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Photoconductivity and Photoluminescence Spectra of $\text{CdIn}_2\text{S}_4:\text{Cr}$

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Photoconductivity and photoluminescence spectra of undoped and Cr-doped samples of CdIn_2S_4 have been measured.

Ligand-field-induced photoconductivity and photoluminescence have been observed in the Cr-doped sample.

A mechanism of the photoconduction is proposed in conjunction with the luminescence process.

§1. Introduction

Pure and chromium-doped CdIn_2S_4 have been studied by many authors in order to get some insights into the electronic structures of the ferromagnetic spinels such as CdCr_2S_4 .

Cr ion has been known to substitute the In-site and become trivalent when doped into the CdIn_2S_4 crystals.¹⁾ Wittekoek *et al.* observed two absorption peaks at $14,800\text{ cm}^{-1}$ and $18,500\text{ cm}^{-1}$, and assigned them to the ligand-field transitions ${}^4A_{2g} - {}^4T_{2g}$ and ${}^4A_{2g} - {}^4T_{1g}$ of Cr^{3+} ion.²⁻⁴⁾ The crystal-field parameters used for the assignment are $10Dq = 14,900\text{ cm}^{-1}$ and $B = 320\text{ cm}^{-1}$. They also assigned some of the peaks of their Kerr spectrum of CdCr_2S_4 to the ligand-field transitions using parameters $10Dq = 14,900\text{ cm}^{-1}$, $B = 380\text{ cm}^{-1}$, and $C = 3,100\text{ cm}^{-1}$. Larsen and Wittekoek reported the "ligand-field-induced" photoconductivity and luminescence on CdCr_2S_4 .⁵⁾

We have grown single crystals of CdIn_2S_4 and $\text{CdIn}_2\text{S}_4:\text{Cr}$ and have measured photoconductivity and photoluminescence spectra, from which we have observed similar phenomena as reported on CdCr_2S_4 . In this article photoconductivity (PC) and photoluminescence (PL) spectra for undoped and Cr-doped single crystals of CdIn_2S_4 are described and a mechanism of the ligand-field-induced PC observed in the Cr-doped sample is discussed.

§2. Experimental Techniques

Single crystals of undoped CdIn_2S_4 and chromium-doped CdIn_2S_4 (1-5% Cr content) were grown by the chemical transport method

as described in ref. 6.

Electrodes for the photoconductivity measurements were either In-amalgam or evaporated gold with the spacing of about 0.5 mm and dc voltage up to 1.3 V was applied between the electrodes. The photocurrent was measured using the chopped light with frequencies of 5 Hz and 187.5 Hz, and the signal was amplified by a phase sensitive detector.

Measurements were carried out in a temperature range between 77 K and 298 K using a glass cryostat with a temperature controller.

Spectral-intensity correction was done with the aid of the light-intensity spectrum measured by a thermopile. All of the PC data in this paper are normalized to unity at the peak of each spectrum.

For the luminescence measurement a 150 W super high-pressure Hg lamp, a Spex-1800 monochromator and a photomultiplier with S-20 response were employed. Samples were immersed in the dewar with liquid nitrogen or liquid helium.

PL excitation spectrum was measured using a 150 W Xenon illuminator (Varian Inc.) combined with a double-monochromator (Carl-Leiss) as the excitation source and a Nikon P-250 grating monochromator followed by a S-20 photomultiplier as the detection system. Spectral distribution of the light measured by the thermopile was used for the correction.

§3. Photoconductivity Spectra

The photoconduction of the undoped sample is characterized by a large photoresponse and a long recombination lifetime (usually a few

tenth of second) indicating the trapping and the thermal release of photocarriers have important roles on the photoconduction processes.

Therefore we had to carry out the photoconduction measurements at a low chopping frequency; 5 Hz-chopper was employed. PC spectra at 77 K and 298 K are given in Fig. 1. Two photoconductivity-edges can be seen in curve (b)—one at $18,000\text{ cm}^{-1}$, the other at $20,000\text{ cm}^{-1}$. They agree with the energy position of the indirect and direct band gaps reported by Radautsan *et al.*, respectively.⁷⁾

Cr-doped samples show much smaller photoresponse than the undoped ones presumably due to the shortened recombination lifetime of carriers.

In this case we adopted 187.5 Hz as a chopping frequency. The temperature dependence of the PC spectra of a Cr-doped sample is shown in Fig. 2, in which we find at room temperature

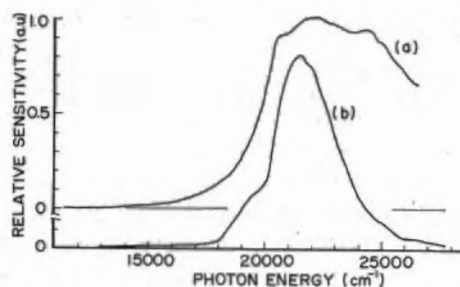


Fig. 1. Photoconductivity Spectrum of CdIn_2S_4 at (a) 298 K and (b) 77 K.

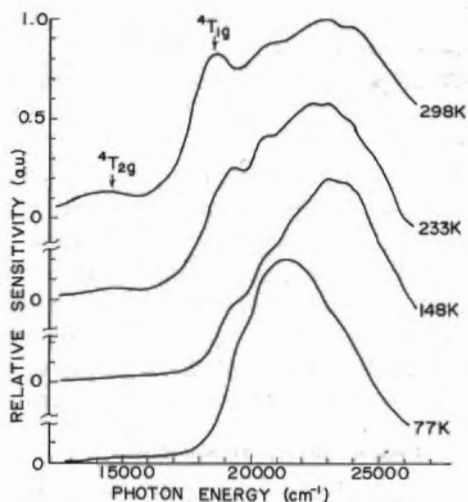


Fig. 2. Temperature variation of photoconductivity Spectrum of $\text{CdIn}_2\text{S}_4:\text{Cr}$.

two PC bands peaked at $14,500\text{ cm}^{-1}$ and $18,500\text{ cm}^{-1}$ in addition to the PC structure associated with the fundamental absorption edge of the host crystal. The energy positions of the additional peaks agree very well with those of the ligand-field transitions of $\text{CdIn}_2\text{S}_4:\text{Cr}$ mentioned in §1. The relative intensity of the ligand-field-induced PC against the absorption-edge-induced PC decreases as the temperature is lowered as seen in Fig. 2.

§4. Photoluminescence Spectra

As illustrated by the curve (a) in Fig. 3 CdIn_2S_4 shows a PL spectrum with a broad maximum around $15,000\text{ cm}^{-1}$ at low temperatures.*

Since the peak position is far below the absorption edge of CdIn_2S_4 , the emission band is considered to be originated from some kinds of imperfections. Czaja *et al.* have pointed out that the partial inversion of Cd and In between tetrahedral(A) and octahedral(B) sites usually occurs in CdIn_2S_4 and have ascribed the broad emission bands below the absorption edge to Cd ion at B-site and In ion at A-site.^{8,9)}

By chromium-doping the emission band loses most of its intensity; instead, a new emission band with several fine-structures appears in the energy region between $12,500$ and $13,000\text{ cm}^{-1}$, as shown by the curve (b) in

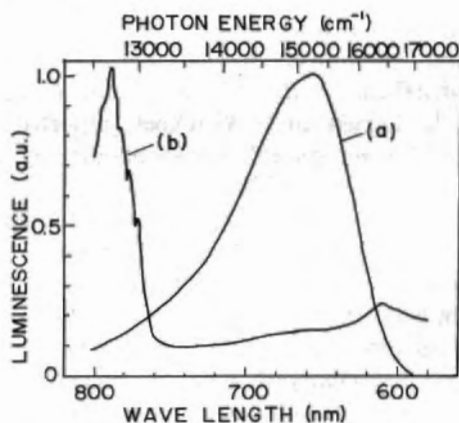


Fig. 3. Photoluminescence Spectrum of (a) CdIn_2S_4 and (b) $\text{CdIn}_2\text{S}_4:\text{Cr}$ at 77 K.

* The PL spectra shown in this figure have not been corrected for the spectral dependence of the photomultiplier sensitivity, so that the observed maximum position does not represent the true peak position of the band. Corrected spectrum should have a maximum about 500 cm^{-1} lower than the observed peak position.

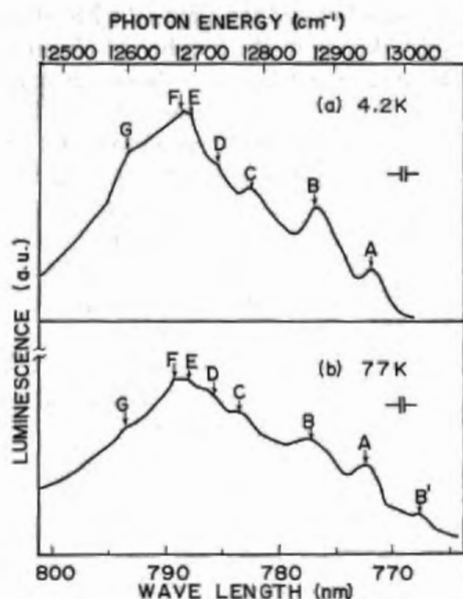


Fig. 4. Photoluminescence Spectrum of $\text{CdIn}_2\text{S}_4:\text{Cr}$ at (a) 4.2 K and (b) 77 K.

Fig. 3. In Fig. 4 are given the details of the new PL spectra at 77 K and 4.2 K. Seven peaks or shoulders (A to G) can be distinguished in the 4.2 K spectrum, whereas 77 K spectrum has an additional peak B' in the higher energy side of A.

In CdCr_2S_4 , a similar band around $13,000\text{ cm}^{-1}$ observed from absorption¹⁰⁾ and emission⁵⁾ experiments has been assigned to the ligand-field transition ${}^4A_{2g} - {}^2E_g$, ${}^2T_{1g}$ (so called R-line) of Cr^{3+} . We adopt the same assignment for the emission band of $\text{CdIn}_2\text{S}_4:\text{Cr}$.

Fine structures of the band may be interpreted as composed of a zero-phonon line and its vibronics. In Table I energy differences of the fine structures measured from A-peak are listed, most of which can be associated with the reported phonon frequencies,¹¹⁻¹⁴⁾ or those multiplied by the integral value. The B' line seen in the 77 K spectrum seems to be a hot emission band, i.e. the electronic transition accompanied by the phonon emission.

The excitation peaks of the Cr^{3+} emission are found at $14,900$, $18,500$ and $22,000\text{ cm}^{-1}$ as shown in Fig. 5. First two of them are identified as the ligand-field transitions ${}^4A_{2g} - {}^4T_{2g}$ and ${}^4A_{2g} - {}^4T_{1g}$ respectively and the last clearly corresponds to the absorption edge of the host crystal.

Table I. Peak energy positions of the fine structures observed in the PL spectrum of $\text{CdIn}_2\text{S}_4:\text{Cr}$. Phonon frequencies are also given for comparison.

Peak energy [cm^{-1}] (77 K)	Energy difference [cm^{-1}]	Phonon frequencies ¹¹⁾ [cm^{-1}]	
		I.R. active phonon (T_{1u}) (85 K)	Raman active phonon (85 K)
B' 13029	76		
A 12953	0		
B 12870	83	71	96 (T_{2g})
C 12771	182	(172) ¹¹⁾	191 (E_g)
D 12723	230		246 (T_{2g})
E 12690	263		
F 12674	279	278	314 (T_{2g})
G 12602	351	345	372 (A_{1g})

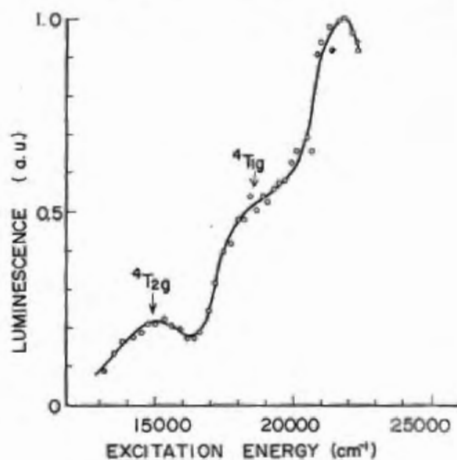


Fig. 5. Excitation spectrum of Cr^{3+} -emission at 77 K.

The temperature behaviors of the ligand-field-induced PL and PC seem to be complementary; at higher temperatures PC is observed but PL does not appear, whereas at lower temperatures PC decreases and PL increases. There is a similarity between the PC spectrum at room temperature (Fig. 2) and the PL-excitation spectrum at 77 K (Fig. 5).

§5. Discussions and Conclusions

The ligand-field transition has long been considered to have essentially no contribution to PC, because of its highly localized nature. It has been turned out, however, that the transition gives rise to PC in many crystals such as $\text{CdIn}_2\text{S}_4:\text{Cr}$, $\text{ZnS}:\text{Co}$,¹⁵⁾ MnS ¹⁶⁾ and CdCr_2S_4 .⁵⁾ This fact suggests that the ligand-field-induced PC is rather a popular phenomenon in the chalcogenides. Therefore it has a

significant physical meaning to clarify the mechanism how the ligand-field absorption gives rise to the photoconduction, since it gives us a clue to understanding of the linkage between localized and band systems.

In the following we propose a speculation on the mechanism of the ligand-field-induced PC in $\text{CdIn}_2\text{S}_4:\text{Cr}$. In Fig. 6 is illustrated a schematic energy diagram of $\text{CdIn}_2\text{S}_4:\text{Cr}$, the left hand side of which represents the 'many-electron' energy-level scheme of Cr^{3+} in the octahedral site, while the right hand side of which gives a 'one-electron' picture of the CdIn_2S_4 itself. The energy levels of Cr^{3+} are determined from the absorption spectrum reported by Wittekoek *et al.* and also from our emission spectrum described in §4. V.B. and C.B. in the right scheme represent the valence band and the conduction band respectively. About $5,000\text{ cm}^{-1}$ below the bottom of C.B. we put unidentified intermediate levels 'I.L.', the presence of which is determined from the observation of the broad emission band in undoped CdIn_2S_4 as shown in Fig. 3. As pointed out in §4, partial inversion between A and B sites usually occurs in CdIn_2S_4 . Moreover ternary sulfides often contain cation or anion vacancies, stacking faults and dislocations. It is quite probable to ascribe the origin of I.L. to one or two of these imperfections.

It should be noted that any transition

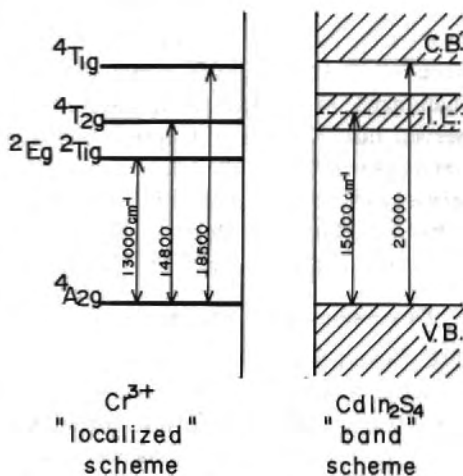


Fig. 6. A schematic diagram of the electronic structures of $\text{CdIn}_2\text{S}_4:\text{Cr}$ and a mechanism of the ligand-field-induced photoconductivity. left scheme-many-electron energy levels of Cr^{3+} ion. right scheme-one-electron energy bands of CdIn_2S_4 .

between the left and the right schemes of Fig. 6 brings a change in the number of electrons of the left system, which makes the energy diagram invalid. Therefore no transition should be imagined between these diagrams. However, these two systems are not completely independent; 3d-electrons relating to the 'many electron levels' are hybridized with 3p-electrons of the anion, which form simultaneously the valence band orbitals. Therefore there may occur a transfer of excitation energy between these two systems. An evidence of such energy transfer is provided by the fact that the broad emission band around $15,000\text{ cm}^{-1}$ of undoped CdIn_2S_4 is almost quenched by chromium-doping, giving rise to the Cr^{3+} R-line emission around $13,000\text{ cm}^{-1}$ as seen in Fig. 3; i.e. energy-transfer has occurred from the right (I.L.) to the left (${}^2E_g, {}^2T_{1g}$).

With these preparations we now proceed to propose a mechanism of the ligand-field-induced PC in $\text{CdIn}_2\text{S}_4:\text{Cr}$, which is illustrated in Fig. 7(a).

- (1) Electrons are excited from ${}^4A_{2g}$ to ${}^4T_{2g}$ (or ${}^4T_{1g}$) by absorption of light.
- (2) The excited electrons relax to the ground state without radiation.
- (3) Giving the energy to the right or the 'one electron' system through the energy transfer process denoted by a broken line in the figure.
- (4) Electrons are excited from the V.B. to I.L. by absorbing the transferred energy.
- (5) Some of the electrons populated in I.L. are excited thermally into C.B.
- (6) The excited electrons migrate in C.B. and induce photoconduction.
- (7) They find recombination centers somewhere in the crystal and recombine with holes.

At low temperatures thermal excitation process (5) becomes less frequent and ligand-field-induced PC becomes less prominent; so that electrons which remain occupying the I.L. prevent further occurrence of the energy-transfer process (3). In this case processes are (1)→(2')→(3') of Fig. 7(a).

- (1) Electrons in the Cr^{3+} center are excited to ${}^4T_{2g}$ (or ${}^4T_{1g}$).
- (2') Transition occurs from ${}^4T_{2g}$ or ${}^4T_{1g}$ to the lowest excited states ${}^2E_g, {}^2T_{1g}$ with the aid of the spin-orbit interaction.

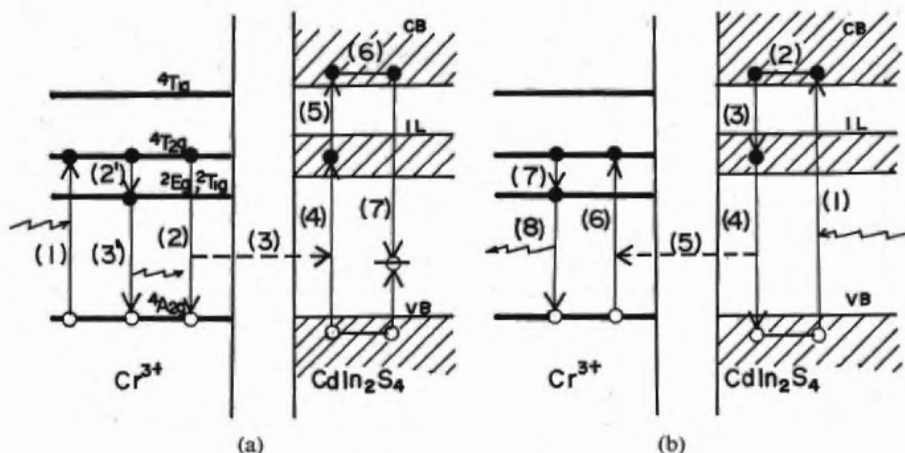


Fig. 7. Schematic diagrams for the proposed mechanisms of (a) the ligand-field-induced PC; (1) to (7) and the ligand-field-induced PL; (1) (2') (3') (b) the R-line emission by the absorption edge excitation: (1) to (8).

(3') ${}^2E_g, {}^2T_{1g}$ relaxes to the ground state ${}^4A_{2g}$ emitting the light; R-line emission band shown in Fig. 4.

As illustrated in Fig. 5 the R-line emission also occurs by stimulating the conduction band. This phenomenon can be understood by the processes (1) to (8) illustrated in Fig. 7(b).

- (1) Electron in V.B. is excited into C.B. by light absorption.
- (2) Electrons migrate in C.B. resulting in the photoconduction (see 77 K spectrum of $\text{CdIn}_2\text{S}_4:\text{Cr}$ in Fig. 2).
- (3) They are trapped by I.L. levels.
- (4) Electrons occupying the I.L. recombine with V.B. holes through the radiationless transition.
- (5) The energy is transferred to the left system.
- (6) The ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition occurs in the Cr^{3+} level-scheme.
- (7) Electrons in ${}^4T_{2g}$ relax to ${}^2E_g, {}^2T_{1g}$ state.
- (8) ${}^2E_g, {}^2T_{1g}$ levels relax to ${}^4A_{2g}$ emitting the light.

The mechanisms shown in Fig. 7(a) and (b) can, thus, explain most of the experimental results on PL and PC observed in $\text{CdIn}_2\text{S}_4:\text{Cr}$ without inconsistency. However, for full understanding of the mechanisms further theoretical analysis on a microscopic origin of the energy transfer process between the localized and the band schemes is required. The authors have no intention to claim that the above-postulated mechanism is always valid for any case of the ligand-field-induced PC previously reported.

There is still a possibility of an 'intrinsic' mechanism as suggested in ref. 16.

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