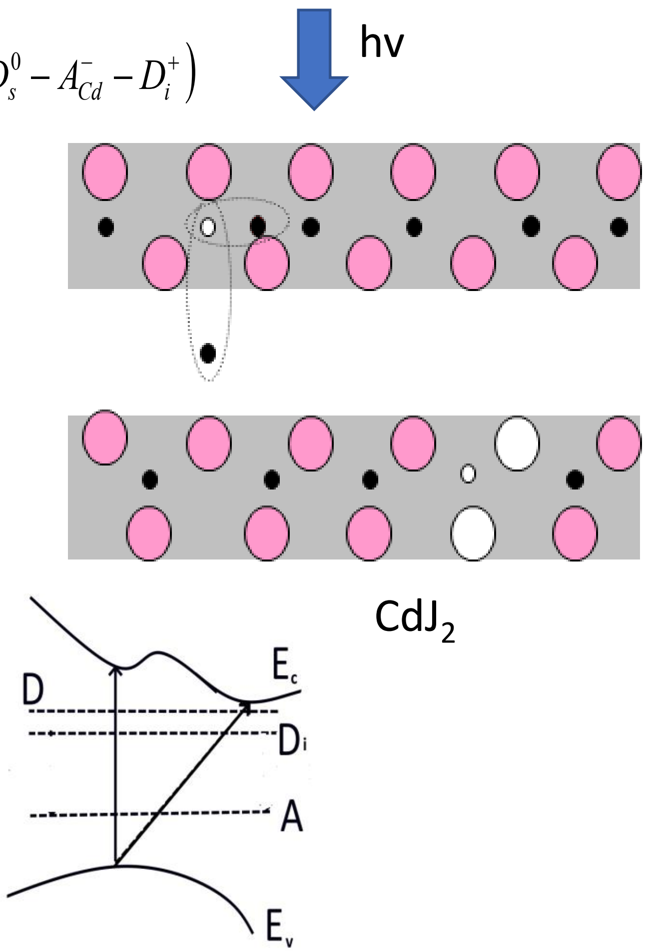
Models of complex trimer defects have been proposed

1. M.M. Rudka, *Visnyk (Official Gazette) of Lviv Polytechnic National University. Physical and Mathematical Sciences*, **566**, 97 (2006) (in Ukrainian)

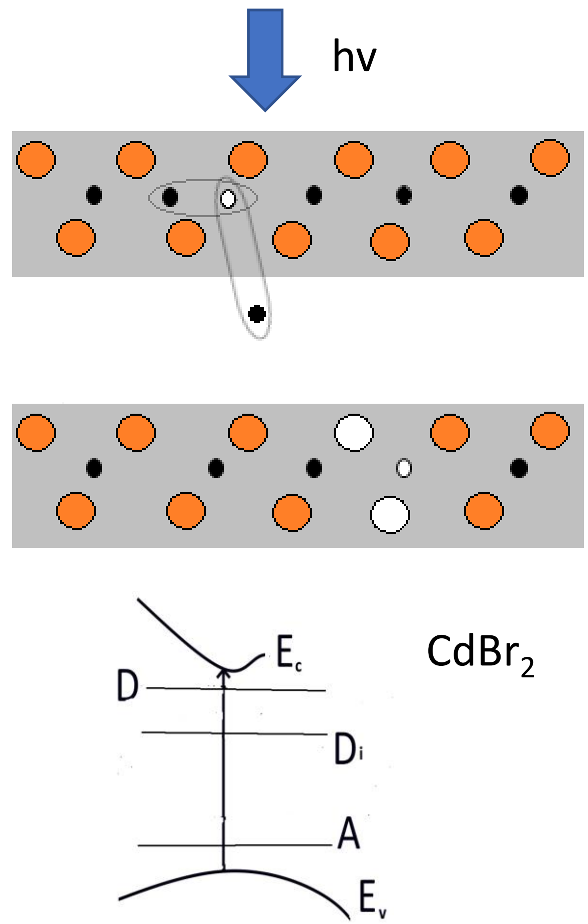
Models of dominant complex donor-acceptor luminescence centers – trimers in layered crystals CdX_2

- Pure crystals:
  - ***DAD****$_i$* –axis depending on the crystal structurcomplexes of intrinsic defects differently spatially oriented relative to the C6 axis depending on the crystal structure
  - Vacancy trimmers (V_X - V_{Cd} – V_X)
- In activated crystals:
  - ***DAD****$_i$* – complexes of intrinsic, intrinsic-impurity and impurity (depending on the impurity concentration) defects differently spatially oriented relative to the C6 axis depending on the crystal structure

$\left(D_s^0 - A_{Cd}^- - D_i^+\right)$



$\left(D_s^0 - A_{Cd}^- - D_i^+\right)$



$CdBr_2$

Model of virtual crystal, when the vacancy Cd with the same probability occurs in every cell

To study the behavior of localized states and their influence on the photoelectric and optoluminescence properties of $CdBr_2$ (ε_g=6 eV), depending on the energy microscopic parameters and the concentration of complex defects we will use quantized functions

$$\Psi(\vec{r}) = \sum_{\vec{n}}\{C_{c\vec{n}}\psi_c(\vec{r}) + p_1(\vec{n})a_{\vec{n}}\varphi_{1\vec{n}}(\vec{r}) + p_2(\vec{n})b_{\vec{n}}\varphi_{2\vec{n}}(\vec{r}) + C_{\vec{n}}\psi_\upsilon(\vec{r})\} \quad , \quad (1)$$

where the sum is taken for all cells; $\psi_c(\vec{r}), \psi_v(\vec{r})$- the wave function of an electron or hole at a layered crystal node, $\varphi_{1\vec{n}}(\vec{r})$ - on the donor-acceptor pair for which energy level E_D which corresponds to (Fig. 6a) or $\varphi_{2\vec{n}}(\vec{r})$ which corresponds to the energy E_a of the trimmer (Fig. 6b).
In the case of the one-electron approach

$$H(\vec{r}) = H_0(\vec{r}) + H_{da}(\vec{r}) + H_{int}(\vec{r}),$$

we proceed to the representation of the secondary quantization.

The displacement of various impurity subbands and the conduction band is calculated from the corresponding Green's functions.

These displacements are defined as poles or as roots of the following equation:

$$D = (\hbar\omega\text{-}\varepsilon_c)[(\hbar\omega\text{-}p_1^2\varepsilon_1)(\hbar\omega\text{-}p_2^2\varepsilon_2) - p_1p_2V_{12}^2] + p_1V_1\left[-p_1V_1(\hbar\omega\text{-}p_2^2\varepsilon_2) - p_2\sqrt{p_1p_2}V_2V_{12}\right]$$
$$- p_2V_2\left[p_2V_2(\hbar\omega\text{-}p_1^2\varepsilon_1) + p_1\sqrt{p_1p_2}V_1V_{12}\right]$$

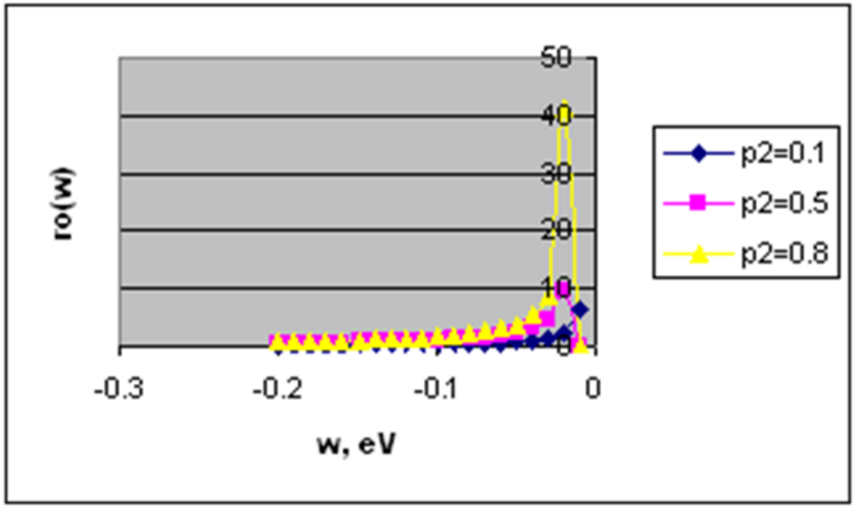
For CdI_2 [2]: Tovstyuk N., Rudka M., et.al. LTP, 2026, N1.

$$\varepsilon(\vec{\chi}, k) = \alpha_c\chi^2 + t_c(1 - cos\, kd),$$

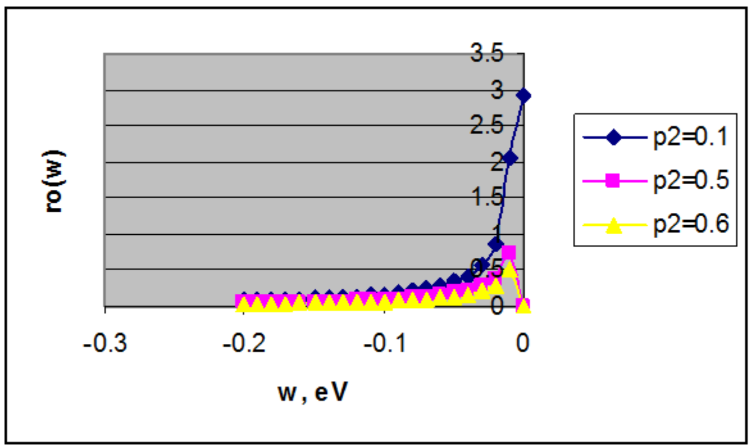
$$\varepsilon_1(\vec{k}) = \alpha_1\chi^2 + t_1(1 - cos\, kd) + \frac{\varepsilon_{01}}{p_1},$$

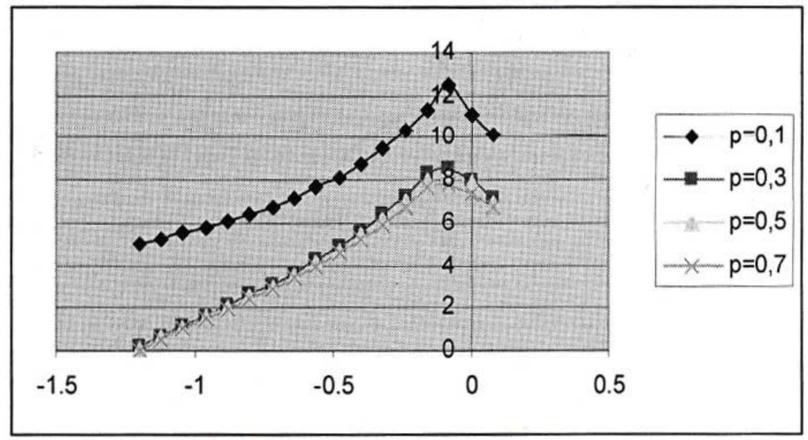
$$\varepsilon_2(\vec{k}) = \alpha_2\chi^2 + t_2(1 - kd) + \frac{\varepsilon_{02}}{p_1}$$

For $CdBr_2$ energy spectrum was taken as strong anisotropic one, with α=0,1 eV and t=0, 08eV



Density of electron states of trimmer with p_1=0.1, ε_{01}=-0.23eV, and different concentations of DA and ground energy state a) ε_{02}=-0.02eV b) ε_{02}=0.02eV





Density of electron states of trimmer with p_1=0.1, ε_{01}=-0.23eV, and different concentations of the DA and ground energy state a) ε_{02}=-0.02eV including interaction between different type of intercalate

CONCLUSIONS

In CdX_2 ($X = F, Cl, Br, I$) crystals the dominance within the structural layer of the covalent bond over the ionic bond and the size of the halogens are the reason of:

- generation of donor-acceptor (DA) complexes of intrinsic defects of the type $Cd_i^0 - V_{Cd}^- - Cd_i^+$ specifically oriented relative to the main crystallographic axis C_6 – trimers, one wing of which lies in the layer, and the other – at some angle to the layer plane. The angle between the trimer wings depends on the parameters of the crystal lattice.
- The significant volatility of the halogen, depending on the size of the anion and the ability of the cation to move from the nodal position to a distance greater than the lattice parameter a, controls the structural stability of the material and is also the cause of the generation of vacancy trimers ($\boldsymbol{V_X}$ - $\boldsymbol{V_{Cd}}$ – $\boldsymbol{V_X}$) , as defects, which are vacancies in the molecule (V_{CdX2}) of the CdX_2 material.
- Activation by impurities stimulates the process of filling molecular vacancies and generating intrinsic-impurity DADi defect complexes, which are the dominant luminescence centers.

- Comparing calculations with the case of $CdBr_2$ crystal with DA centers only, it is clear that the energy region is significantly narrower in the case of trimmer appearance.

THANK YOU FOR YOUR ATTENTION!