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Influence of indium dilution level on magnetic properties and photoconductivity of $Cd_{1-y}Cr_{2-2x}In_{2x+y}Se_4$ magnetic semiconductors

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Magnetic semiconductors of $CdCr_2Se_4$ diluted by indium belong to the class of soft magnetic materials. The amount of indium alters the energetic structure of chalcogenide spinel. For $CdCr_2Se_4$:In magnetic semiconductor the state with reentrant transition (REE) is achieved. In the case of $Cd_{1-y}Cr_{2-2x}In_{2x+y}Se_4$ dilution, the spin glass (SG) state and the randomly canted state is obtained. Chalcogenide spinel could be used as the element of a near-infrared detector. Then the photoconductivity properties – the voltage sensitivity versus the light wavelength – are of interest. This parameter is also affected by the dilution level. The polycrystalline $Cd_{1-y}Cr_{2-2x}In_{2x+y}Se_4$ thin films obtained by rf-sputtering technique were studied. It was found that the dependence of voltage sensitivity of the photoresponse on the wavelength differs significantly for samples with REE and in the SG state. For both types of magnetic ordering, the photoresponse below the critical magnetic temperature is larger than above it.

Key words: *magnetic semiconductor; reentrant transition; spin glass; photoconductivity*

1. Introduction

The energy-band structure of $CdCr_2Se_4$ magnetic semiconductors is influenced by long-range magnetic order. The top of the valence band and the bottom of the conduction band are split due to “spin up” and “spin down” configurations (Fig. 1) [1]. There is a non-zero density of states in the forbidden gap of the doped $CdCr_2Se_4$: In, which is presented in Fig. 2 [2]. From the experiment data it is known that the samples:

- $CdCr_2Se_4$ and $CdCr_2Se_4$: In are in the state with reentrant transition (REE),
- $CdCr_{2-2x}In_{2x}Se_4$ (In substitutes Cr) are in spin glass state (SG),
- $Cd_{1-y}In_yCr_2Se_4$ (In substitutes Cd) are in spin glass state,
- $Cd_{1-y}Cr_{2-2x}In_{2x+y}Se_4$ (In substitutes Cd and Cr) are in the randomly canted state [3, 4].

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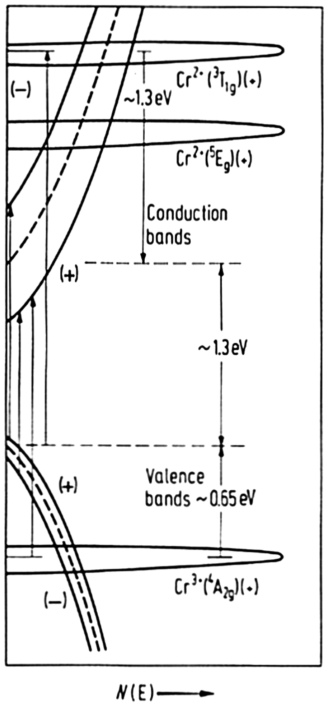

Fig. 1. Energy level diagram of $CdCr_2Se_4$ at $T < T_c$ [1]. Conduction and valence bands at $T > T_c$ are indicated by dashed lines

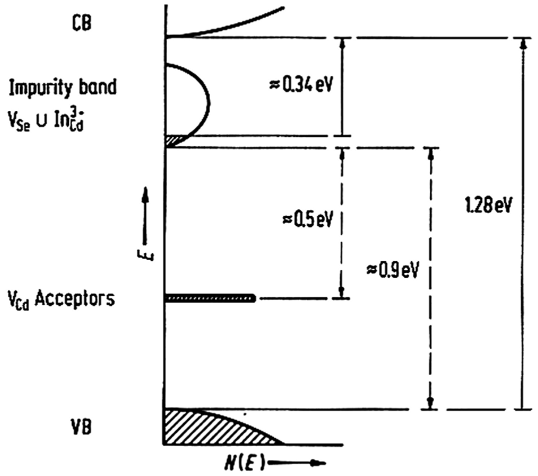

Fig. 2. Tentative energy level diagram at $T = 80$ K for In-doped n-type $CdCr_2Se_4$ [2]. $N(E)$ is the density of states, V_{Cd} is the Cd vacancy. Impurity band is formed by Se vacancies and In^{3+} ions on Cd-lattice sites

We investigated thin films of chalcogenide magnetic semiconductors obtained by the rf-sputtering technique. The magnetic state was classified based on the temperature dependence of the magnetization M and unidirectional magnetic anisotropy H_{an}. Both parameters were determined from the ferromagnetic resonance experiments (FMR).

The modified energetic structure affects the character of voltage sensitivity in the photoconductivity measurements. The photoconductivity measurements were carried out in the temperature range of 77–300 K. A different behaviour of a voltage sensitivity for the magnetic semiconductors with REE transition in comparison with the samples in SG state was observed.

2. Experiment

The chalcogenide semiconductor thin-film layers were fabricated by the co-sputtering from the three powdered cathodes (CdSe, Cr, Cr_2Se_3) on Corning glass substrates with controlled temperature. The dilution level was controlled with the amount of uniformly spotted pieces of In_2Se_3 on the Cr_2Se_3 cathode. Polycrystalline layers were obtained after a heat treatment process. Composition of the samples was analysed using X-ray microprobe and the thickness was measured with Talysurf 4 profilometer. Samples were 300–800 nm thick. The technology details are presented in the paper [5]. The samples of $CdCr_{2-2x}In_{2x}Se_4$ thin films with $0 < 2x < 0.70$ and $y = 0$ have been investigated. The results for samples with $y > 0$ were presented earlier [3].

The dependencies of magnetization M and of unidirectional magnetic anisotropy field H_{an} on temperature were considered as the criteria of magnetic ordering. Both magnetic parameters were determined from the ferromagnetic resonance (FMR) data at X-band for perpendicular and parallel geometry and for temperature range from 4 to 125 K. The dispersion relation for uniform mode has the form [6]:

- for the perpendicular geometry (the external magnetic field is perpendicular to the film plane)

$$\frac{\omega}{\gamma} = H_{\perp} + H_{an} - 4\pi M \tag{1}$$

- for the parallel geometry (the external magnetic field is within the film plane)

$$\left(\frac{\omega}{\gamma}\right)^2 = (H_{\text{II}} + H_{an})(H_{\text{II}} + H_{an} + 4\pi M) \tag{2}$$

where $\omega = 2\pi\nu$, ν – the microwave frequency, γ – the gyromagnetic factor, $H_{\perp}$ and H_{II} – resonance fields of the uniform mode for the perpendicular and parallel geometry, respectively. Both equations are applied to determine $M(T)$ and $H_{an}(T)$ when the temperature dependencies of $H_{\perp}$ and H_{II} are known.

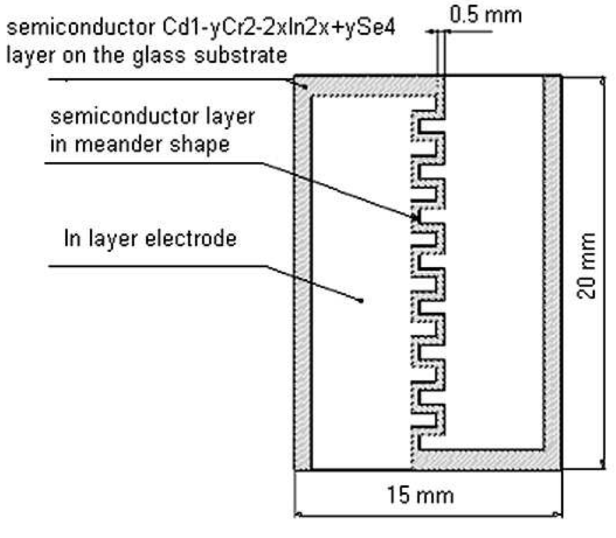

Fig. 3. Thin film sample with the indium electrodes system

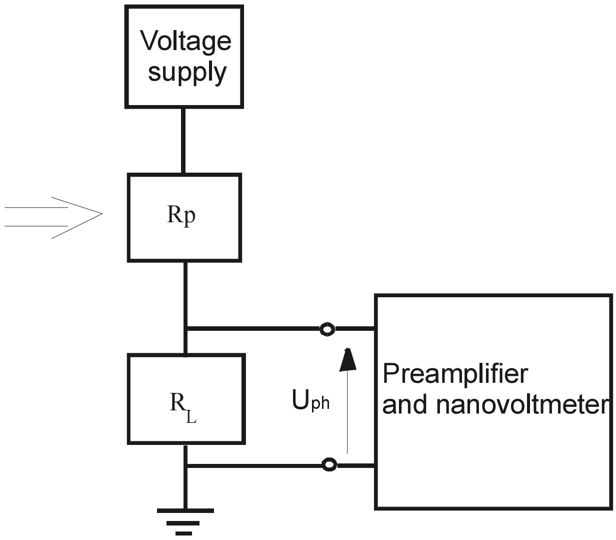

Fig. 4. Scheme of the voltage photoresponse measurements

To prepare the sample for the photoconductivity measurements, indium electrodes were carefully placed on the samples. Indium layer was evaporated on the semiconductor thin film to obtain a proper meander shape (Fig. 3). Such an action lowers the resistance R_p of the samples, which is important in a photoresponse signal. The photosignal was detected as a voltage response U_{ph} on the load resistor R_L, as is shown in Fig. 4. The illuminating light within the wavelength range from 400 nm to 1000 nm was chopped with the frequency of 90 Hz. The measurements were carried out under the condition $R_L = R_p$. The samples of 0.02–2 MΩ resistance (at 298 K) were biased with 30 V voltage. The temperature was changed from 77 K to 300 K. The voltage photo-signal was detected using a Selective Nanovoltmeter Lock-in SR830.

3. Results

The temperature dependencies of magnetization M and the unidirectional magnetic anisotropy field H_{an} obtained from the FMR experiment at X-band for thin films of $CdCr_2Se_4$:In (REE) and $CdCr_{1.7}In_{0.3}Se_4$ (SG) are shown in Figs. 5 and 6. Spectral sensitivity R_v of the voltage response is obtained from the photoconductivity measurements of the $Cd_{1-y}Cr_{2-2x}In_{2x+y}Se_4$ thin films. The data for $CdCr_2Se_4$:In (REE) and $CdCr_{1.9}In_{0.1}Se_4$ (SG) are presented. The experimental data are illustrated as a voltage sensitivity of the photoresponse vs. the wavelength (Figs. 7a 7b) for different temperatures. The transitions are indicated in the figures with dotted lines. The differences in the character of spectral sensitivity are observed depending on the temperature. Figures 8a and 8b present the voltage sensitivities for the temperatures $T < T_c$ and $T > T_c$, respectively.

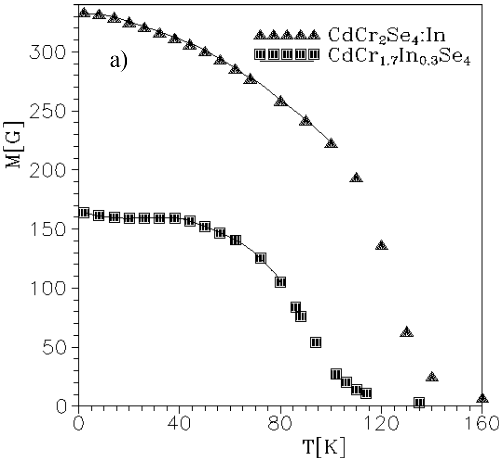

Fig. 5. Dependence of magnetization on temperature

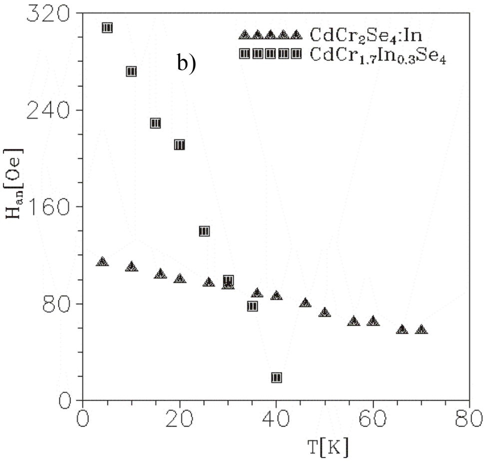

Fig. 6. Dependence of H_{an} on temperature

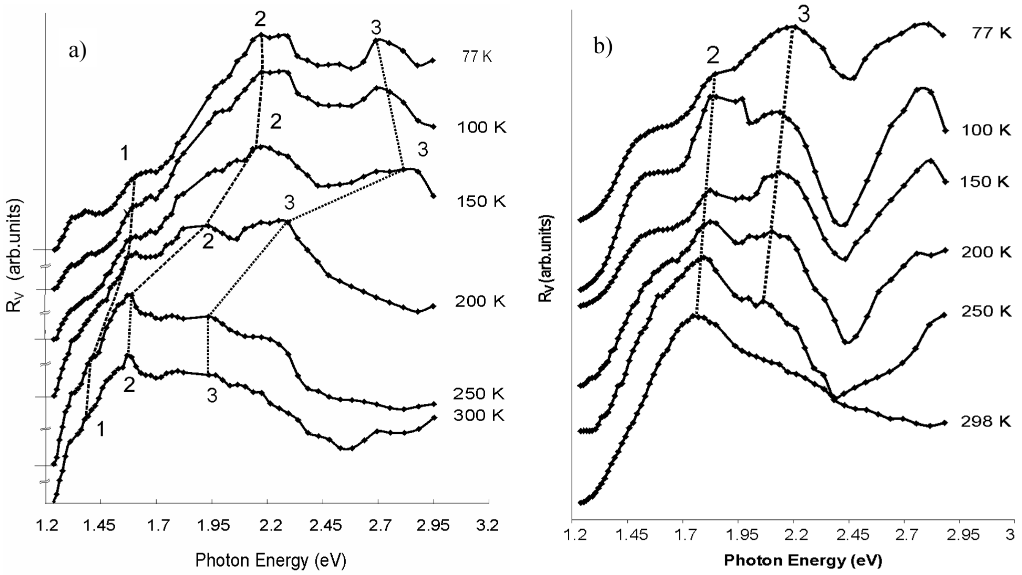

Fig. 7. The voltage sensitivity vs. the photon energy of the incident light for:
a) the undoped $CdCr_2Se_4$ thin film, b) the $CdCr_{1.9}In_{0.1}Se_4$ thin film

4. Discussion

4.1. Magnetic parameters

For both types of magnetic ordering (REE and SG), the dependence of magnetization on temperature does not obey the Bloch law. For the state with REE transition, the Bloch law is modified due to a non-zero density of states in the energy gap. The dependence of magnetization on temperature is described by Eq. (3) [6]

$$\frac{M(0)-M(T)}{(0)}=BT^{3/2}\sum_{n=1}^{\infty}\frac{\exp\left(-n\Delta_r/k_BT\right)}{n^{3/2}} \tag{3}$$

where:

$$B=\xi\cdot\frac{3}{2}\cdot\frac{g\mu_B}{M(0)}\cdot\left(\frac{k_B}{4\pi D}\right)^{3/2}$$

$\xi\cdot(3/2)$ stands for the Riemann ξ-function, Δ_r is the energy gap and D is the spin-wave stiffness constant.

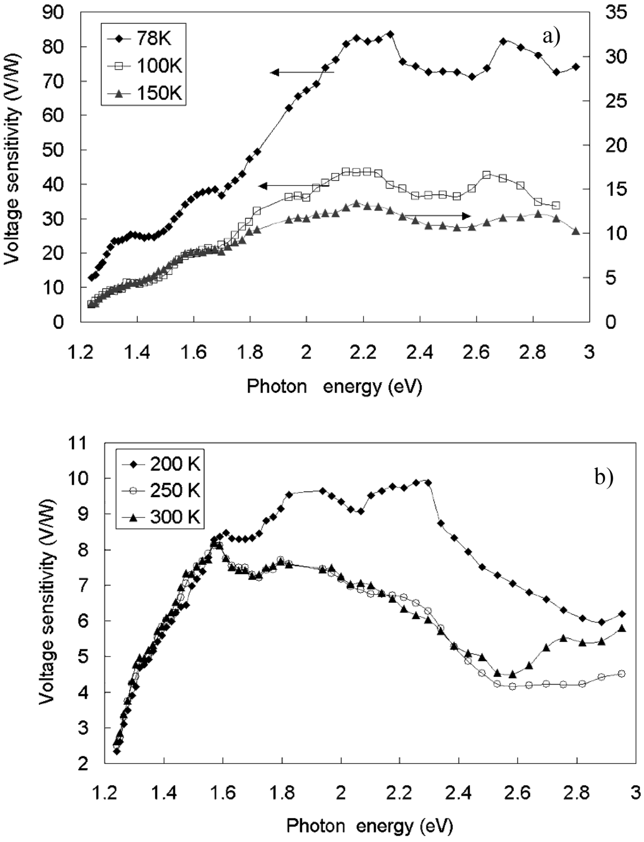

Fig. 8. The voltage sensitivity of the undoped $CdCr_2Se_4$ thin film (REE):
a) for the temperatures below the Curie temperature, b) for the temperatures higher than T_c

For the SG state, the dependence $M(T)$ is described by the equation

$$\frac{M(0)-M(T)}{M(0)}=\frac{C_S}{\exp(\Delta_S/kT)-1} \tag{4}$$

where C_s is responsible for the density of states in the energy gap and Δ_S is a measure of the intercluster interaction. The temperature dependence of magnetization presented in Fig. 5 is in a good agreement with the theoretical prediction for samples with REE transition $CdCr_2Se_4$:In and also for $CdCr_{1.7}In_{0.3}Se_4$ SG state. Following Eq. (3), the theoretical calculations for REE are presented for fitting parameters $M(0)$ = 330 G and Δ_r = 10 K, while for SG (Eq. (4)) $M(0)$ = 162 G, C_s = 11.8 and Δ_s = 270 K. The values of $M(T)$ calculated theoretically are represented by solid lines. It is seen in Fig. 6 that the unidirectional magnetic anisotropy field H_{an} in $CdCr_{2-2x}In_{2x}Se_4$ thin films decreases with increasing temperature and depends on the amount of In (H_{an} increases with increasing dilution level). H_{an} depends on the field-induced remanent magnetization and keeps the direction of the cooling field, which means that the spins have some memory of the cooling field direction. H_{an} is influenced by the dilution level and, being related to the induced magnetization, is also temperature-dependent. The dependence $H_{an}(T)$ is available only from the experimental data, since no comprehensive theoretical model of the temperature dependence of H_{an} is known.

4.2. Photoconductivity

The voltage sensitivity of undoped $CdCr_2Se_4$ thin films (REE) is presented in Fig. 7a. The transition is marked by three lines: for the energy about 1.6 eV (line 1), for the energy about 2.2 eV (line 2) and for the energy about 2.7 eV (line 3). Line 1 exhibits a blue shift. Line 2 also exhibits a blue shift which is significant for $T > T_c$. Line 3 exhibits a more complicated energy transition: we have a blue shift for $T > T_c$ and a red shift for $T < T_c$. The voltage sensitivity of diluted (SG) samples, $CdCr_{1.9}In_{0.1}Se_4$, is presented in Fig. 7b. Two transitions are observed for the energy about 1.8 (line 1) and 2.2 eV (line 2). For both cases a blue shift is observed.

Those shifts for samples with REE transition as well as for the samples with SG state result from a mechanism related to the magnetic ordering and interatomic exchange interaction [7–9].

For all samples investigated, the spectral response – voltage sensitivity is about one order of magnitude higher below the Curie temperature than above T_c. As an example, we present the data for the sample with REE transition (Figs 8a, b). For the potential application as the photodetectors, magnetic semicondutors working below T_c could be taken into consideration. The voltage sensitivity and its maximum are influenced by the dilution level.

5. Conclusions

Magnetic semiconductors of $Cd_{1-y}Cr_{2-2x}In_{2x+y}Se_4$ chalcogenide spinel exhibit different types of magnetic ordering, depending on the dilution level. For the samples $CdCr_2Se_4$: In, the state with REE is obtained, for diluted samples an SG state appears. We classify the magnetic states of thin films of $Cd_{1-y}Cr_{2-2x}In_{2x+y}Se_4$ based on the dependence of the magnetization and the unidirectional magnetic anisotropy field on the temperature and concentration.

The photoconductivity measurements show the influence of the type of magnetic ordering on the character of voltage sensitivity. We can conclude from our experimental results that the voltage sensitivity is higher in the case of state with reentrant transition than for the spin glass state. These differences are more pronounced below the critical magnetic temperature.

The voltage sensitivity exhibits its maximum at different energies, depending on the temperature: it appears in the high-energy region below T_c shifting towards lower energies above T_c. The exchange interactions in the magnetic semiconductor result in shifts of the energy transitions when the temperature changes. When the amount of indium increases, the maximum sensitivity shifts to the higher energies. Finally we can conclude that there is a possibility of controlling parameters of $CdCr_{2-2x}In_{2x}Se_4$ near-infrared detectors with the temperature and dilution level.

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