Anomalies of the photoconductivity in the region of the Curie point of the compound CdCr₂Se₄ weakly doped with gallium

K. P. Belov, L. I. Koroleva, S. D. Batorova, M. A. Shalimova, V. T. Kalinnikov, T. G. Aminov, G. G. Shabunina, and N. P. Shapsheva

Moscow State University (Submitted July 3, 1974) ZhETF Pis. Red. 20, 191-195 (August 5, 1974)

We have investigated the photoconductivity of the single-crystal semiconductors $\operatorname{Cd}_{1-x}\operatorname{Ga}_x\operatorname{Cr}_2\operatorname{Se}_4$ (x=0.007 and x=0.01) as a function of the temperature and of the magnetic field. A minimum of the photocurrent and a maximum of the negative photomagnetoresistance was observed in the region of the Curie temperature. Three possible causes of these extrema are suggested: 1) capture of the photoelectrons by magnetic polarons in the region of the Curie point; 2) scattering of the photoelectrons by magnetic polarons; 3) spin-disordered scattering of the photoelectrons in the region of the Curie point.

We have investigated the photoconductivity of single-crystal ferromagnetic semiconductors with composition $Cd_{1-x}Ga_xCr_2Se_4$ (x=0.007 and x=0.01) as a function of the temperature and of the magnetic field. We observed various anomalies of the photoconductivity of these compounds in the region of the Curie point.

The single crystals were grown by the method of chemical transport reactions. The samples were regular octahedra with edge dimensions from 0.3 to 1 mm. The Ohmic contacts were produced by fusing-in indium or by rubbing-in indium-gallium paste, and the resistance of the contacts was $<\!10\%$ of the sample resistance.

The photoconductivity was measured by the voltammeter method, using an electrostatic voltmeter, since the resistance of the samples was $\leq 10^8 \Omega$. The accuracy of the measurement of R was better than 6%. During the time of the measurements the sample was in vacuum and was illuminated with an incandenscent lamp whose power was varied in the range from 0 to 400 W. The cryostat was carefully darkened when the dark current was measured. A rough estimate of the photoconductivity region, obtained with the aid of factory-certified glasses, was 100-1400 nm (1.24-0.886 eV). To prevent photoconductivity in the contacts, the latter were coated with black lacquer. In this case the photoconductivity remained the same in the entire investigated temperature interval as in the case of uncovered contacts. The differences in the chemical and mechanical surface finish caused likewise no changes in the photoconductivity. We investigated also the effect of light of the conductivity of undoped CdCr2Se4. In the entire investigated temperature interval, the photocurrent did not exceed 20% of the dark current, and it appears therefore that the photoconductivity investigated by us was of the impurity and volume type.

Figure 1a shows the temperature dependence of the photocurrent density at a voltage 30 V, for a sample

with x=0.01, at difference powers of the illuminating lamp. The same figure shows the density of the dark current (dashed curve). We see that in the region of the Curie temperature (120.5 °K) the j(T) curves have deep minima. Below the Curie temperature, e.g., at 77 °K, the photocurrent is higher by approximately two orders of magnitude than the dark current, whereas above the Curie point it is smaller by approximately one order.

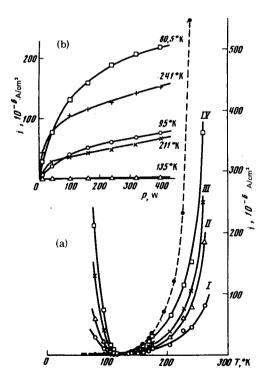


FIG. 1. ${\rm Cd_{0.99}Ga_{0.01}Cr_2Se_4}$ sample: a) temperature dependence of the photocurrent density j (voltage 30 V) at different illuminating lamp powers: I-W, II-40 W, III-100 W, IV-400 W. The dashed line shows the density of the dark current; b) dependence of the photocurrent on the lamp power at various temperatures.

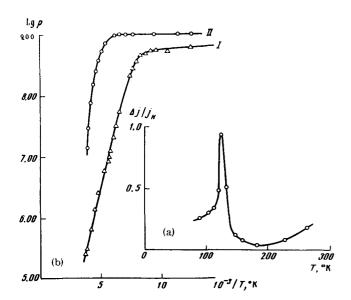


FIG. 2. a) $Cd_{0.99}Ga_{0.01}Cr_2Se_4$: temperature dependence of the relative change of the photocurrent in a magnetic field $\Delta j/j_H$ (H=6.65 kOe). b) Dependence of the logarithm of the resistivity ρ on the reciprocal temperature of samples with compositions $Cd_{0.99}Ga_{0.01}Cr_2Se_4$ (I) and $Cd_{0.993}Ga_{0.007}Cr_2Se_4$ (II).

Figure 1b shows the dependence of the photocurrent on the lamp power for different temperatures. The curves for the composition with x = 0.007 are similar, but the photoconductivity turns out to be lower by 1-0.5 orders than for the composition with x = 0.01.

Figure 2a shows the temperature dependence of the relative change of the photocurrent in a magnetic field, $\Delta j/j_H$ (at H=6.65 kOe). Here j_H is the photocurrent density in the magnetic field, and $\Delta j = j_H - j_{H=0}$. It is easily seen that the ratio $\Delta j/j_H$ is none other than the magnetic resistance of the sample relative to the photoelectrons, taken with the opposite sign. As seen from the figure, $\Delta j/j_H$ has a maximum in the regions of the Curie temperature; the photocurrent increases here by almost a factor of two when the magnetic field H=6.65 kOe is turned on.

Figure 2b shows the dependence of the logarithm of the resistivity ρ of the investigated samples on the reciprocal temperature. The resistivity was defined as the voltage applied to the sample divided by the dark-current density multiplied by the sample length. It is seen from the figure that at the Curie point the lines $\log \rho(1/2)$ T) have sharp kinks, but the maximum obtained in[1] for a hot-pressed Cd_{0.98}Ga_{0.02}Cr₂Se₄ sample was not observed here.

We believe that the effect observed by us, namely the decreases of the photoconductivity in the region of the Curie point, is due mainly to the onset of magnetopolaron states, theoretically predicted in [2-4], near the Curie point. It appears that much below the Curie point the irregular ions or lattice defects serve as trapping centers for the photoelectrons, whereas in the Curie region these ions become recombination centers—the photoelectrons are localized in the region of the impurity ions and maintain the magnetic order around these ions. The scattering of photoelectrons by magnetic polarons, which was predicted theoretically in [5] is also possible. This would explain the strong influence of the magnetic field in the region of the Curie point on the photocurrent, which prevents the destruction of the magnetic long-range order.

Studies of the photoconductivity [6,7] and of the absorption and reflection of light[8,9] in pure and doped InCdCr₂Se₄ have revealed in the main two absorption peaks: one narrow (I) at 1.2-1.3 eV, and the other smeared at 1.8-2 eV (II). Peak II is usually regarded as the width of the forbidden band. The first narrow peak has a rather large red shift (~0.2 eV when the temperature is lowered from 150 to 77 °K).

It appears that the photoconductivity described in the present paper is due to absorption in the region of the peak I.

The red shift of peak I also contributes to a decrease of the photocurrent when the Curie point is approached from the low temperature side, but the increase of the photocurrent above the Curie point cannot be connected with peak I, since its blue shift is extremely small.

The photoconductivity in the region of the Curie point can also be decreased by the spin-disordered scattering considered by Haas[10] in order to explain the resistance maximum at the Curie points of n-type CdCr2Se4 and CdCr₂S₄.

In conclusion, we are grateful to E.L. Nagaev and A.P. Grigin for a discussion of the work.

¹C. Haas, A.M.J. G. van Run, P.F. Bongers, and W. Albers, Solid State Comm. 5, 657 (1967).

²A. Vanase and T. Kasuya, J. Phys. Soc. Japan 25, 1025 (1968).

³M. A. Krivoglaz and A. A. Trushchenko, Fiz. Tverd. Tela 11, 3119 (1969) [Sov. Phys.-Solid State 11, 2621 (1970)].

⁴E. L. Nagaev, Zh. Eksp. Teor. Fiz. 56, 1013 (1969) [Sov. Phys.-JETP 29, 545 (1969)]; Fiz. Tverd. Tela 11, 3438 (1969) [Sov. Phys.-Solid State 11, 2899 (1970)].

⁵A.P. Grigin and E.L. Nagaev, ZhETF Pis. Red. 16, 438 (1972) [JETP Lett. 16, 312 (1972)].

⁶K. Sata and T. Teranishi, J. Phys. Soc. Japan 29, 523

⁷A. Amith and S. B. Berger, J. Appl. Phys. 42, 1472 (1971). ⁸G. Harbeke and H.W. Lehmann, Solid State Comm. 8, 1281 (1970).

⁹G. Harbeke and H. Pinch, Phys. Rev. Lett. 23, 438 (1966).

¹⁰C. Haas, IMB J. Res. Dev. 14, 282 (1970).