Absorption spectrum of *n*- and *p*-type single crystals of ferromagnetic semiconductor $HgCr_2Se_4$ in a magnetic field

M. I. Auslender, E V. Barsukova, N. G. Bebenin, B. A. Gizhevskiĭ, N. N. Loshkareva, Yu. P. Sukhorukov, and N. M. Chebotaev

Institute of Metal Physics, Ural Division of the Academy of Sciences of the USSR, Sverdlovsk

(Submitted 15 June 1988)
Zh. Eksp. Teor. Fiz. **95**, 247–252 (January 1989)

An investigation of the absorption spectra of single crystals of a magnetic semiconductor $HgCr_2Se_4$, carried out at photon energies corresponding to the interaction with charge carriers, revealed a strong influence of a magnetic field on the absorption coefficient. A sharp magnetoabsorption peak was observed for *n*-type $HgCr_2Se_4$ single crystals at the Curie temperature $T = 114$ K. The magnetoabsorption in *p*-type crystals was considerable throughout the ferromagnetic range of temperatures and it reached 25%. The dependences of the absorption spectrum on the applied magnetic field in the Faraday and Voigt geometries were similar to the field dependences of the magnetization. A strong magnetic linear dichroism was observed when linearly polarized light was absorbed in the Voigt geometry. The results were explained using a one-electron model allowing for the complex structure of the valence band and its changes in the ferromagnetic temperature range.

1. INTRODUCTION

The spinel $HgCr_2Se_4$ differs from other magnetic semiconductors by a small effective mass of electrons (down to $0.15m_0$) and a comparatively high mobility (up to $\sim 10^3$ $cm^2 \cdot V^{-1} \cdot s^{-1}$). The mobility of holes is considerably lower (subject to a large error because of a strong anomalous Hall effect), but its values (> 5 $cm^2 \cdot V^{-1} \cdot s^{-1}$) indicate that in a wide range of temperatures including the Curie point the conductivity is essentially of band nature.

Investigations of $HgCr_2Se_4$ from the point of view of semiconductor physics, i.e., of the relationship between the transport properties and the energy-band structure near extrema, are just beginning. At present we know of the anisotropy of the magnetoresistance and piezoresistance, and of certain features of the absorption of light near the fundamental band edge. The next step is reported below in the form of an experimental and theoretical study of optical properties of *n*- and *p*-type $HgCr_2Se_4$ single crystals in the spectral range where light interacts mainly with free carriers.

2. INVESTIGATION METHOD AND RESULTS

We investigated the absorption spectra of $HgCr_2Se_4$ single crystals using a modernized version of an IKS-21 spectrometer[1] in the spectral range 2.3–10 μm. Linearly polarized light was created using polyethylene and Teflon grating polarizers (with 1200 and 2400 lines/mm, respectively). The polarizing power of the monochromator was allowed for in the polarized-light measurements. The absorption coefficient was deduced allowing for the reflection coefficient *R*:

$$K = \frac{1}{d} \ln \frac{1}{T} (1-R)^2, \tag{1}$$

where *T* is the transmission of a sample and *d* is its thickness. The influence of a magnetic field was investigated in the Faraday geometry with light propagating along the applied magnetic field ($\mathbf{k} \| \mathbf{H}$) and also in the Voigt geometry with light propagating at right-angles to the magnetic field ($\mathbf{k} \perp \mathbf{H}$). We also used the Voigt geometry to determine rotation of the polarization ellipse of light emerging from a sample subjected to a magnetic field. Our $\lambda/4$ plate was a Fresnel rhomb made of NaCl and placed behind a cryostat with a sample. The polarization was analyzed by rotation of an analyzer behind the Fresnel rhomb.

Single-crystal $HgCr_2Se_4$ plates were cut at right-angles to the [111] axis to within 0.3°. The following samples were investigated: 1) *p*-type $HgCr_2Se_4$ with a high resistivity $\rho_{80\ K} = 10^6$ $\Omega \cdot cm$ and an activation energy $E_A = 0.2$ eV at temperatures $T > 200$ K; 2) $HgCr_2Ce_4$ annealed in Hg vapor and exhibiting *n*-type conduction throughout the investigated temperature range, with a resistivity $\rho_{300\ K} = 0.18$ $\Omega \cdot cm$ and a metallic nature of its temperature dependence $\rho(T)$; 3) $HgCr_2Se_4$ annealed in Se vapor and exhibiting *p*-type conduction throughout the investigated temperature range, with resistivities $\rho_{300\ K} = 0.05$ $\Omega \cdot cm$, $\rho_{80\ K} = 10$ $\Omega \cdot cm$, $\rho_{25\ K} = 3 \times 10^2$ $\Omega \cdot cm$, and an activation energy $E_A = 0.05$ eV at temperatures $T > 80$ K.

In the investigated spectral range the absorption spectra included a fundamental edge which was shifted in the red direction as a result of cooling. At longer wavelengths the absorption coefficient of the high-resistivity sample 1 was constant and low: $K = 10$ cm^{-1} (the spectrum is given in Ref. 1). The absorption spectra of the *n*-type sample (Ref. 2) and of the *p*-type sample 3 (Fig. 1) exhibited a characteristic rise of the absorption due to the interaction of light with carriers. In the fundamental absorption region ($\lambda < 4$ μm) the change in the absorption in a magnetic field, representing the magnetoabsorption $\Delta K/K \equiv (K_H - K_0)/K_0$, was observed for all the samples.

The temperature dependence of the magnetoabsorption at wavelengths $\lambda > 4$ μm is shown in Fig. 2. In this spectral range the magnetic field influenced the absorption spectra of the *p*-type sample at all temperatures $T < 140$ K and the spectra of the *n*-type sample in a narrow temperature interval near the Curie Point T_c. The application of a magnetic field reduced the absorption, i.e., it bleached the samples 2 and 3. At 80 K we found that the change in the absorption on application of a magnetic field to *p*-type $HgCr_2Se_4$ (Fig. 1)

0038-5646/89/010139-04$04.00

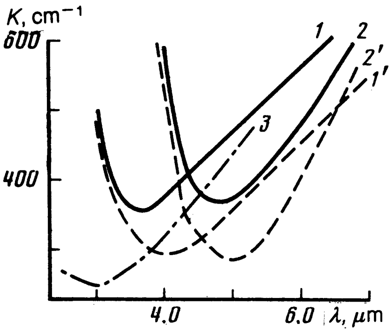

FIG. 1. Absorption spectra of a p-type single crystal of $HgCr_2Se_4$ in the absence of a magnetic field (1–3) and in a magnetic field of 4.3 kOe (1′, 2′) at different temperatures: 1), 1′) 80 K; 2), 2′) 25 K; 3) 293 K.

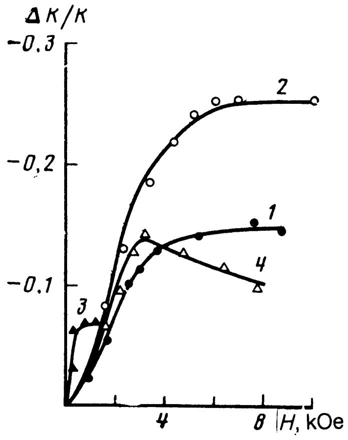

FIG. 3. Dependence of the magnetoabsorption on an external magnetic field applied to p-type $HgCr_2Se_4$ single crystals: 1) $T = 80$ K, $\lambda = 5.5\,\mu$m, k⊥H; 2) $T = 25$ K, $\lambda = 5.5.\mu$m, k⊥H; 3) $T = 80$ K, $\lambda = 5.5.\mu$m; k‖H; 4) $T = 80$ K, $\lambda = 2.3\,\mu$m, k⊥H.

was practically the same at all wavelengths in excess of 4 μm. At 25 K the slopes of the $K_0(\lambda)$ and $K_H(\lambda)$ curves were different. The magnetic-field dependences of the magnetoabsorption obtained in the Faraday and Voigt geometries were similar to the magnetization curves (Fig. 3). For example, in the Faraday geometry the high demagnetizing fields resulted in saturation of the magnetoabsorption in much lower fields than when the sample was magnetized along the plate (in the Voigt geometry). Magnetoabsorption saturation at 25 K occurred in higher fields than at 80 K, in accordance with an increase in the demagnetizing field due to cooling.

All the measurements were made after cooling the samples in a magnetic field close to the saturation field for the given geometry of the field and light beam. The magnetoabsorption was much stronger in the case of cooling in the absence of the field than for cooling in the field, but the results were not reproducible.

In the case of sample 3 (p-type) in the Voigt geometry the dependence of the magnetoabsorption on the angle between the polarization vector of the incident light and the direction of the magnetic field exhibited 180° oscillations (Fig. 4a). The absorption was minimal for e‖H and maximal for e⊥H, where **e** is the electric vector of the incident light wave. The magnetic linear dichroism was $K_\perp - K_\parallel = 110\ \text{cm}^{-1}$ and the peak-to-peak amplitude of the magnetoabsorption oscillations was ~21%. The field dependence of the oscillation amplitude was exactly the same as the field dependence of the magnetoabsorption. There were no such oscillations in the case of the n-type sample 2.

An analysis of the polarized radiation emerging from a sample of p-type $HgCr_2Se_4$ in the Voigt geometry showed that linearly polarized light became partly depolarized when the sample was cooled below the Curie temperature. The depolarization decreased on application of a magnetic field and it practically disappeared in fields exceeding the saturation value. The plane of polarization of light was rotated: for $\varphi = (\widehat{\mathbf{e},\mathbf{H}}) = 45°$ the angle of rotation reached ≈15°.

3. DISCUSSION OF RESULTS

The results of electrical measurements showed that the p-type sample 3 of $HgCr_2Se_4$ was a nondegenerative semiconductor. At room temperature the conduction was mainly due to holes in the valence band. Cooling increased the elec-

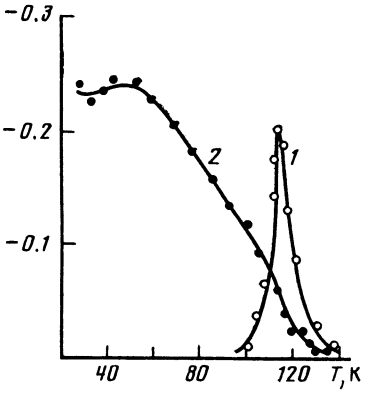

FIG. 2. Influence of temperature on the absorption spectrum of light of a single crystal in a magnetic field: n-type $HgCr_2Se_4$ at $\lambda = 8\,\mu$m (1) and p-type $HgCr_2Se_4$ at $\lambda = 5.5\,\mu$m (2).

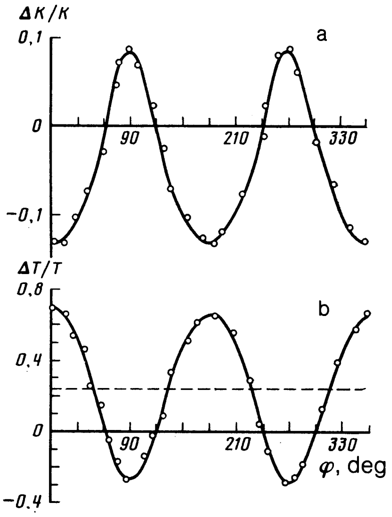

FIG. 4. Dependences of the magnetoabsorption (1) and the magnetotransmission (b) of p-type $HgCr_2Se_4$ on the angle between the polarization vector of the incident light and the magnetization at $\lambda = 5.5\,\mu$m and $T = 80$ K in a field $H = 4.3$ kOe. The dashed line represents the dependence of $\Delta T/T$ on the angle φ for unpolarized light.

trical resistivity and p-type conduction was maintained, although the absorption spectra recorded at 25 K (Fig. 1) indicated that the density of electrons increased as a result of cooling and electrons began to play an important role. The contribution of highly mobile electrons was probably responsible for an increase in the slope of the $K(\lambda)$ curves at 25 K.

The application of a magnetic field increased the shift of the fundamental absorption edge of ferromagnetic semiconductors. The field dependence of the magnetoabsorption observed at $\lambda = 2.5\ \mu$m (Fig. 3), which was typical of all the samples, indicated that the absorption first decreased (as also found at wavelengths $\lambda = 4\ \mu$m) in magnetic fields less than the saturation value, but the absorption began to increase on further increase in the field and this was due to the "red shift" of the absorption edge.

The absence of magnetoabsorption at wavelengths in excess of 4 μm in the case of the high-resistivity sample and the different temperature dependences of the magnetoabsorption near the edge and at $\lambda > 4\ \mu$m indicated that the magnetoabsorption observed at wavelengths in excess of 4 μm was due to the interaction of the magnetic field with charge carriers. The characteristics of such magnetoabsorption can be explained on the basis of the band structure model proposed in Ref. 3.

The exchange interaction of electrons with localized moments was strong and it induced a clear anomaly near T_c for n-type $HgCr_2Se_4$ (Fig. 2). In the case of holes the exchange interaction parameter was at least an order of magnitude less than for electrons[3] and this accounted for the absence of significant anomalies in the temperature dependence of $\Delta K/K$ recorded for p-type $HgCr_2Se_4$ near T_c (Fig. 2).

The piezoresistance[4] and magnetoresistance[3,5] experiments had demonstrated that the conduction band of $HgCr_2Se_4$ is spherically symmetric which was why n-type $HgCr_2Se_4$ did not exhibit a magnetoabsorption anisotropy.

The valence band of the investigated spinel is known to be complex.[3] In the paramagnetic temperature range it is quadruply degenerate at the point Γ (when the symmetry is Γ_8), whereas at temperatures $T < T_c$ the exchange field imposed on carriers by localized spins lifts the degeneracy. The constant-energy surfaces near the point $\mathbf{k} = 0$ are transformed into ellipsoids and the directions of the principal axes of these ellipsoids depend on the orientation of the magnetization vector relative to the cubic axes. It has been shown earlier that such an energy band scheme makes it possible to explain satisfactorily the magnetoabsorption anisotropy at temperatures $T < T_c$ (Refs. 3 and 5), so that it is natural to use the results of Ref. 3 also to account for the magnetoabsorption anisotropy of doped $HgCr_2Se_4$.

The permittivity tensor can be written in the form

$$\hat{\varepsilon} = \hat{\varepsilon}^{(0)} + i4\pi\hat{\sigma}/\omega,$$

where $\hat{\varepsilon}^{(0)}$ is the permittivity tensor of an undoped crystal and $\hat{\sigma}$ is the conductivity tensor of holes. In the approximation of an isotropic frequency-dependent relaxation time, we find that $\hat{\sigma} \propto M^{-1}$, where M is the effective mass tensor. Using the results of Ref. 3 and assuming that holes fill only the lowest ellipsoid, we obtain

$$\sigma_{ij}(\omega) = \sigma(\omega)\left[(1+\gamma_2^* - 3\gamma_2^* n_i^2)\delta_{ij} - 3\gamma_3^*(1-\delta_{ij})n_i n_j\right],$$
$$i, j = x, y, z, \tag{2}$$

where $\sigma(\omega)$ is a scalar function; $\gamma^*_{2,3} = \gamma_{2,3}/\gamma_1$; γ_i are the Luttinger parameters; $\mathbf{n}$ is a unit vector in the direction of the magnetization; the coordinate axes are parallel to the fourfold axes.

A standard analysis yields the following expression for the wave vectors of optical waves with the positive and negative polarizations, traveling along the $\mathbf{M} \parallel [111]$ direction:

$$k_\pm = \frac{n\omega}{c}\left[1 \pm \frac{g}{2n^2} + i\frac{2\pi\sigma(\omega)}{\omega n^2}(1+\gamma_3^*)\right], \tag{3}$$

where n is the refractive index and g is the gyration. The presence of holes gives rise to an additional absorption contribution, but since it is the same in both polarizations it does not give rise to ellipticity. This conclusion is in agreement with the experimental results.

We shall now consider the effects observed in the Voigt geometry. It is convenient to adopt a coordinate system with unit vectors $\mathbf{e}_1 \parallel [111]$, $\mathbf{e}_2 \parallel \mathbf{n}$. In this coordinate system we have

$$\hat{\sigma} = \sigma(\omega)\begin{pmatrix} 1+\gamma_3^* & \frac{\gamma_2^*-\gamma_3^*}{\sqrt{2}}\sin 3\theta & -\frac{\gamma_2^*-\gamma_3^*}{2}\cos 3\theta \\ \frac{\gamma_2^*-\gamma_3^*}{\sqrt{2}}\sin 3\theta & 1-\frac{\gamma_2^*+3\gamma_3^*}{2} & 0 \\ -\frac{\gamma_2^*-\gamma_3^*}{2}\cos 3\theta & 0 & 1+\frac{\gamma_2^*+\gamma_3^*}{2} \end{pmatrix}, \tag{4}$$

where θ is the angle between the magnetization vector and the $[1\bar{1}0]$ axis. The tensor $\hat{\varepsilon}^{(0)}$ has the same structure. The eigenwaves traveling parallel to $\mathbf{e}_1$ are (approximately) polarized parallel and at right-angles to the direction of magnetization (see, for example, Ref. 6) and the wave vectors are $k = k' + ik''$:

$$\begin{aligned} k_\parallel &= \frac{\omega n_\parallel}{c}\left[1 + i\frac{2\pi\sigma(\omega)}{\omega n_\parallel^2}\left(1 - \frac{\gamma_2^*+3\gamma_3^*}{2}\right)\right], \\ k_\perp &= \frac{\omega n_\perp}{c}\left[1 + i\frac{2\pi\sigma(\omega)}{\omega n_\perp^2}\left(1 + \frac{\gamma_2^*+\gamma_3^*}{2}\right)\right], \end{aligned} \tag{5}$$

where $n_{\parallel,\perp}$ are the corresponding refractive indices and the terms $\sim(\gamma_2^* - \gamma_3^*)^2$ are omitted because of their smallness. The absence of a significant ellipticity means that $n_\perp \approx n_\parallel \approx n$, so that the observed effects are associated mainly with a magnetic linear dichroism.

We can easily see that the transmission T_H is an oscillatory function of the angle $\varphi = (\mathbf{e},\mathbf{H})$ between the plane of polarization of the incident light and the magnetization:

$$T_H=\exp\left[-(k_\parallel''+k_\perp'')d\right]\left[\mathrm{ch}\,(k_\perp''-k_\parallel'')d - \cos(2\varphi)\,\mathrm{sh}\,(k_\perp''-k_\parallel'')d\right]. \qquad (6)$$

Since $k_\perp'' - k_\parallel'' = (2\pi\,\mathrm{Re}\,\sigma/nc)(\gamma_2^* + 2\gamma_3^*) > 0$, which follows from the positive nature of γ_2^* and γ_3^* in Ref. 3, the minima of T_H should occur at $\varphi = \pi n$ and the maxima at $\varphi = \pi(n + 1/2)$; the average value $\bar{T}_H$, near which T_H oscillates, should be identical with the value of the transmission of unpolarized light. Precisely this type of angular dependence of $(T_H - T_0)/T_0$ is observed experimentally (Fig. 4b).

In the case of the absorption coefficient found from Eq. (1) the cosinusoidal dependence is only asymptotic for $(k_\perp'' - k_\parallel'')d \ll 1$, when

$$K_H \approx k_\perp''+k_\parallel''-(k_\perp''-k_\parallel'')\cos 2\varphi. \qquad (7)$$

Since the inequality $(k_\perp'' - k_\parallel'')d \lesssim 1$ was obeyed in our case it follows that near the point where $|\cos 2\varphi| = 1$ the series for the logarithm converges poorly and the dependence (7) is greatly distorted.

Using the values $\gamma_2^* = 0.11$ and $\gamma_3^* = 0.07$ obtained from the magnetoresistance data,[3] we find that the peak-to-peak oscillation amplitude is

$$2(k_\perp''-k_\parallel'')/(k_\perp''+k_\parallel'') \approx 25\%,$$

which is in good agreement with the experimental value 21%.

A linear magnetic dichroism rotates the plane of polarization by an angle

$$\psi=\mathrm{arctg}\,\{\mathrm{tg}\,\varphi\exp\left[-(k_\perp''-k_\parallel'')d\right]\}-\varphi. \qquad (8)$$

An estimate of ψ obtained using this expression is in satisfactory agreement with the experimental value found from $\varphi = \pi/4$.

We considered the effects in a homogeneously magnetized p-type sample. In the absence of a magnetic field (or in a field less than the saturation value) a sample is split into domains and each of them is characterized by its own direction of the magnetization and, consequently, by its own value of the absorption coefficient and angle of rotation of the plane of polarization; the measured quantities are averaged over the distributions of the magnetization directions. On application of a magnetic field a sample is converted to a single-domain state and this is why the transparency increases and the depolarization of light is no longer observed in p–type $HgCr_2Se_4$ samples.

The authors are grateful to A. V. Druzhinin for valuable discussions of the experimental method.

[1] G. V. Pokazan'ev, N. N. Loshkareva, Yu. P. Sukhorukov, and A. I. Trofimov, Prib. Tekh. Eksp. No. 5, 205 (1986).

[2] N. N. Loshkareva, Yu. P. Sukhorukov, B. A. Gizhevskiĭ, N. M. Chebotaev, and A. A. Samokhvalov, Fiz. Tverd. Tela (Leningrad) **30**, 906 (1988) [Sov. Phys. Solid State **30**, 526 (1986)].

[3] M. I. Auslender, N. G. Bebenin, B. A. Gizhevskiĭ, *et al.*, Preprint No. 87/2 [in Russian], Institute of Metal Physics, Ural Division of the Academy of Sciences of the USSR, Sverdlovsk (1987).

[4] A. Galdikas, S. Grebinskiĭ, and S. Mitskyavichus, Deposited Paper No. 4374-V-87 [in Russian], VINITI, Moscow (1987).

[5] A. Galdikas, S. Grebinskiĭ, and S. Mitskyavichus, Litov. Fiz. Sb. **27**, 309 (1987).

[6] F. F. Sizov and Yu. I. Ikhanov, *Magnetooptic Faraday and Voigt Effects in Applications to Semiconductors* [in Russian], Naukova Dumka, Kiev (1979).

Translated by A. Tybulewicz