Energy band structure and anomalies of the photoconductivity, electrical resistivity, and magnetoresistance of chalcogenide compounds $Cd_{1-x}Ga_xCr_2Se_4$

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An experimental study was made of the photoconductivity, electrical conductivity, magnetoresistance, and photomagnetoresistance of $Cd_{1-x}Ga_xCr_2Se_4$ single crystals ($0 \leq x \leq 0.091$). In the range $x \leq 0.01$, the photoconductivity in the ferromagnetic state was two or three orders of magnitude higher than the dark conductivity. The temperature dependence of the photoresistivity had a maximum in the region of the Curie point, whereas the dark resistivity ρ_d had only a kink in the dependence $\rho_d(T)$. The photoresistivity was affected strongly by a magnetic field, whereas this field did not influence ρ_d. When the amount of gallium was increased, the photoconductivity disappeared rapidly and was not observed in compositions with $x \geq 0.019$. The disappearance of the photoconductivity was accompanied by a maximum of the dependences $\rho_d(T)$ and the resistivity was then affected strongly by a magnetic field. The anomalies observed in samples with low concentrations of gallium were attributed to the photogeneration of magnetic polarons, whereas the anomalies observed at high gallium concentrations were explained by fluctuations of the magnetization due to fluctuations of the carrier density. Such carrier states were predicted in theoretical papers of Yanase, Kasuya, Krivoglaz, Nagaev, and Grigin (1965–1972). Some hypotheses were made about the possible band structure of the investigated materials and about the nature of the photoferromagnetic effect observed by other workers in samples of the same compositions.

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We reported earlier[1] a study of the photoconductivity of $Cd_{1-x}Ga_xCr_2Se_4$ spinel crystals lightly doped with Ga ($x = 0.007$ and 0.01). We extended this study to the temperature dependences of the photoconductivity, resistivity, and magnetoresistance of the same compound with larger amounts of gallium ($x \leq 0.091$). Single crystals were grown from molten solutions. The samples were regular octahedra with an edge from 0.3 to 1 mm. Ohmic contacts were formed by alloying with indium or by rubbing-in an indium–gallium paste; the contact resistance was less than 10% of the resistance of the sample. The single-phase nature of the samples was established by x-ray diffraction to within 2.5%. The gallium concentration was determined by the atomic absorption method.

The Curie temperature of all the investigated compositions was deduced from the magnetization curves by the method of thermodynamic coefficients.[2] The magnetization was determined with a vibration magnetometer. The Curie temperature was found to be independent of the composition and it was within the range 134.5–142.5 °K.

The electrical resistivity and photoconductivity were measured by the voltammeter method using an electrostatic voltmeter since the resistance of some of the samples was of the order of 10^8 Ω. A TR-1452 picovoltmeter–nanoammeter was used to measure the current. The measurements were made to within 6%. An incandescent lamp, whose power was varied from 0 to 400 W, was used to generate the photoconductivity in a sample kept in vacuum.

In measurements of the dark current, a cryostat was carefully screened from the light. The range of wavelengths in which the photoconductivity was observed was estimated roughly with calibrated glass filters. At 77 °K, the photoconductivity range was 1000–1400 μ (1.24–0.886 eV).

Contact photoconductivity was avoided by covering the contacts with a black lacquer. It was found that, throughout the investigated temperature range, the photoconductivity was the same with contacts covered or exposed. Various chemical and mechanical surface treatments also had no influence on the photoconductivity. We investigated additionally the effect of illumination on the conductivity of undoped $CdCr_2Se_4$. Throughout the range of temperatures employed, the photocurrent in $CdCr_2Se_4$ represented no more than 20% of the dark current so that we concluded that the observed photoconductivity was a bulk effect associated with the Ga^{3+} ions.

A minimum of the photocurrent in the vicinity of the Curie point was observed in our earlier study[1] of samples with small amounts of gallium ($x = 0.007$ and 0.010). In the present study, we determined the influence of illumination and temperature on the resistivity of one of these samples (Fig. 1). We found that illumination of a sample in the ferromagnetic state reduced the resistivity by two or three orders of magnitude. The resistivity ρ of an illuminated sample had a maximum in the region of the Curie point, whereas the dark resistivity ρ_d had no such maximum but only a kink near the Curie point. Below the Curie point, the dark resistivity (curve 5) was practically independent of temperature. The temperature dependences of ρ_d of the samples with $x = 0.007$ and $x = 0.010$ were very similar to the dependence $\rho(T)$ of pure $CdCr_2Se_4$ shown in Fig. 2 ($x = 0$).

We determined the temperature dependence of the relative change in the photocurrent $\Delta j / j_H$ ($\Delta j = j_H - j_{H=0}$)
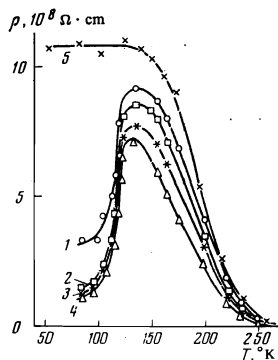
FIG. 1. Dependences of the resistivity of a sample with $x = 0.007$ on temperature and power supplied to an illumination source (incandescent lamp). Curve 1 was obtained for the power $P = 10$ W, curve 2 for $P = 80$ W, curve 3 for $P = 160$ W, curve 4 for $P = 340$ W, and curve 5 for $P = 0$.

FIG. 3. Temperature dependence of the relative change in the photocurrent in a magnetic field $H = 6.65$ kOe applied to $Cd_{0.99}Ga_{0.01}Cr_2Se_4$.

in a magnetic field $H = 6.65$ kOe applied to a sample with $x = 0.01$ (Fig. 3). The ratio $\Delta j/j_H$ was simply the magnetoresistance of a sample due to photoelectrons but with its sign reversed. It is clear from Fig. 3 that the value of $\Delta j/j_H$ had a maximum in the region of the Curie point; at this maximum, the photocurrent increased almost twofold on the application of a magnetic field $H = 6.65$ kOe. On the other hand, the dark current was hardly affected by a magnetic field. For example, the application of a field $H = 6.65$ kOe changed the dark resistivity by an amount smaller than the experimental error in the range from 77 to 273 °K.

An increase in the amount of gallium caused a rapid fall of the photoconductivity; the photoconductivity was hardly observed in samples with $x \geqslant 0.019$. On the other hand, there was no clear correlation between the relative magnitude of the photoconductivity and the amount of gallium. However, the lower the ratio of the photocurrent to the dark current, the stronger was the maximum of $\rho_d(T)$ in the region of the Curie point (Fig. 2). In addition to the maximum in the dependence $\rho_d(T)$ of the samples with high gallium concentrations, the dark resistivity was now affected strongly by a magnetic field. For example, in the case of a sample with $x = 0.019$, the magnetoresistance in a 6.65 kOe field was of the order of 0.8 in the region of the Curie point. In the case of a sample with $x = 0.091$, a field of 6.65 kOe reduced the resistivity almost twofold near the Curie point (Fig. 4).
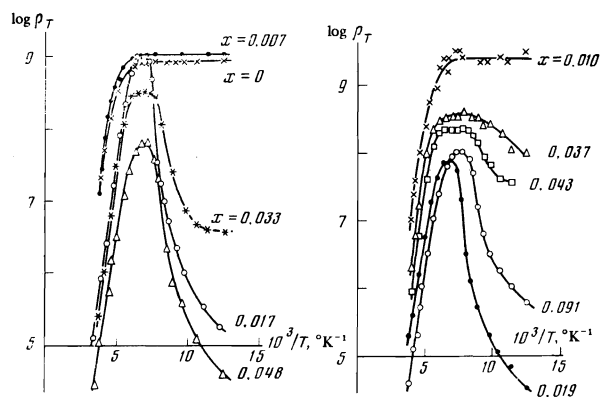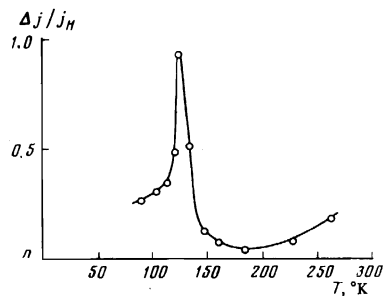
The reported studies of the photoconductivity[3,4] and

luminescence,[5] and studies of the absorption and reflection of light[6,7] in pure and indium-doped $CdCr_2Se_4$ revealed several absorption (luminescence) peaks. Peak II at ~1.8 eV, which exhibits a weak blue shift when the temperature is lowered, is usually regarded as representing the forbidden band width. Peak I at 1.25 eV exhibits a strong red shift, particularly in the region of the Curie point. Thus, when the temperature is lowered from 150 to 77 °K, peak I shifts approximately by 0.2 eV. As pointed out above, the investigated photoconductivity was observed in the photon energy range 1.24–0.886 eV. Therefore, the photoconductivity was clearly due to the absorption in the region of peak I. However, the origin of peak I is not yet clear.

We shall explain the observed photoconductivity anomalies and the red shift of peak I on the basis of a band structure of $CdCr_2Se_4$ shown in Fig. 5. Clearly, in the absence of calculations or reliable optical determinations of the band structure, the proposed model is only tentative and it is only in qualitative agreement with the experimental results.

The top of the valence band is formed by the p orbitals of anions, whereas the bottom of the wide conduction band is due to the $5s$ orbitals of cadmium. The $4s$ orbitals of chromium lie somewhat above the bottom of the conduction band. The forbidden band is ~1.8 eV wide. A level (or a narrow band) due to a deficiency of selenium is located approximately 0.2 eV below the bottom of the conduction band. It is reported in the literature[8–11] that $CdCr_2Se_4$ is almost always selenium-deficient. Other authors also report the same position for the selenium-deficiency level. For example, Amith and Friedman[10] reached this conclusion by investigating the temperature dependence of the electrical resistivity, Hall effect, and thermoelectric power. Miyatani et al.[7] studied the absorption spectra of this compound

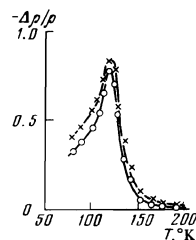FIG. 2. Temperature dependences of the dark resistivity of $Cd_{1-x}Ga_xCr_2Se_4$ samples with $x = 0-0.91$.

FIG. 4. Magnetoresistance of a sample of $Cd_{0.909}Ga_{0.091}Cr_2Se_4$ plotted as a function of temperature in two magnetic fields H (kOe): $\times$) 6.65; o) 5.
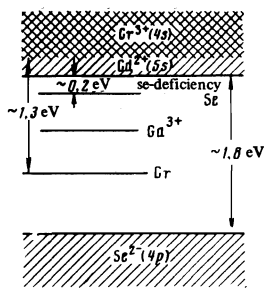
FIG. 5. Proposed energy band structure of gallium-doped CdCr$_2$Se$_4$.

and observed a similar absorption peak whose intensity increased after vacuum annealing which magnified the selenium deficiency.

Figure 2 shows the temperature dependence of the electrical resistivity of undoped CdCr$_2$Se$_4$ ($x = 0$). In the paramagnetic state, cooling clearly freezes-out conduction electrons at the selenium-deficiency donor level whose activation energy is ~0.2 eV. Amith and Friedman observed a similar dependence $\rho(T)$ for a selenium-deficient CdCr$_2$Se$_4$ single crystal. They concluded that the conductivity in the ferromagnetic region could be due to the hopping of electrons inside the narrow selenium-deficiency band. The weak influence of the magnetic field on the electrical conductivity of selenium-deficient CdCr$_2$Se$_4$ observed in our study suggested that carriers at the bottom of the conduction band and in the selenium-deficiency band interacted weakly with the magnetic moments of Cr^{3+}. Hence, we concluded that the bottom of the conduction band was more likely to be formed by the $5s$ states of nonmagnetic cadmium than by the $4s$ states of chromium. We were then able to explain also the absence of a red shift of the forbidden band width. Moreover, the top of the valence band was formed by the $4p$ selenium orbitals interacting weakly with the magnetic moments of Cr^{3+}.

According to our hypothesis, the gallium donor level is located much lower than the selenium-deficiency level. No studies have yet been made of the optical spectra or of the temperature and magnetic-field dependences of the transport coefficients of stoichiometric gallium-doped CdCr$_2$Se$_4$ single crystals. However, such work has been carried out on indium-doped CdCr$_2$Se$_4$ crystals. Indium resembles gallium in acting as a donor impurity but the ionic radius of Ga^{3+} (0.62 Å according to Ahrens) is somewhat smaller than the ionic radius of In^{3+} (0.81–0.92 Å). A calculation carried out by Amith and Friedman[10] showed that the addition of indium corresponding to $x = 0.01$ should produce an indium impurity band. Therefore, in the case of gallium-doped samples, one would expect the formation of an impurity band at somewhat higher gallium concentrations because the ionic radius of Ga^{3+} is smaller than that of In^{3+}. We shall assume that the donor levels of indium and gallium are located close to one another in the forbidden band. Amith and Friedman annealed a Cd$_{0.973}$In$_{0.027}$ single crystal in a selenium atmosphere, which removed the selenium deficiency and found that the activation energy increased from 0.22 to 0.66 eV. This activation energy was attributed to the donor level of Ga^{3+}.

Miyatani et al. studied the absorption spectrum of indium-doped CdCr$_2$Se$_4$ and found an absorption peak at 0.57 eV. The intensity of this peak was a function of the indium concentration but the peak was also exhibited by undoped nonstoichiometric low-resistivity samples. Miyatani et al. attributed this peak to defects at A positions, which could be due to, in particular, doping with In. We shall assume (Fig. 5) that the gallium band (or donor level) lies below the selenium-deficiency level at approximately the same depth as the indium level.

Moreover, we shall assume that the $3d$ states of chromium form a narrow acceptor band located near the midpoint of the forbidden gap. In the absence of donor impurities, this is the level of trivalent chromium formed by the t_{2g} orbitals of the $3d$ electrons. However, when a donor impurity is introduced, it becomes "compensated" by the acceptor impurity, i.e., electrons are transferred from the indium or gallium donor level to the chromium level. The conduction then occurs in a narrow chromium band. In fact, experiments indicate[9] that the electron mobility in n-type CdCr$_2$Se$_4$ is approximately two orders of magnitude lower than the mobility of holes in p-type CdCr$_2$Se$_4$.

However, electrons transferred from the donor level to the $3d$ chromium band are strongly affected by the crystal field which forces these "excess" electrons to occupy the high-spin ^1e_g state. According to Nagaev,[14] in the case of conduction within a narrow band, a magnetic semiconductor exhibits a strong exchange interaction between carriers and a magnetic subsystem. In this case, the carriers are spin polarons, i.e., electrons whose spin is strongly coupled to the magnetic moment of an ion at which the electron is located at a given moment. In our case, this strong exchange interaction is clearly more important than the crystal-field splitting of the high-spin state of Cr^{2+} and it stabilizes the low-spin $^4t_{2g}$ state. The low-spin state of Cr^{2+} is also stabilized by an increase in the covalence of CdCr$_2$Se$_4$ compared with CdCr$_2$S$_4$. Then, the "excess" electron spin becomes oriented antiparallel to the magnetic subsystem, which reduces the magnetic moment, as observed experimentally in[8].

We shall start by considering the case of low gallium concentrations, when the wave functions of gallium ions do not yet overlap. Photons of ~1.3 eV energy excite electrons from the $3d$ state of Cr to the $4s$ state of Cr located higher than the bottom of the conduction band. These electrons experience a strong exchange interaction with Cr^{3+} ions. Since the $4s$ states of neighboring Cr ions overlap much more strongly than the $3d$ states of Cr, such excited electrons become smeared out between the nearest $4s$ states of Cr. The s–d exchange interaction of these electrons with the $3d$ states of Cr surrounding the central Cr ion produces magnetic polarons and inside these polarons the ferromagnetic order is maintained even when the long-range magnetic order in a crystal is already destroyed.

It is shown in the theoretical work of Yanase and Kasuya,[12] Krivoglaz,[13] and Nagaev[14,15] that, from the energy point of view, an electron is likely to be localized near a donor ion producing magnetic order

around it. Slightly above the Curie temperature, the $s-d$ exchange clearly no longer affects the energy of an excited electron, whereas, in the ferromagnetic temperature range, the energy of such an electron is reduced by the $s-d$ exchange energy. Therefore, an absorption edge or peak shifts toward lower energies on transition from the paramagnetic to the ferromagnetic state. This explains the red shift of peak I. In the region of the Curie point, where the long-range magnetic order disappears, the activation energy rises strongly since the transfer of an electron to a new site is accompanied by the creation of a magnetic cluster which is still ordered. Therefore, there should be a resistivity peak in the region of the Curie point. The application of a magnetic field should reduce strongly this peak since the field maintains the magnetic order in the crystal matrix and reduces the activation energy.

It is clear from Fig. 2 that the dark resistivity of a lightly doped ($x \leqslant 0.01$) sample varies with temperature in the same way as the resistivity of an undoped crystal. Moreover, the values of the resistivity are similar. A magnetic field has almost no influence on the dark resistivity of doped samples. As mentioned earlier, conduction above the Curie point is due to electrons near the bottom of the conduction band which are excited from the selenium-deficiency band. Below the Curie point, the electrons jump within the selenium-deficiency band and the activation energy of such jumps is very low ($\sim 10^{-3}$ eV). Photons of ~ 1.25 eV energy create magnetic polaron states and this is most likely to occur in the region of the Curie point. A photoconductivity minimum and a maximum of the giant photomagnetoresistance are observed near the Curie point. Another possible cause of these anomalies is the scattering of carriers by moments of magnetic clusters predicted theoretically by Grigin and Nagaev.[16]

It is also interesting to note that the photoferromagnetic effect has been observed[17,18] in similar $CdCr_2Se_4$ samples doped lightly with gallium. This effect can be described as follows: illumination of a sample cooled in darkness with light of the same wavelength as in our study causes its initial permeability to rise steeply and the hysteresis loop expands and becomes rectangular. The initial permeability is known to depend strongly on the displacement of boundaries between domains. We may assume that optically created magnetic polarons are inhomogeneous inclusions which act as obstacles to the domain boundary motion. The hysteresis loop is then governed largely by the rotation of these magnetic polarons and, therefore, becomes rectangular under the influence of light.

We shall consider separately the case of heavily doped $CdCr_2Se_4$ samples containing large amounts of Ga. As shown above, the donor electrons of gallium are in the collective state (itinerant) in samples with $x \geqslant 0.017$. The semiconductor $CdCr_2Se_4$ then becomes degenerate. As shown by Grigin and Nagaev,[18] there is a strong correlation between fluctuations of the carrier density Δn and of the magnetic moment ΔM in heavily doped ferromagnetic semiconductors. Thus, an increase in the electron density near an ionized donor enhances the

ferromagnetic coupling between spins of atoms in its vicinity because electrons ensure the indirect exchange between them. Since the electron energy decreases as a result of an increase in the local magnetic order (the $s-d$ exchange energy becomes larger), there is a tendency to a further increase in Δn. Therefore, the density of electrons screening a charge increases. This effect increases in strength with decreasing magnetic order in a crystal, i.e., with increasing temperature. In this case, the scattering by magnetization fluctuations begins to predominate. This is why the resistivity rises with temperature. After passing through the Curie point, the magnetization fluctuations decrease with rising temperature and the scattering becomes weaker so that a resistivity maximum is observed near the Curie point. The application of an external magnetic field increases the magnetic order throughout the crystal and this reduces the relative fluctuations of the magnetization. Consequently, the field reduces the electrical resistivity, particularly in the region of the Curie point, where magnetization fluctuations in the absence of the field are strongest. The scattering of electrons by magnons, discussed by Haas[19] in the explanation of the conductivity of anomalies of the same compound in the region of the Curie point, is hardly likely to be important because it is two orders of magnitude weaker than the scattering by ΔM.

Clearly, these phenomena occur in samples with $x \geqslant 0.017$. It is clear from Figs. 2 and 4 that the dependences $\rho(T)$ and $\Delta\rho/\rho$ have a maximum in the region of the Curie point. Moreover, the above discussion explains the absence of the photoconductivity in samples of these compositions. In the light doping case, a magnetic polaron is formed from a $3d$ electron of Cr by excitation to a $4s$ state. In a heavily doped semiconductor $Cd_{1-x}Ga_xCr_2Se_4$ ($x \geqslant 0.017$), electrons in the gallium impurity band are in the collective state and they drift inside this band. The fluctuations of Δn, causing fluctuations of ΔM, then appear as described above. Since the impurity electrons are in the collective state, they do not have to be excited particularly by light or in another way to create mangetization fluctuations.

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K. P. Belov *et al.*

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Thermodynamics of the semiconductor-metal transition in Ni₁₋ₓS

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A calorimetric study was made of the semiconductor-metal phase transition in Ni₁₋ₓS samples with different critical temperatures (160–265°K). The contribution of the electron, spin, and phonon degrees of freedom to the change in the thermodynamic properties of the system was determined. Some of the concomitant phenomena—the dependence of the kinetics of the transition on the crystal size, discrete nature of the thermal effects in bulk crystals, and the fracture of the latter as a result of multiple crossing of the transition point—were attributed to the influence of stresses created by the structural transition accompanied by a change in the specific volume.

Nickel sulfide (NiS) with the hexagonal NiAs-type lattice is an example of a substance in which the insulator–metal (IM) phase transition occurs, with rising temperature, due to a simultaneous change in the electronic and magnetic sybsystems of a crystal.[1-7] At low temperatures, NiS is a semiconducting antiferromagnet with a magnetic moment, per nickle atom, close to two Bohr magnetons ($\sim 1.7\ \mu_B$). At a first-order transition point, $T_c \sim 265\ °K$, the magnetic order disappears suddenly (the sublattice moment falls from a value approximately equal to 0.9 of the maximum moment) and, at the same time, the substance becomes a metal. The conductivity increases abruptly by about two orders of magnitude, which corresponds to the collapse of an energy gap of ~ 0.2 eV.[8] Above T_c, there is no magnetic diffuse neutron scattering (the magnetic moment is $\sim 0.5\ \mu_B$) and the high-temperature phase exhibits properties of a d-band Pauli paramagnet. The transition is accompanied by a change in the sign of the carriers from positive to negative,[3,4] and by abrupt changes in the magnetic susceptibility[2,5] and lattice parameters[1,9,10]: the specific volume and the axial ratio c/a decrease correspondingly by 1.9 and 1%. The symmetry of the NiS lattice is not affected by the IM transition.[9] The temperature of the electronic transition in Ni₁₋ₓS depends strongly on the composition, decreasing with deviation from stoichiometry, and it vanishes at $x = 0.03–0.04$.[1,6,7] The fall of T_c is accompanied by a reduction in the conductivity jump.[7]

An agreed interpretation of the properties of the

Ni₁₋ₓS system has not yet been worked out. In particular, the thermodynamic stimulus and the nature of the IM transition in this system at finite temperatures remains unresolved. The present paper reports a calorimetric investigation of the IM transition in Ni₁₋ₓS samples with controlled compositions (with different values of T_c). We shall separate the contributions of the various degrees of freedom to the change in the thermodynamic properties of the system.

METHOD AND EXPERIMENTAL RESULTS

The compositions and morphology of the investigated samples are given in Table 1. Polycrystalline samples (sintered aggregates and powders) were synthesized from very pure components by the usual method.[7] Single crystals were prepared by crystallization from the melt at a rate of 3.6 mm/h in a furnace with a temperature gradient of 70 deg/cm. The NiAs-type structure was frozen by quenching from 400 °C in water. The quality of the single crystals was determined by x-ray diffraction. A local x-ray spectroscopic analysis, carried out using a JXA-5 microprobe, indicated that the inhomogeneity of the distribution of the components did not exceed ±1 rel.%. The specific heat and thermal effects associated with the IM transition were determined with a recording microcalorimeter of sensitivity down to 1×10^{-7} W.[11] The advantage of this method was the ability to determine (with an error not exceeding 6%) the properties of small samples (1–100 mg) in which the composition and structure inhomogeneities