The effect of copper impurity on photochemical transformations in cadmium iodide

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SCOPE

- **INTRODUCTION**
- layered crystals CdI_2
- Real pure and copper activated crystals CdI_2
- Some physical properties of crystals CdI_2, CdI_2:Cu
- Photochemical reactions and thermochemical reactions in CdI_2 :Cu
- **CONCLUSIONS**

Introduction

layered crystals CdI_2

Features of crystals :

- unique, model, specific, original
- strongly anisotropic (quasi-two-dimensional)
- Cadmium in the I-Cd-I structural layer between iodine occupies half of the voids
- easy to obtain ideal ultrathin samples for research
- the ability to intercalate and obtain ultrathin crystals and nanostructures
- etc.

a = 0,4240 нм
c = 0,6855 нм

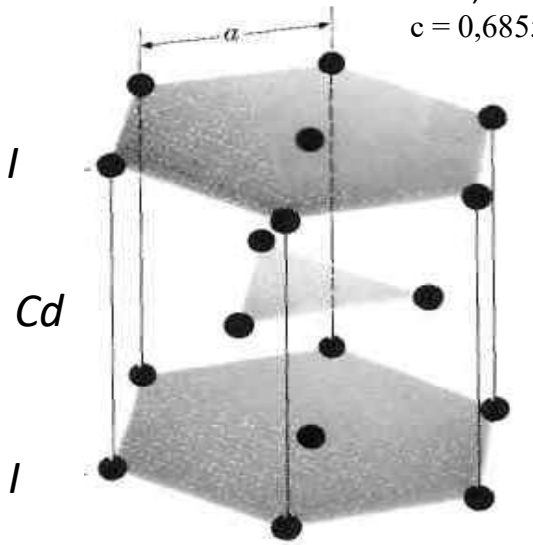


Fig. 1

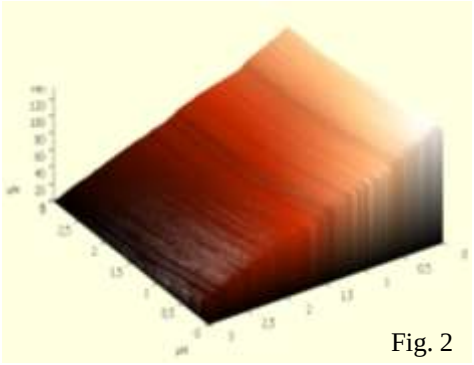
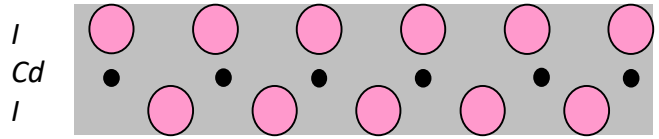


Fig. 2



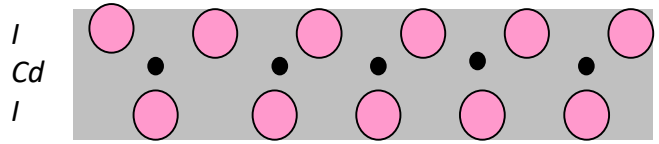


Fig. 3

Coupling force constants:

ionic $(Cd - X)$, ~ 0,277 $mdin/A^0$

covalent $(Cd - Cd)$, $(X - X)$ ~ 1,2 $mdin/A^0$

molecular (interlayer) ~ 0,081 $mdin/A^0$

An estimate of the magnitude of the interaction within the layer gives the following effective charges : $Cd^{+1,30}$, $I^{-0,65}$

Pure crystals are optically and radiation stable,have an indirect long-wavelength absorption edge,at 80 K the band gap is:

- indirect E_g = 3,5 eB
- direct E_g = 3,8 eB

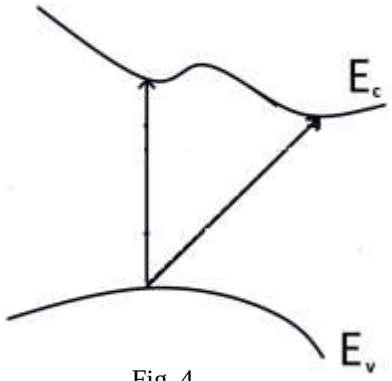


Fig. 4

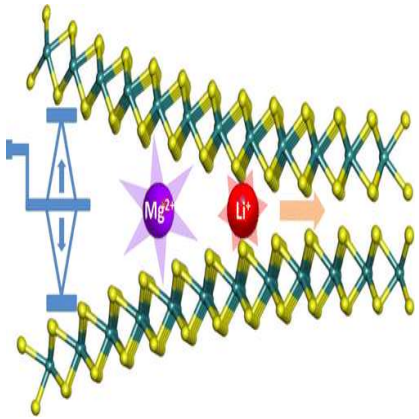


Fig. 5

Real pure and copper activated crystals CdI_2

pure crystals CdI_2

Fig. 6

Fig. 7

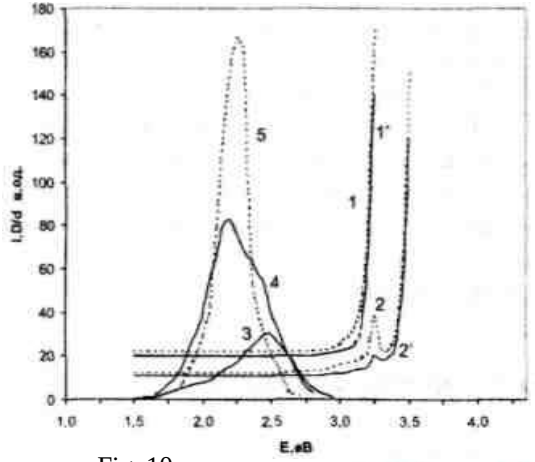


Fig. 10

crystals CdI_2:Cu

Fig. 11 CdI_2:0,5 mjl.%CuI

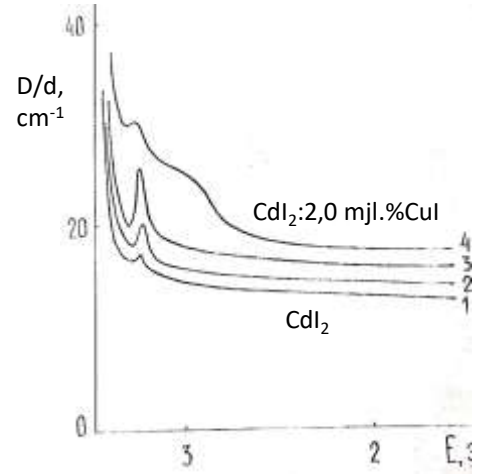


Fig. 16

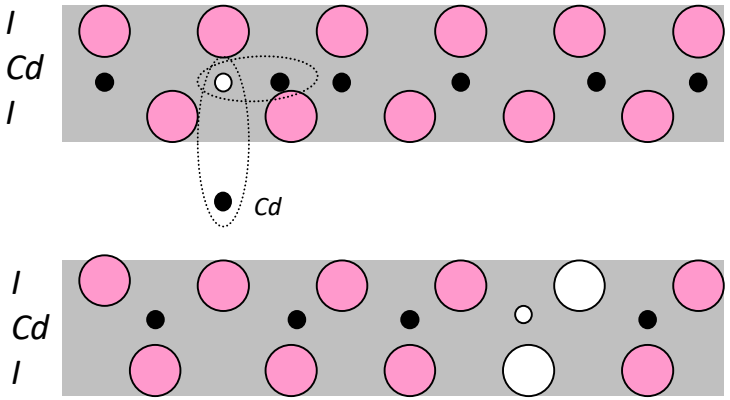


Fig. 8

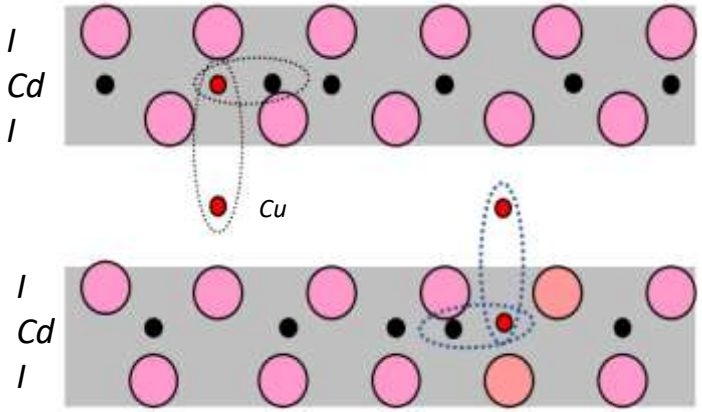


Fig. 14

$I_{PC}\cdot10^{13}$, A

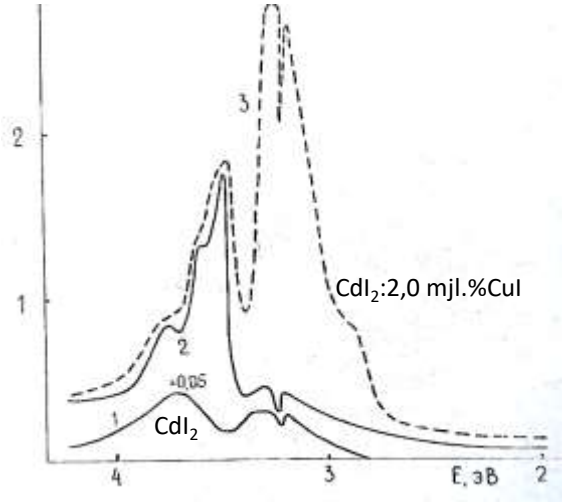


Fig. 17

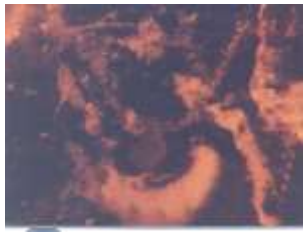


Fig. 9

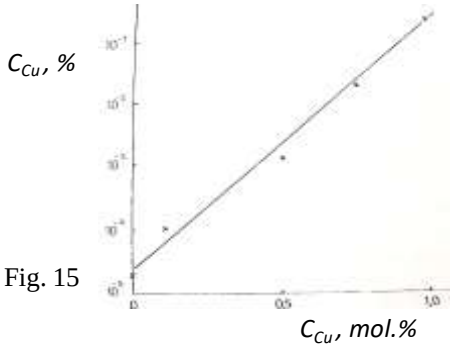


Fig. 15

CdI_2:0,5 mjl.%CuI

Fig. 12

CdI_2:2,0 mjl.%CuI

Fig. 13

[1] M.Rudka, et.al. , *Low Temp. Phys.*, **51**, 43 (2025) [*Fiz. Nyzk. Temp*. **51**, 47 (2025)]. https://doi.org/10.1063/10.0034643

Some physical properties of crystals CdI_2, CdI_2:Cu

- optical-luminescent

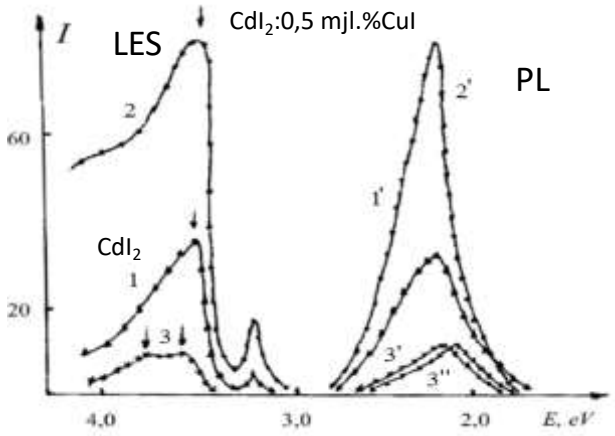


Fig. 18

- photovoltaic

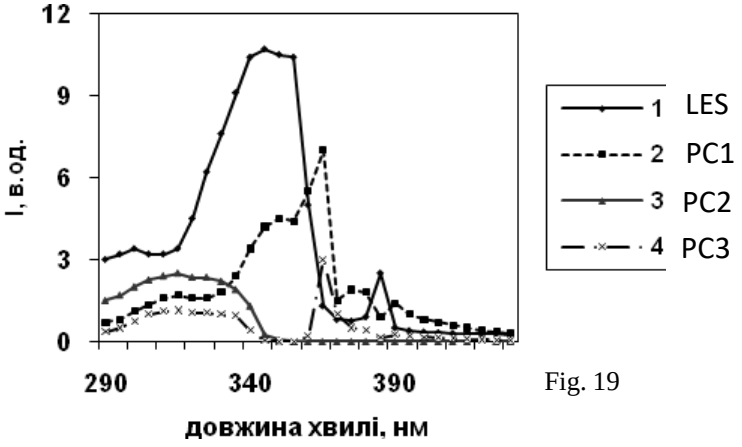


Fig. 19

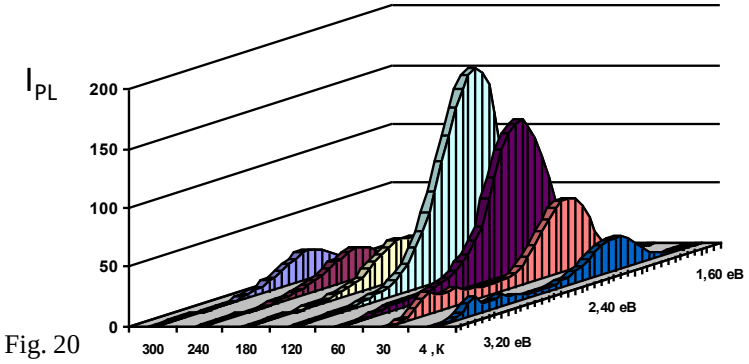


Fig. 20

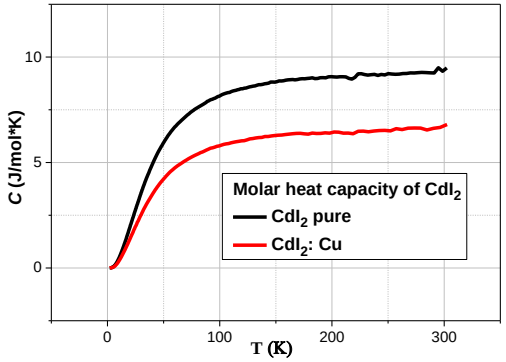
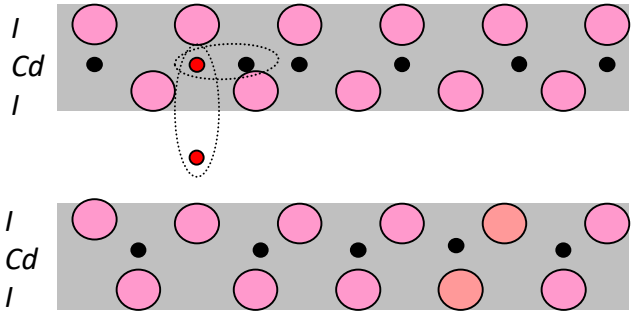


Fig. 23



- thermal activation

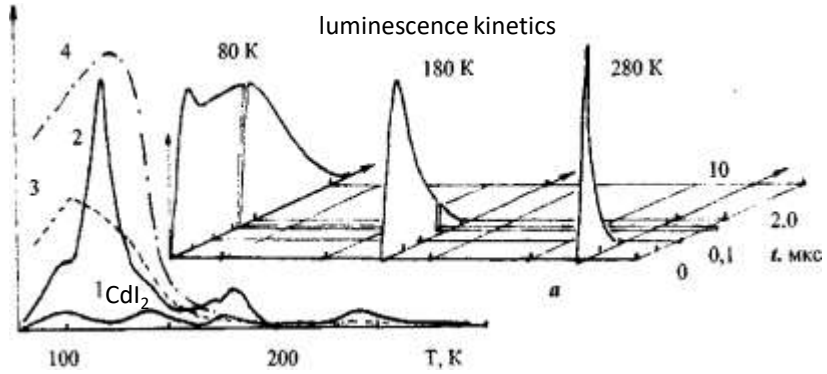
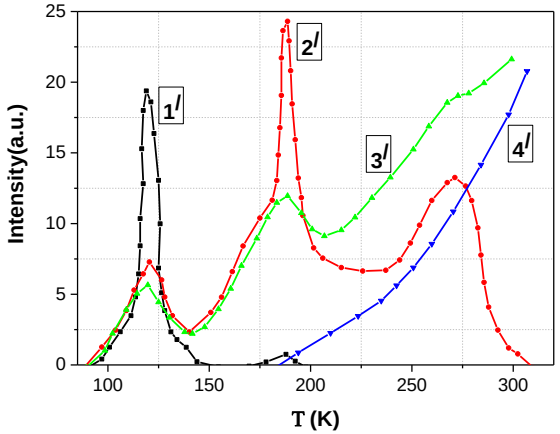


Fig. 21



CdI_2:0,5 mjl.%CuI

1' – TSL
2' – YSD
3' – TSC
4' - I_{dC}

Fig. 22

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

Fig. 24

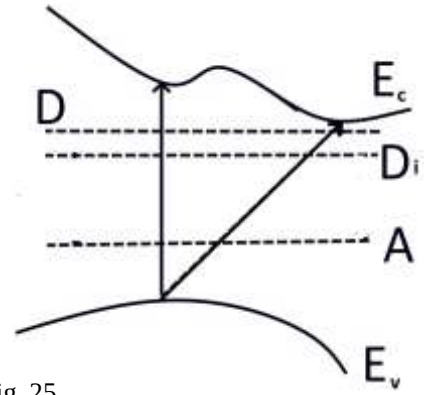


Fig. 25

[2] M. Rudka, et.al , *2020 IEEE 40th International Conference on Electronics and Nanotechnology (ELNANO)*, 268 (2020). https://doi.org/10.1109/ELNANO50318.2020.9088922.

[3] Mykola Rudka, Low Temp. Phys. 52, 200 (2026). https://doi.org/10.1063/10.0042295.

Photochemical reactions (PCR) and thermochemical reactions (TCR) in CdI_2 :Cu

Effect of irradiation on transmission spectra

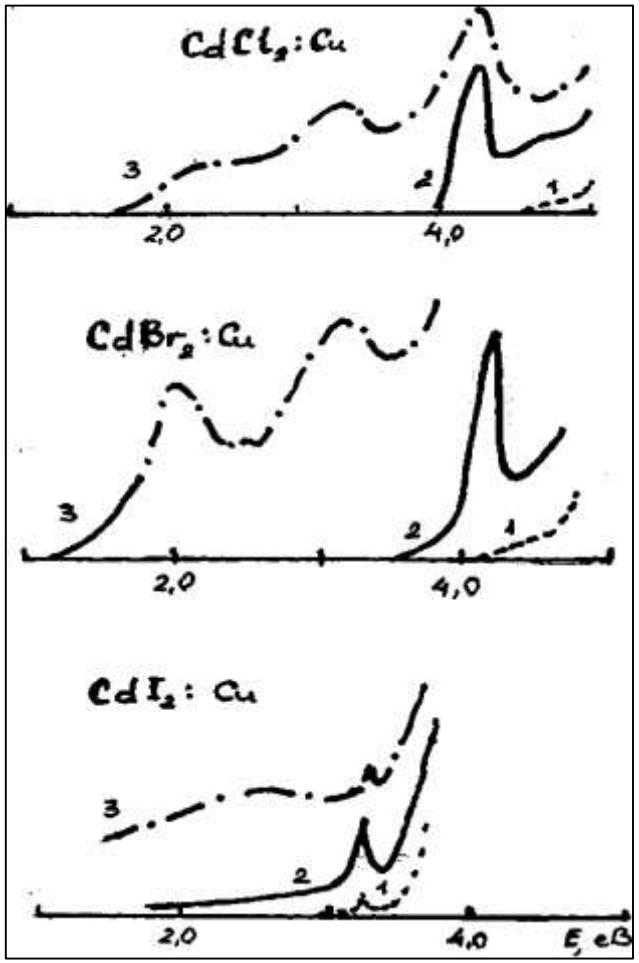


Fig. 28

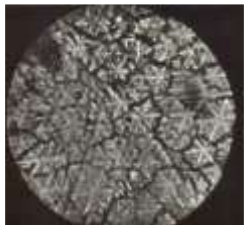
PCR: photostimulated "blackening" of crystals

hv

CdI_2 :Cu

Fig. 26

Fig. 27



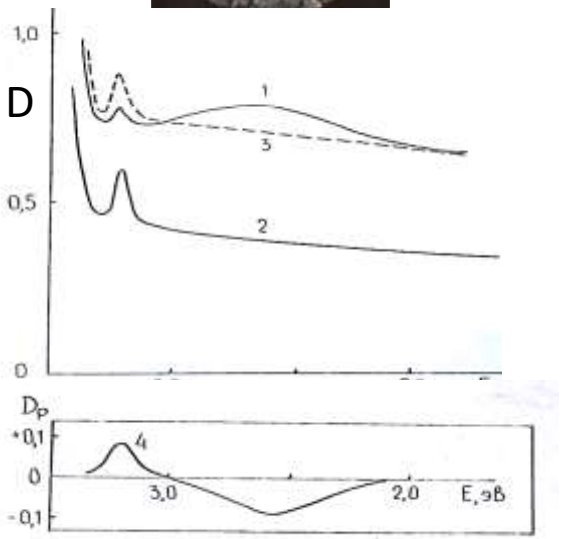


Fig. 29

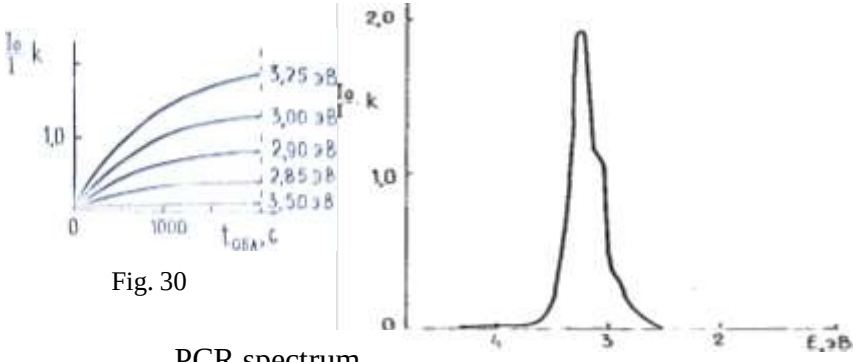
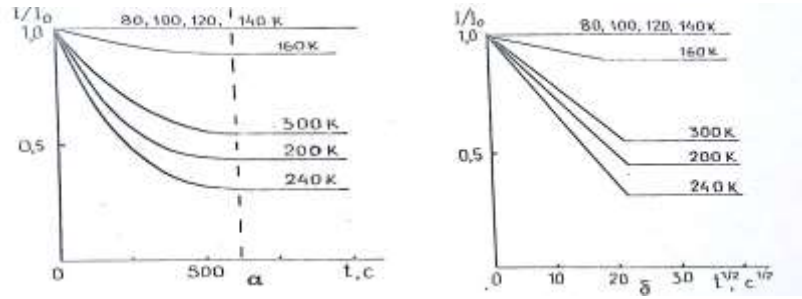


Fig. 30

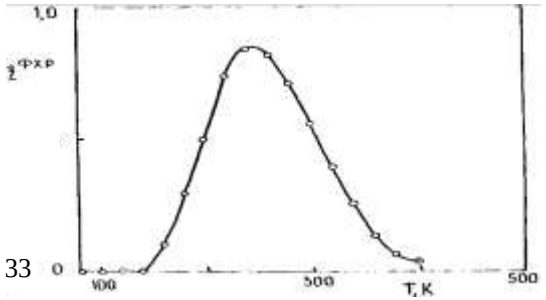
PCR spectrum

Fig. 31



PCR kinetics

Fig. 32



PCR effectiveness

Fig. 33

???: 1) why is this PCR only (!) in the materials ***CdX_2:Me*** (***X*** = ***Cl, Br, I;*** ***Me*** = ***Cu, Ag, Au***)

2) why is the most effective combination CdI_2 : Cu

Summary: *PCR "blackening" is a multi-step process involving several separate PCRs and TCRs*

Effect of irradiation on the *luminescence* and *conductivity* of CdI_2:Cu

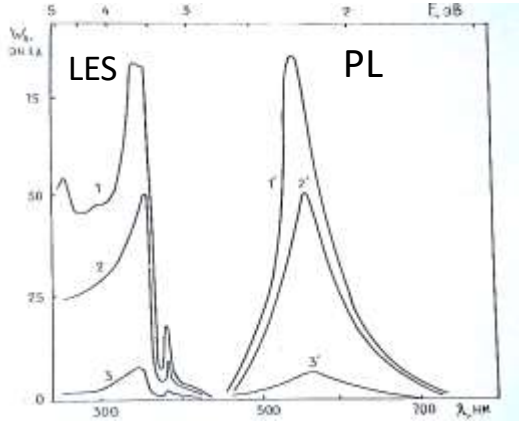
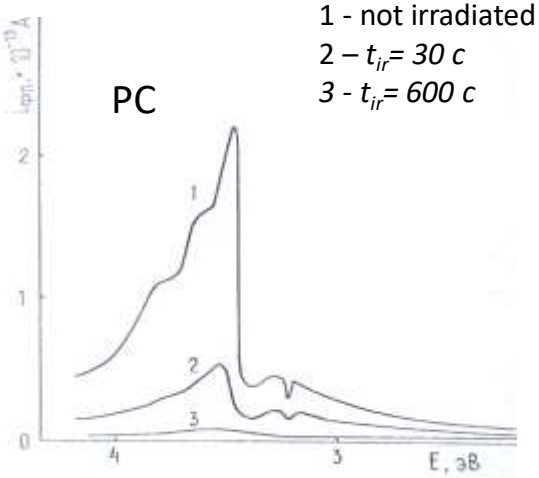
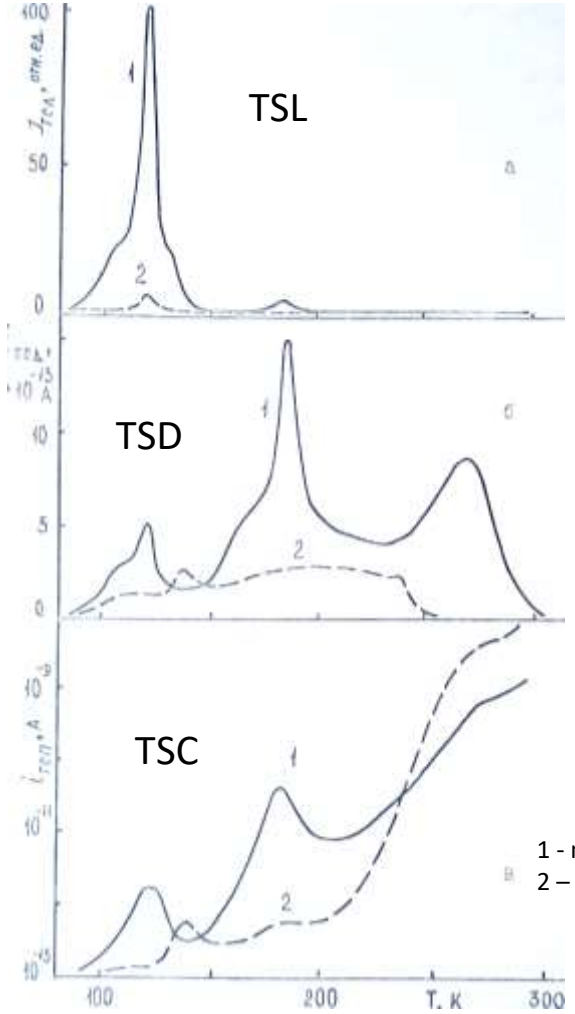


Fig. 34



1 - not irradiated
2 – t_{ir}= 30 c
3 - t_{ir}= 600 c

Fig. 35



1 - not iradiated
2 – t_{ir}= 600 c

T_{ir}=240 K

Fig. 36

PCR: *photo stimulated decay of self-impurity DAD$_i$ centers (Cd_i^0- Cu_{Cd}^-- Cu_i+)*

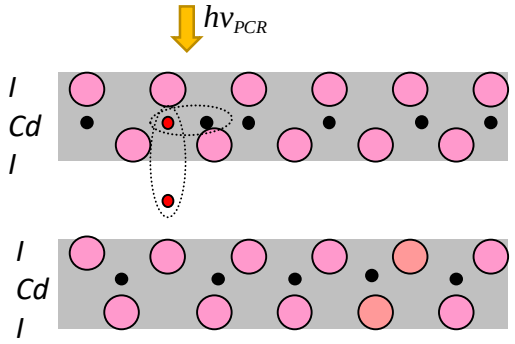


Fig. 37

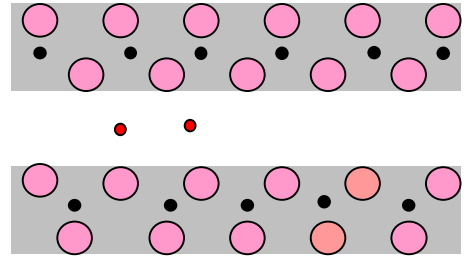


Fig. 38

mechanism: *- photostimulated athermal release of copper from the node to the internode according to the Scheinkman model according to the scheme:*

$Cu_{Cd} + h\nu_{ФХР} = (Cu_{Cd})^* \rightarrow Cu_i + V_{Cd}$ *з наступним* $Cd_s + V_{Cd} = Cd_{Cd}$

PTCR: thermally stimulated diffusion of Cu_i^+ ions into effluents

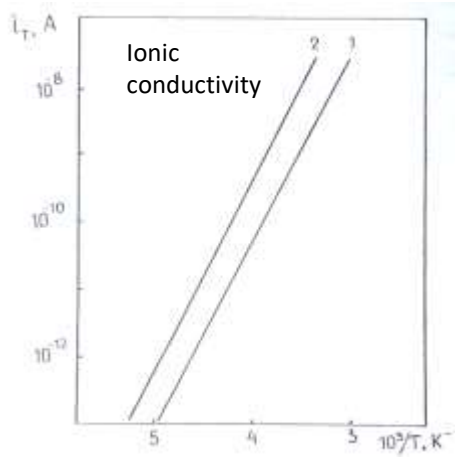


Fig. 39

Fig. 40

Fig. 41

mechanism: *- thermally stimulated diffusion of copper Cu_i^+ through van der Waals gaps and edge dislocations to screw dislocations*

***PCR**: association of copper ions in the coagulate ("decoration" of screw dislocations) - image centers*

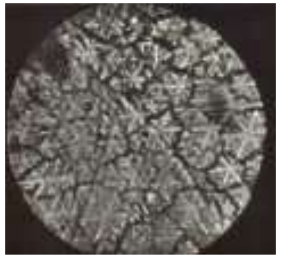


Fig. 42

***mechanism:** - jump-like association of copper ions accumulated on linear defects (LD) when their concentration reaches a certain critical nk according to the scheme :*

$$(Cu_i^+ + Cu_i^+ + Cu_i^+ + \ldots)_n + LD \rightarrow (Cu_n^0 LD)$$

***note:** the mechanism of formation of copper coagulates from ions (!) is similar to the process of dew precipitation and has signs of Bose-Einstein condensation of Cu_i^+ bosons when they accumulate above the critical concentration nk*

PTCR: thermally stimulated decomposition of copper coagulates ($Cu_n^0 LD$) and drift of copper ions throughout the crystal volume

***mechanism:** - decay of image centers with the participation of phonons*

$$h\nu_{ph} + (Cu_n^0 LD) \rightarrow (Cu_i^+ + Cu_i^+ + Cu_i^+ + \ldots)_n + LD$$

TCR: thermally stimulated generation of self-impurity trimers of DAD_i-cents in a crystal CdI_2 :Cu

***mechanism:** - thermally stimulated substitution at high temperatures of the nodal cadmium by a copper ion with the generation of a DAD_i-center complex in the composition* $(Cd_s^0\text{-}Cu_{Cd}^{-}Cu_i^+)$

PTCR

Fig. 44

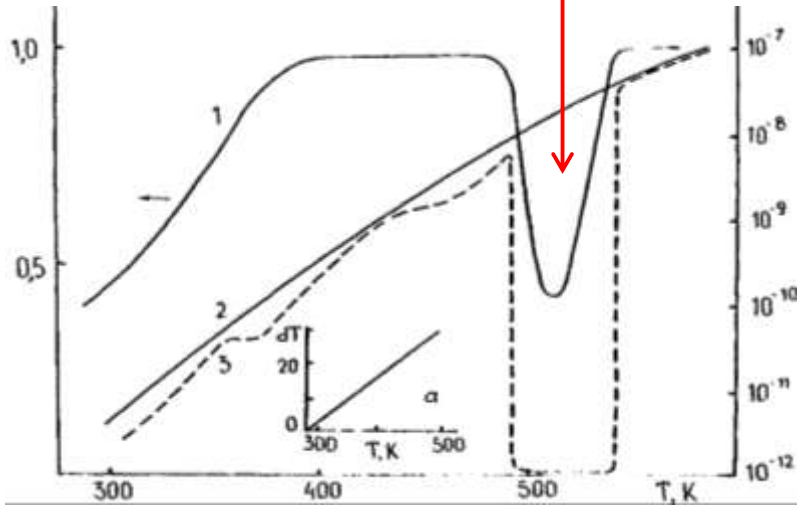


Fig. 43

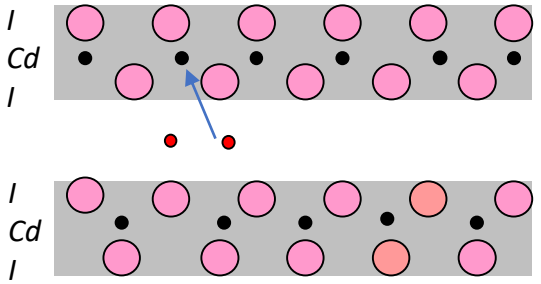


Fig. 45

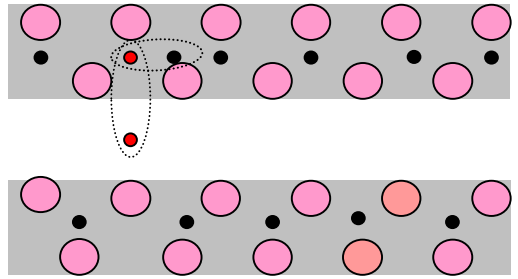


Fig. 46

conclusions

- The main reason for the photochromic properties of CdI_2:Cu crystals is the amphoteric properties of copper in cadmium iodide: copper enters the crystal matrix into van der Waals gaps as donors (Cu_i^+) and as acceptors – substitution ions Cu_{Cd}^-, displacing the nodal cadmium into the adjacent free void and generating complex defects of the type DAD_i- centers.
- Copper-activated crystals significantly increase their luminescent and photoelectric properties due to the increase in the concentration of luminescence centers and recombination centers, which are such self-impurity trimers as ($Cd_s^0 – Cu_{Cd}^- – Cu_i^+$)
- The absence of copper centers in the Cu^{2+} state in cadmium iodide (according to electron paramagnetic resonance studies) makes it unlikely (compared to other halides $CdCl_2$:Cu and $CdBr_2$:Cu) that the process of induced absorption occurs due to photostimulated copper charge transfer from singly charged (Cu^+) to doubly charged (Cu^{2+})
- In CdJ_2:Cu crystals, the "blackening" process is caused by the following sequential series of photochemical reactions PCR :
  - photostimulated dissociation of complex centers – impurity trimers due to the athermal release of the substitutional copper ion from the site to the interstitial space
  - thermally stimulated diffusion of impurity interstitial ions to drains – linear defects
  - association (condensation) of impurity centers on linear structural defects in the coagulate – image centers
  - The discoloration of the crystals is caused by the process of thermally stimulated dissociation of the image centers
- The reversibility of the PCR in CdI_2:Cu indicates the possibility of restoring intrinsic-impurity DAD_i-defect complexes at high temperatures.

Thank You for Your attention !