THE ROLE OF DONOR-ACCEPTOR DEFECT COMPLEXES IN THE RECOMBINATION OF NON-EQUILIBRIUM CARRIERS IN CADMIUM IODIDE

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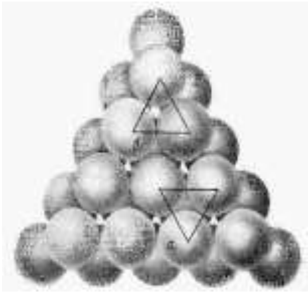
SCOPE

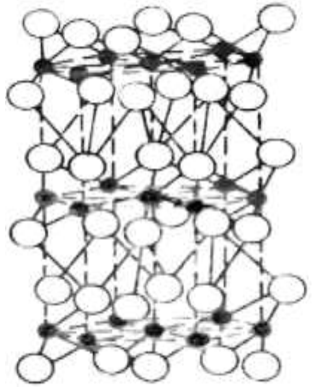
- **INTRODUCTION**
- **STRUCTURE OF** CdX_2
- **SOME OPTICAL, LUMINESCENT AND PHOTOELECTRIC PROPERTIES**
- **MODEL AND CALCULATIONS**
- **CONCLUSIONS**

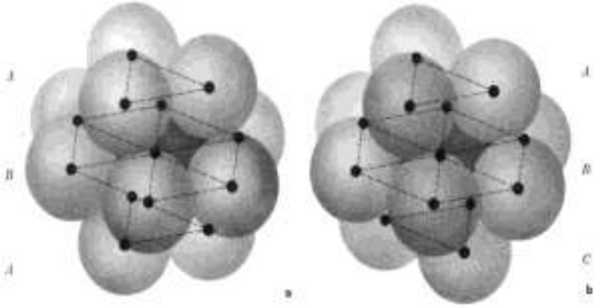
Introduction

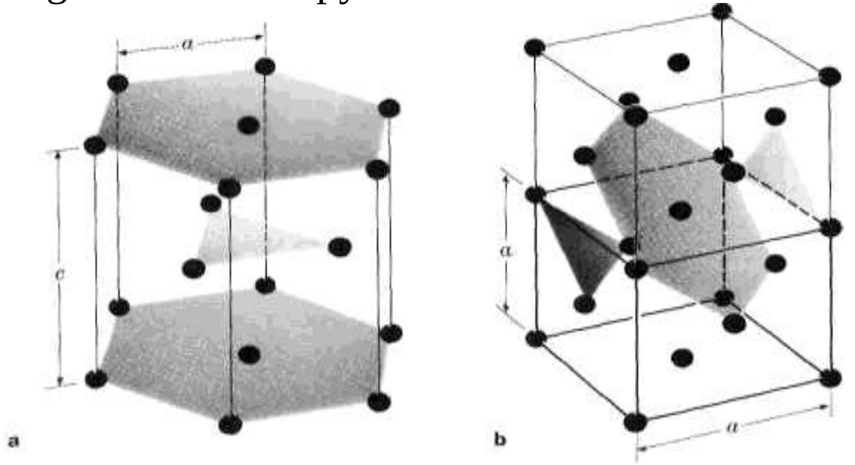
STRUCTURE OF CdX_2

The main feature of crystals of the CdX2 class (X = Cl, Br, J) is the arrangement of atoms in layer packages, within which ionic-covalent bonds operate, between the layers there are weak van der Waals interactions, the degree of anisotropy increases with the size of the halogen compared to the size of the cation.









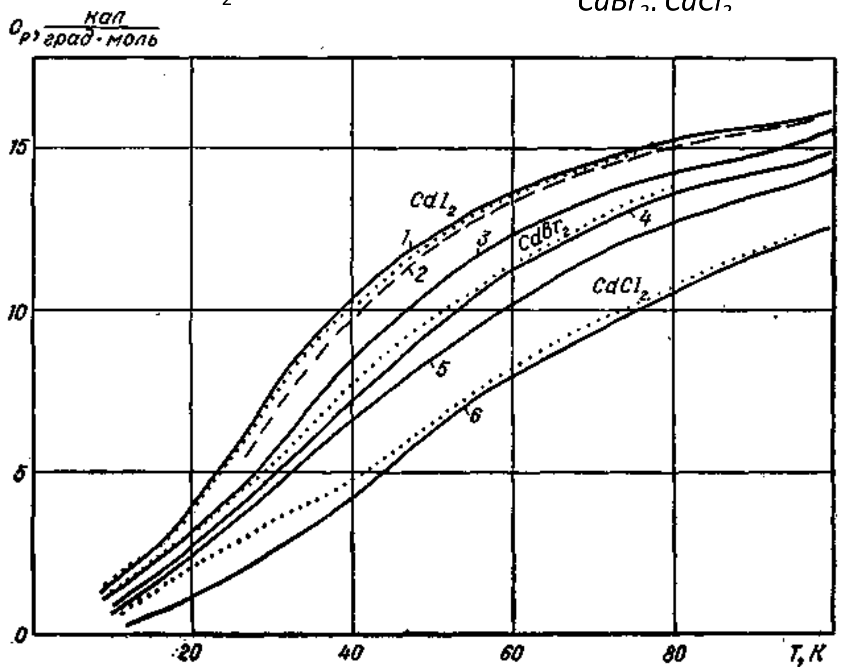
CdJ_2 $CdBr_2$, $CdCl_2$

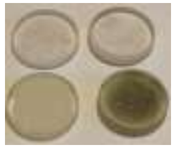
Professor Kityk I.V. established the force constants of the coupling:

	ionic, $(Cd-X)$	***covalent*** $(Cd-Cd)$, $(X-X)$	and molecular *міжшарового*
for $CdBr_2$ -	0,472 *мдин/А*^{0}	~ 1,2 *мдин/А*^{0}	0,073 *мдин/А*^{0}
for CdJ_2 -	0,277 *мдин/А*^{0}	~ 1,2 *мдин/А*^{0}	0,081 *мдин/А*^{0}

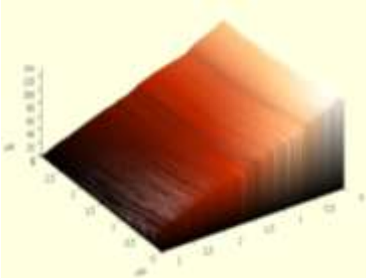
The estimation of the magnitude of the interaction within the layer indicates the dominant influence of the covalent bond due to the significant hybridization of (Cd – Cd) and (X – X) atoms. The calculated effective charges are:

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



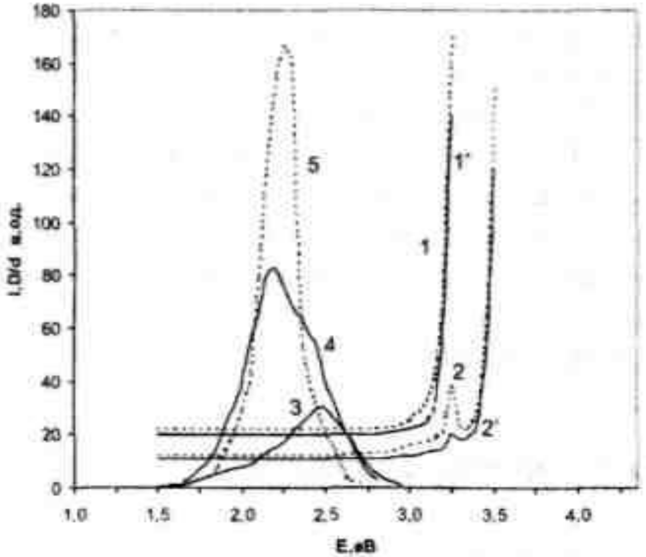


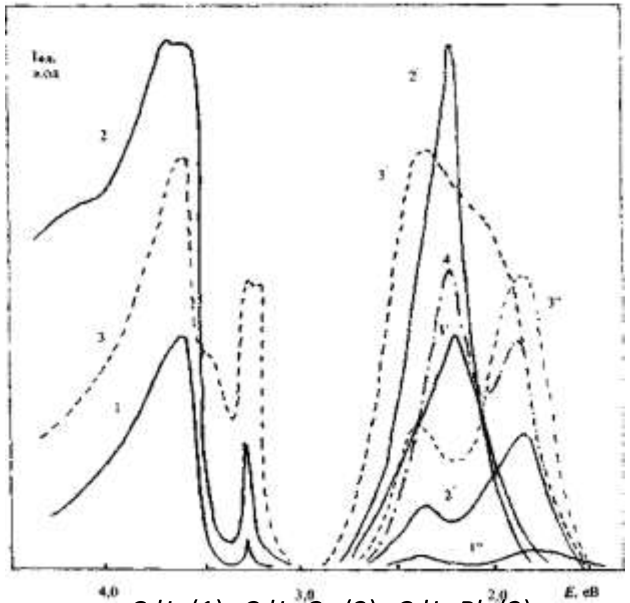
CdJ_2



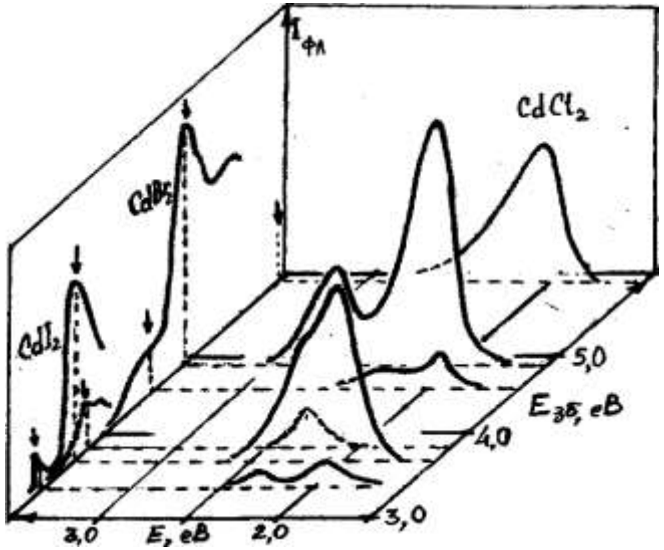
Temperature dependences of the heat capacity of crystals (1. M. S. Brodin, I. V. Blonsky Exciton processes in layered crystals – Kyiv: Nauk. Dumka, 1986. – 256 p.)

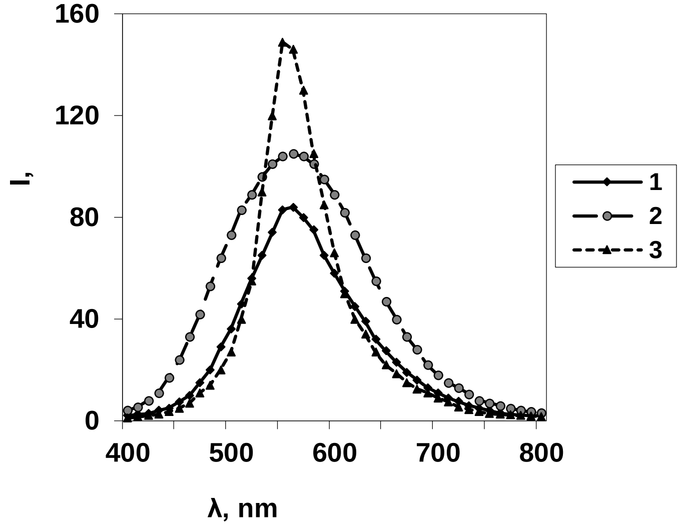
Luminescence excitation spectra (LE) and photoluminescence (PL) $\mathbf{CdX_2}$ (X = **Cl**, **Br**, **J**)



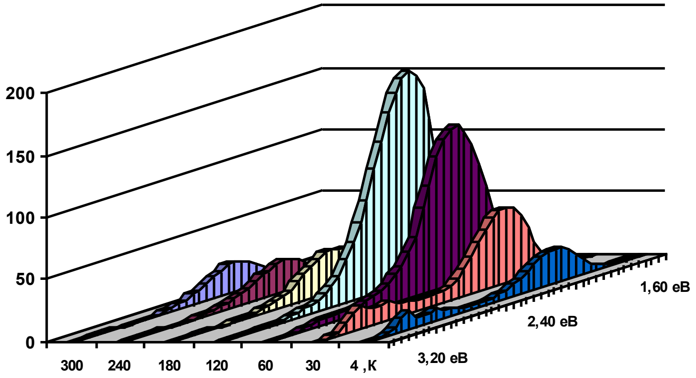


CdJ₂ (1), *CdJ₂:Cu* (2), *CdJ₂:Pb* (3)

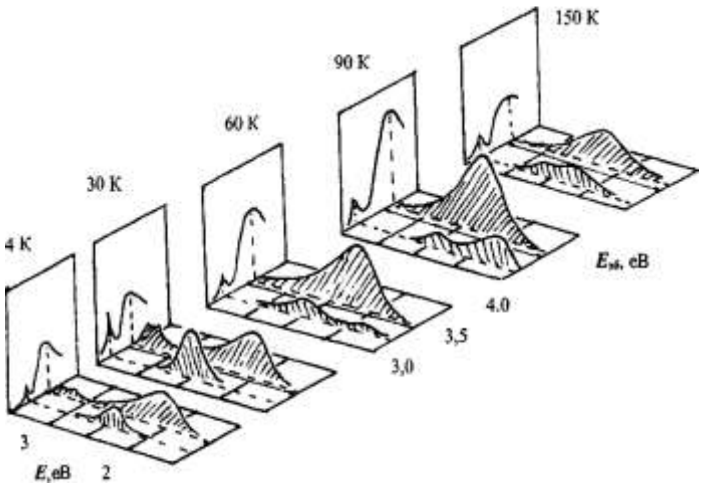




CdJ₂ (1), *CdJ₂:Cu* (2), *CdJ₂:Cs* (3)

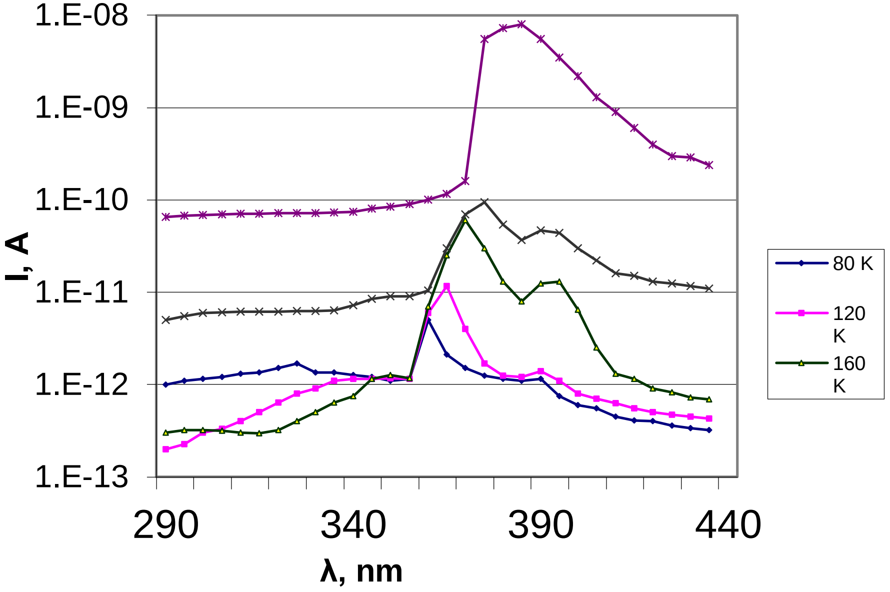


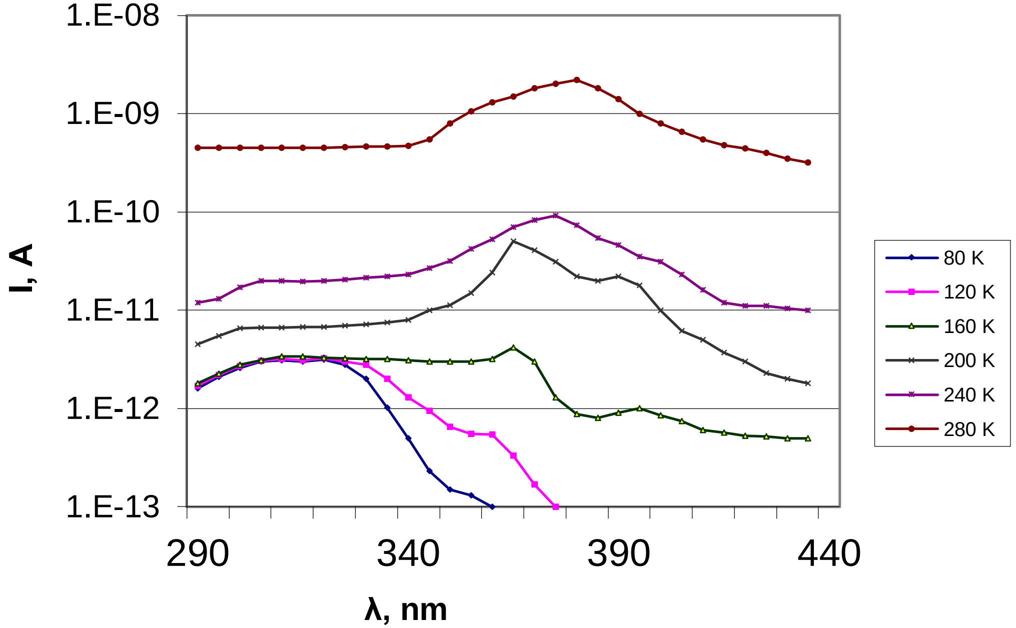
CdJ_2:0,5 мол.%CuJ

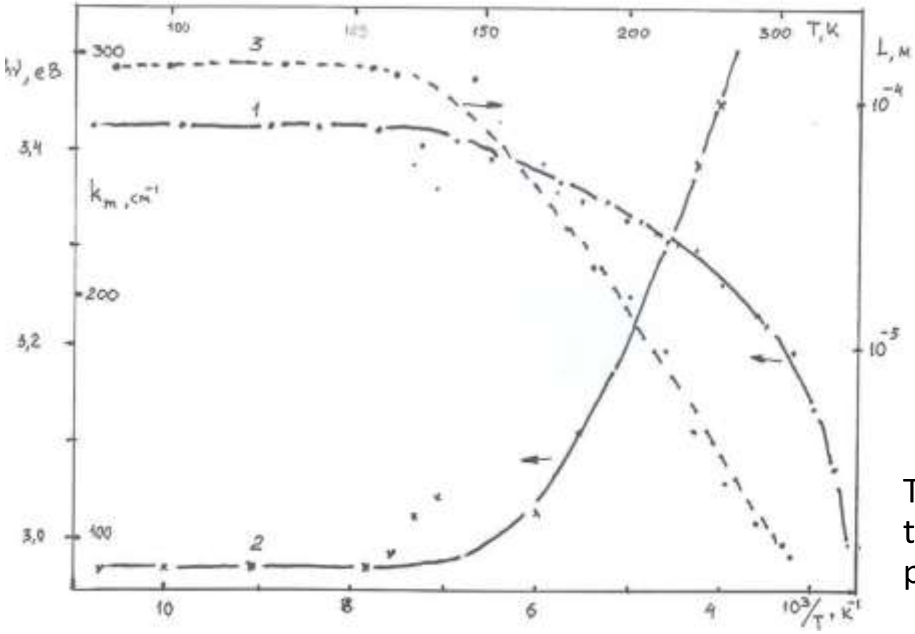


CdJ_2:0,5 мол.%CuJ

Photoconductivity (PC) of CdJ_2

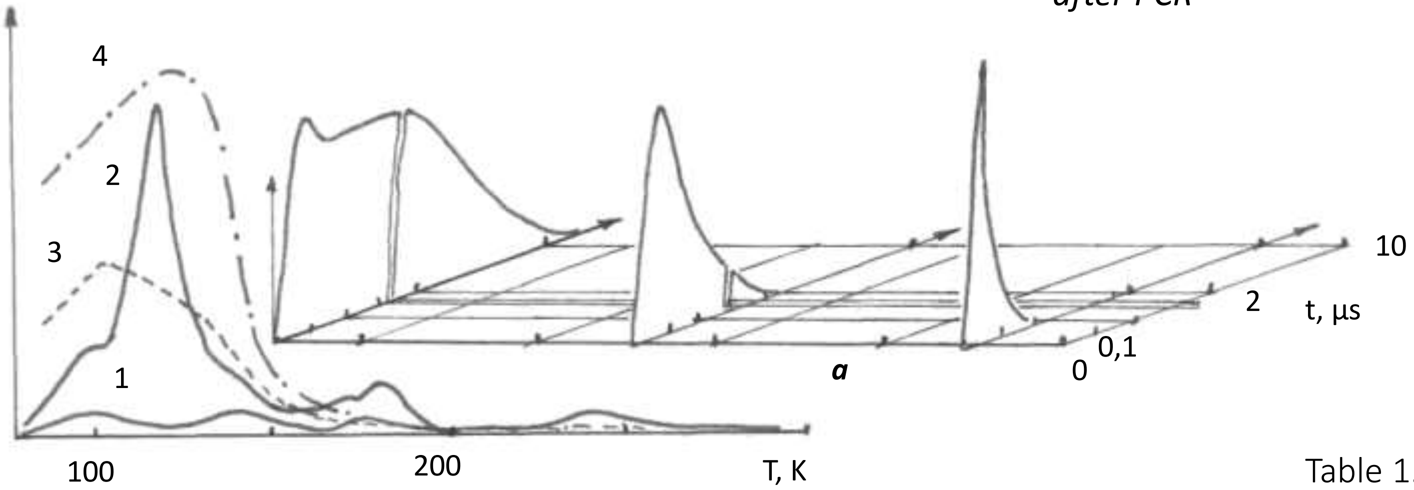




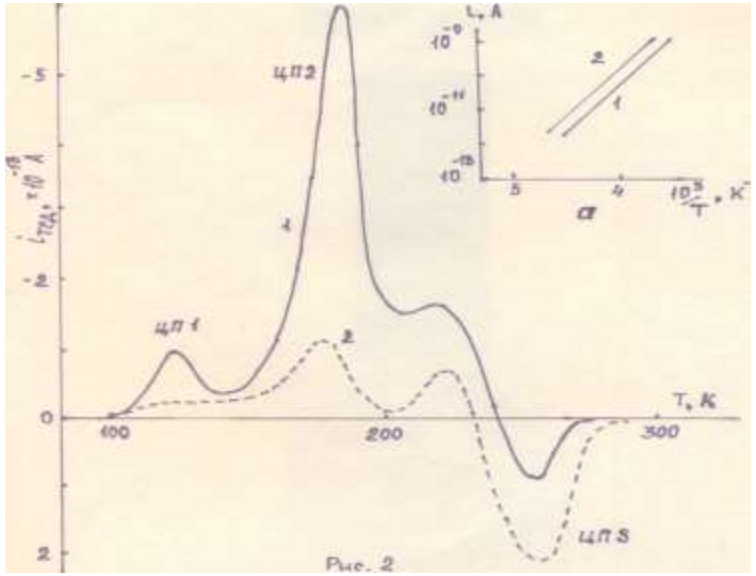


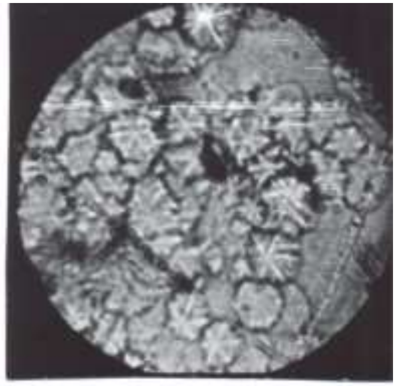
Temperature dependences for cadmium iodide crystals of the absorption coefficient k_m at the photoconductivity maximum (1), the diffusion length of charge currents (2), and the position of the maximum in the photoconductivity spectrum (3).

TSL curves (1,2), temperature dependence of integrated photoluminescence (3,4), CdJ_2 (1,3) and CdJ_2:Cu (2,4).
a – PL kinetic curves upon excitation by 3.68 eV light pulses at different temperatures



Thermally stimulated depolarization (TSD) CdJ_2:Cu thermally stimulated depolarization before (1) and after (2) photochemical reactions (PCR
a *- dark ionic conductivity before and after PCR*





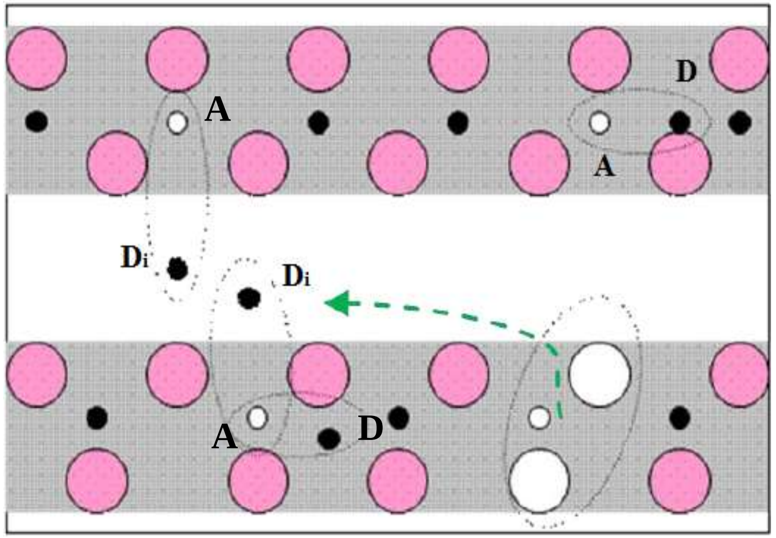
PCR CdJ_2:Cu

Table 1. Main capture centers in crystals CdJ_2 and CdJ_2:CuJ

Temperature maximums $T_м$, K	CdJ_2	CdJ_2:CuJ	ature of adhesion centers	Position of the maximum in the thermal emission spectrum of TSL peaks
105 (TSL, TSD)	+	+	Cd_i^0	2,25
125 (TSL, TSD))	-	+	Cu_i^0	2,25
137 (TSL, TSD))	+	+	ЛД	2,25
175 (TSL, TSD)	+	+	V_{Cd}^-	1,9
185 (TSL, TSD)	-	+	Cu_{Cd}^-	1,9
240 (TSD))	+	-	Cd_i^+	
270 (TSD)	-	+	Cu_i^+	

Model and calculations

In CdJ_2 crystals, there is almost always excess cadmium present, which remains after the anion(s) leaves the sites and iodine bivacancies appear. These structural defects lead to the appearance of local energy levels in the forbidden bands of the layered CdJ_2 crystal, which, according to thermoactive spectroscopy data [2], are located near the allowed energy bands at distances: E_D - about 0.15 eV from one conduction band; E_A - about 0.5 eV above the ceiling of the valence band E_v; E_{Di} - about 1.0 eV from $_{Ec}$.



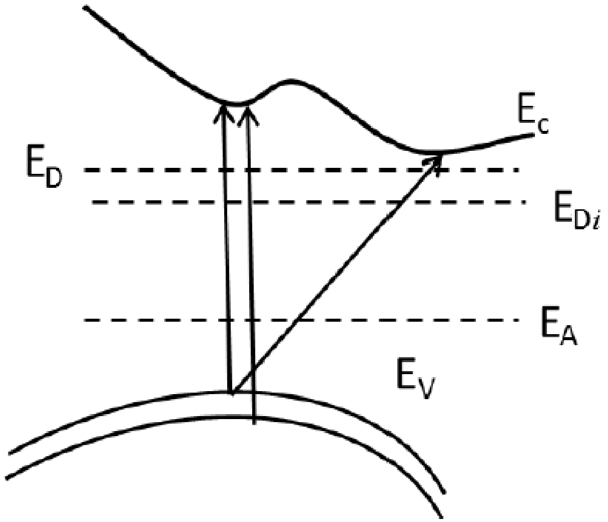
DA models of intrinsic defect complexes

DA1 : $(Cd_i^0 - V_{Cd}^-)$

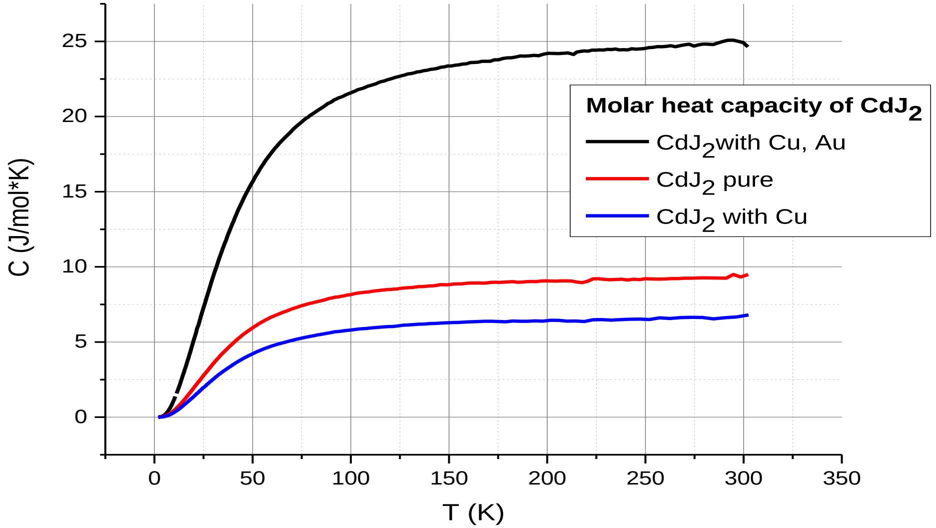
DA2: $(V_{Cd}^- - Cd_i^+)$

DAD_i : $(Cd_i^0 - V_{Cd}^- - Cd_i^+)$

layer vacancy : $(V_X - V_{Cd} - V_X)$



Local energy levels of defects in the band gap of CdJ2 structure

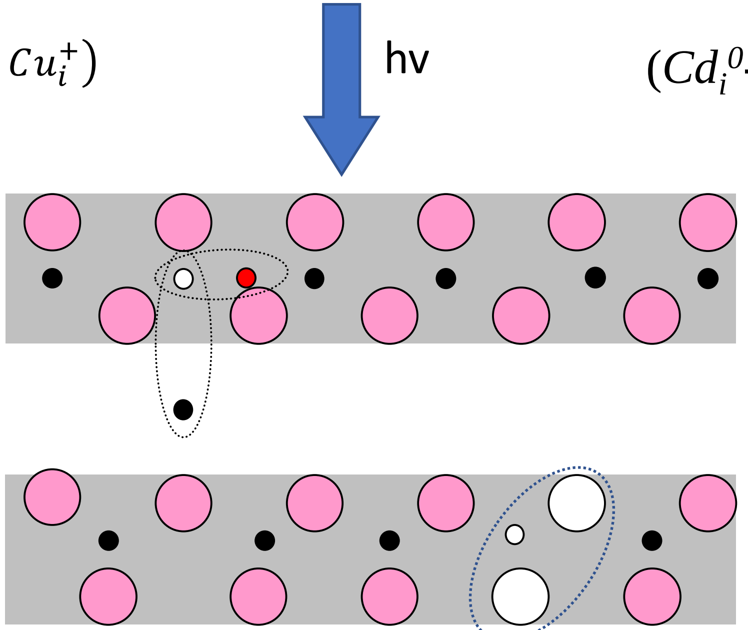


2. M.M. Rudka, "Centers of green-yellow and red luminescence in crystals of cadmium iodide", Visnyk Physical and Mathematical Sciences, vol. 687, 2010, 181-187.

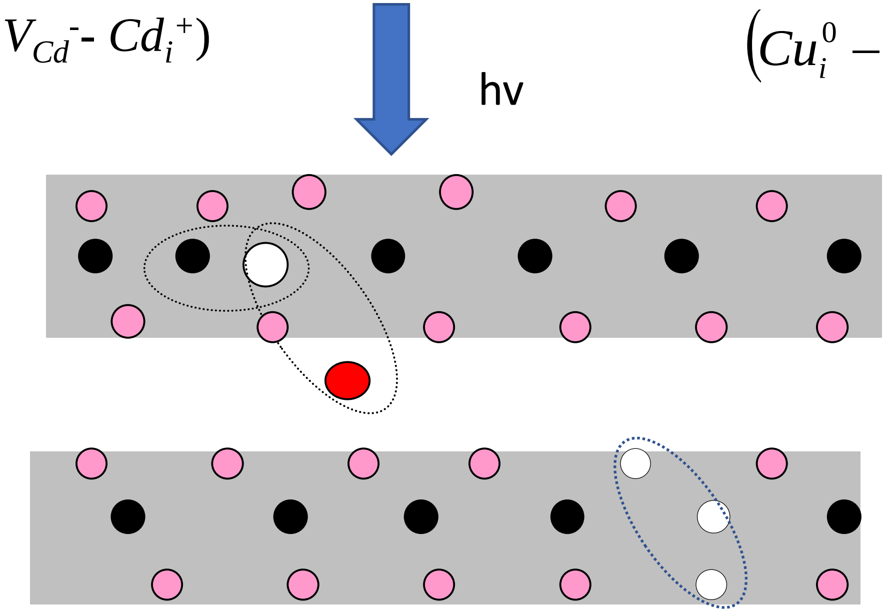
Models of complex defect centers in layered crystals **CdX_2**:

– trimmer ***DAD*$_i$** $\left(D_s^0 - A_{Cd}^- - D_i^+\right)$

$\left(Cd_i^0 - Cu_{Cd}^- - Cu_i^+\right)$



$(Cd_i^0 - V_{Cd}^- - Cd_i^+)$



$\left(Cu_i^0 - Cu_{Cd}^- - Cu_i^+\right)$

CdJ_2

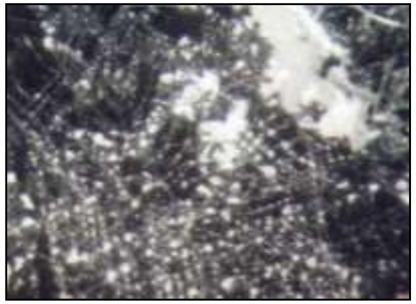
$\left(V_J^{+0,65} - A_{Cd}^{-1,30} - V_J^{+0,65}\right)$

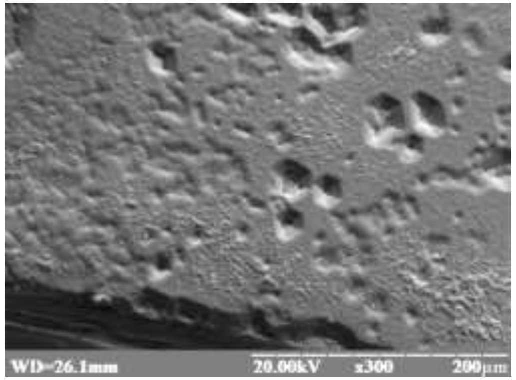
– layer vacancy

(V_X - V_{Cd} – V_X)

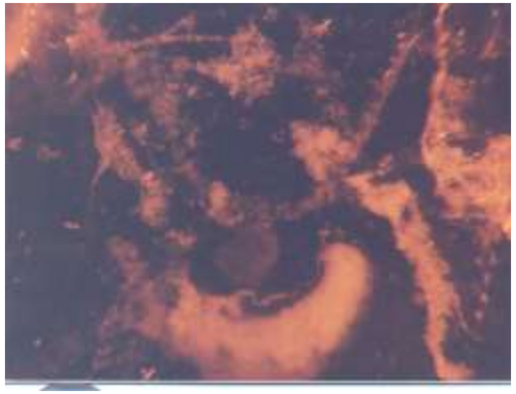
$\left(V_{Br}^{+0,69} - A_{Cd}^{-1,38} - V_{Br}^{+0,69}\right)$

$CdBr_2$





CdJ_2



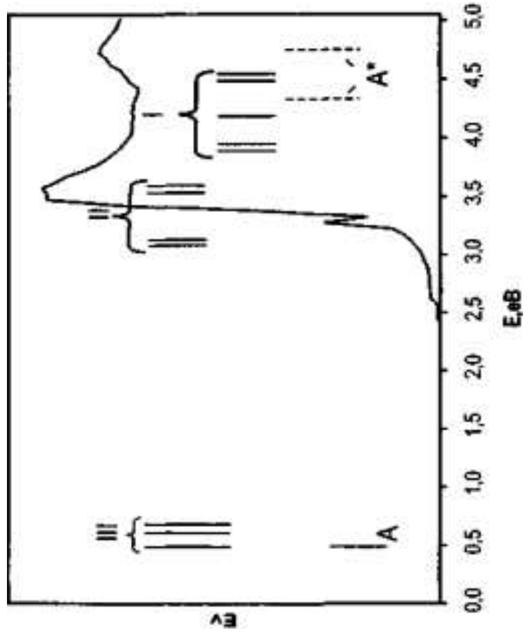
$CdBr_2$

Model of the dominant luminescence center:

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

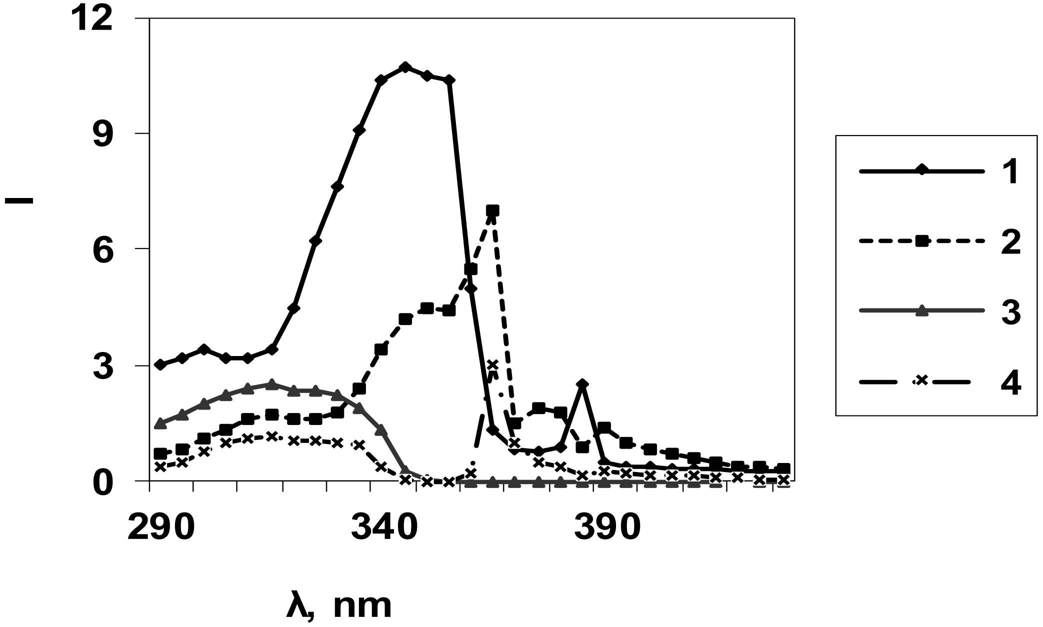
LES of CdJ_2:Cu crystals and theoretically calculated positions of impurity energy levels of copper centers included in the associated DADi complex

$$\left(Cu_s^0 - Cu_{Cd}^- - Cu_i^+\right)$$

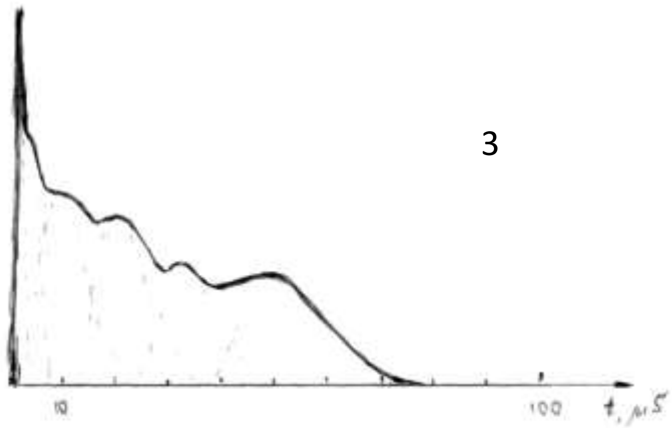


Impurity center in CdJ_2	*Energy position of the level*	*orbital*
Cu_{Cd}^-	E_v + 0,50 eB E_v + 0,70 eB E_v + 0,78 eB	x^2-y^2 *xz* *yz*
Cu_i^+	E_v + 3,03 eB E_v + 3,12 eB E_v + 3,60 eB E_v + 3,70 eB	x^2-y^2 *xz* *yz* *xy*
Cu_s^0	E_v + 3,72 eB E_v + 3,76 eB E_v + 4,18 eB E_v + 4,57 eB E_v + 4,59 eB	x^2-y^2 *xy* $3z^2$-r^2 *yz* *xz*

$E_{макс}$, eB (experiment)	**$E_{макс}$, eB** (theory)	**identification**
4,7	4,6	$E_v \rightarrow Cu^0_{i(yz,xz)}$
4,2	4,25 4,18	$E_v \rightarrow (Cu_{Cd}^-)^*$ $E_v \rightarrow Cu^0_{i(3z^2-r^2)}$
3,8	3,8 3,68	$E_v \rightarrow Cu^+_{i(xy,yz)}$ $Cu^-_{Cd(x^2-y^2)} \rightarrow Cu^0_{i(3z^2-r^2)}$
3,22	3,22	$Cu^-_{Cd(x^2-y^2)} \rightarrow Cu^0_{i(x^2-y^2)}$
край плато - 2,6	2,53	$Cu^-_{Cd(x^2-y^2)} \rightarrow Cu^+_{i(x^2-y^2)}$



LES (1) and PC (2,3,4) spectra for orientation I (2), orientation II (3) and orientation III (4) of crystals CdJ_2:Cu. T = 80 K



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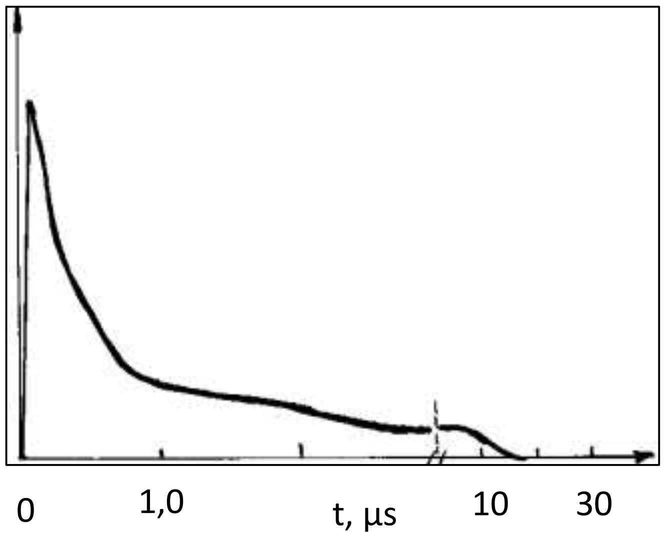
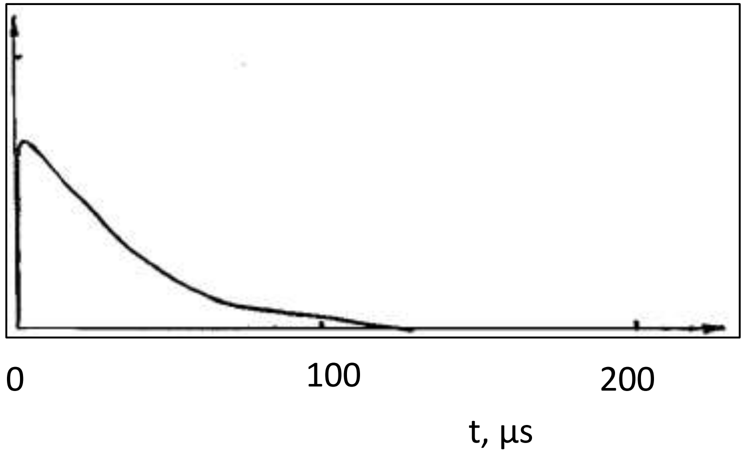


1

kinetics of PL (1, 3) and PC(2) CdJ_2:Cu ($E_{зб}$ = 3,68 eV, $t_{імп}$ = 8 nc). T = 80 K



2

The mechanism of DA luminescence is cascade:

Conclusions

- the dominant centers of luminescence and recombination in CdJ2 are associated donor-acceptor complexes of intrinsic and impurity defects of the structure; the features of the crystalline structure of the matrix cause the spatial orientation of the centers
- non-equilibrium genetic electron-hole pair (GEHP) is a carrier of both luminescence and conduction in layered cadmium halides
- luminescence mechanism: cascade recombination (annihilation) of GEDP on associated DA-complexes of structural defects
- the phenomena of luminescence and conduction are two competing branches of relaxation of energy absorbed by the crystal
- the decay of non-equilibrium GEHP and the capture of “fragments” by different DA centers cause the appearance of maxima on the curves of thermally stimulated luminescence and conductivity.

Thank You for Your attention !