Changes in the photoluminescence spectra of the magnetic semiconductor CdCr$_2$Se$_4$ under high-power picosecond-laser excitation which determine that the fundamental gap is direct

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Changes in the photoluminescence spectra of the magnetic semiconductor CdCr$_2$Se$_4$ at 80 K were measured at high picosecond-laser pulse intensities from 0.3 to 20 GW cm^{-2}. Evidence is presented for the formation of the electron-hole plasma. Theoretical fitting of the spectral data determined that CdCr$_2$Se$_4$ is a direct-band-gap semiconductor.

The steady-state photoluminescence from the ferromagnetic semiconductor CdCr$_2$Se$_4$ was published earlier by Yao *et al.*[1] The emission centered at 1.81 eV was ascribed to the transition from the fundamental gap. In that report[1] it was not determined whether the transition was direct or indirect. Picosecond spectroscopy is important in investigating the underlying physics of highly photoexcited semiconductors. It can be used to extract basic information on the properties of semiconductors and on elementary excitations and coupled modes. Furthermore, picosecond pulses can be used at ultrahigh intensity without causing substantial damage or heating. This is a great advantage of picosecond pulses as compared with nanosecond pulses. In this paper, we report changes in the spectra of the photoluminescence emitted from CdCr$_2$Se$_4$ excited with intense picosecond light pulses. It was found that the luminescence shifted to red and broadened as the excitation intensity increased from 0.3 to 20 GW cm^{-2}. These changes are ascribed to the formation of high-density electron-hole plasma. Theoretical fitting of the spectral profiles associated with electron-hole plasma formation at different intensities determines for the first time that the fundamental band gap of CdCr$_2$Se$_4$ is a direct band gap.

A 6-ps 527-nm pulse was used to excite the sample CdCr$_2$Se$_4$ on the front surface. The excitation area on the sample was 0.5×0.6 mm^2. The sample was placed in an optical Dewar at 80 K. The luminescence emitted from the front surface of CdCr$_2$Se$_4$ was detected and analyzed using a $\frac{1}{4}$-m Spex spectrometer coupled to a PAR silicon intensified target (SIT) camera and an optical multichannel analyzer II.

In Fig. 1 a series of time-integrated spectra for CdCr$_2$Se$_4$ at 80 K as a function of the picosecond-laser pulse intensity from 0.3 to 20 GW cm^{-2} are displayed. With increasing excitation intensity the peak of the luminescence shifts to lower energy and the spectral linewidth becomes broader. In Fig. 2 the spectral linewidths of the emission from CdCr$_2$Se$_4$ for these different pumping intensities are plotted. The peak energy of the emission from CdCr$_2$Se$_4$ as a function of the picosecond-laser excitation intensity is plotted in Fig. 3. The linewidth increases from 10 to 30 meV and the peak energy shifts to red from 1.79 to 1.76 eV as the pumping intensity increases from 0.3 to 20 GW cm^{-2}. Figure 4 shows the intensity dependence of the integrated emission spectra with respect to the exciting intensity. The emission intensity increases linearly with the excitation intensity.

The peak energy of the photoluminescence at lowest excitation intensity is 1.789 eV (693 nm)
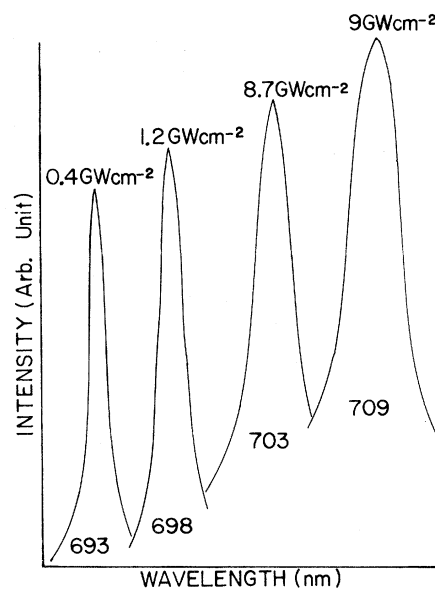

FIG. 1. Series of time-integrated spectra, as a function of the excitation level P, for 0.3 GW cm$^{-2} \leq P \leq 20$ GW cm^{-2}, at 80 K.
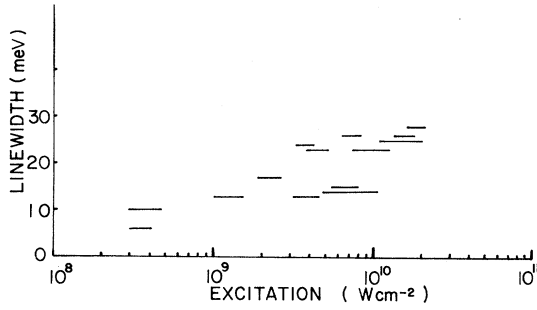
FIG. 2. Linewidth of the emission of CdCr$_2$Se$_4$ under picosecond-laser excitation as a function of the pumping intensity.

FIG. 4. Intensity dependence of the integrated emission spectra with respect to the exciting intensity.

which is 18 meV smaller than the peak energy of 1.807 eV (686 nm) measured by the low-power steady-state luminescence[1] work. Since the exciton state in CdCr$_2$Se$_4$ has not been observed at 80 K, the effect of exciton emission and other exciton effects are not possible. Therefore, the related spontaneous and stimulated exciton-exciton scattering emissions are not possible either. The red shift of the peak energy in Fig. 3 may point to stimulated emission of exciton-exciton collisions because it also has a red shift as the excitation increases.[2] We can still exclude this possibility because of the intensity dependence shown in Fig. 4 for CdCr$_2$Se$_4$. Spontaneous exciton-exciton scattering emission would increase quadratically[3] with the exciton density and a stimulated emission should have more than square dependence of the exciton density. At high excitation intensities, the densities of electrons and holes are proportional to the square root of excitation,[4] therefore the luminescence intensity from electron-hole plasma should be linearly proportional to the excitation intensity which is shown in Fig. 4.

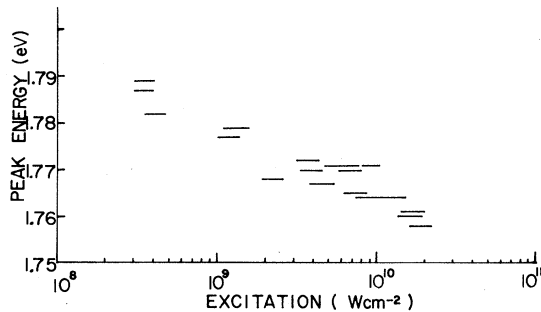The spontaneous emission spectrum of electron-hole plasma is described by[5] either

FIG. 3. Peak energy of emission of CdCr$_2$Se$_4$ under picosecond-laser excitation as a function of the pumping intensity.
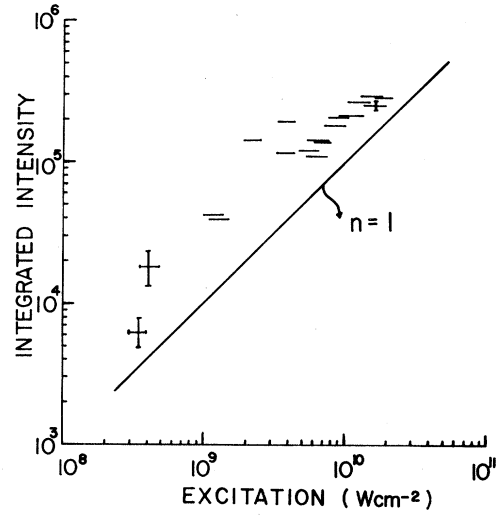
$$I(h\nu) \propto (h\nu - \widetilde{E}_g)^{1/2} f_e \left[(h\nu - \widetilde{E}_g) \frac{m_h}{m_e + m_h} \right]$$

$$\times f_h \left[(h\nu - \widetilde{E}_g) \frac{m_e}{m_e + m_h} \right] \qquad (1)$$

for K selection (direct gap transition), or by

$$I(h\nu) \propto \int_0^{h\nu - \widetilde{E}_g} (h\nu - \widetilde{E}_g - E)^{1/2} E^{1/2} f_e$$

$$\times (h\nu - \widetilde{E}_g - E) f_h(E) dE , \qquad (2)$$

for non-K-selection (indirect transition) for degenerate semiconductors, where f_e and f_h are Fermi-Dirac distributions of electrons and holes, respectively, $\widetilde{E}_g$ is the reduced band gap, and m_e and m_h are the effective masses of electrons and holes, respectively. We assume at the present time $m_e = m_h = 0.5 m_0$. The carrier temperatures were extracted from the high-energy tails of the emission curves in nondegenerate cases, assuming that the carrier distributions are Maxwellian. The distribution was nondegenerate below 10^{18} cm^{-3} for input power density of 17 GW cm^{-2}. The carrier density at the largest excitation intensity (20 GW cm^{-2}) was chosen to be 1.25×10^{18} cm^{-3} to fit the data and the lower carrier densities were accordingly determined. For all the emission spectra of CdCr$_2$Se$_4$ for the high excitation intensity, the carrier temperatures were all close to the lattice temperature ~ 80 K. This is expected because of ultrafast recombination[1] time of carriers ≤ 20 ps. As shown in Fig. 5, the theoretical curve for K selection (direct gap transition) fits the experimental data well from 0.4 to 15 GW cm^{-2} and the theoretical curve without K selection (indirect transition) does not fit the data. The
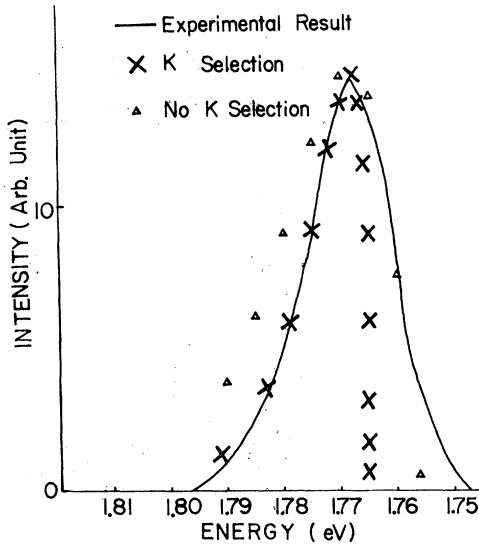
FIG. 5. Emission spectrum of $CdCr_2Se_4$ at the excitation intensity 2.2 ± 0.3 GW cm^{-2}. The experimental data are fitted to a theoretical curve of direct band gap

$$I(h\nu) \propto (h\nu - \widetilde{E}_g)^{1/2} f_e \left[(h\nu - \widetilde{E}_g) \frac{m_h}{m_e + m_h} \right]$$

$$\times f_n \left[(h\nu - \widetilde{E}_g) \frac{m_e}{m_e + m_h} \right]$$

with K selection.

low-energy side of the experimental data is not fitted by the curves because a perfect parabolic band without impurities is assumed for the theoretical curve. When the excitation intensity is below 0.4 GW cm^{-2}, the high-energy side of the spectra can be fitted approximately by $\exp[-(h\nu - \widetilde{E}_g)/kT_{\text{carrier}}]$, and the peak energy equals $\widetilde{E}_g$. Furthermore, the steady-state spectra using low-power cw excitation can also be fitted to the simple exponential expression for Maxwellian distributions below 70 K. It appears the density of states is close to being a constant within 20 meV from band edge. Above 80 K the K-selection form can fit the high-energy side of the spectral profile. Therefore, we conclude that the fundamental gap of $CdCr_2Se_4$ is a direct band gap by picosecond-laser time-integrated spectra.

The reduced band gap $\widetilde{E}_g$, obtained by subtracting $0.0kT_{\text{carrier}}$ to $0.9kT_{\text{carrier}}$ from the peak energy of the emission spectrum,[6] is plotted as a function of the carrier pair density n in Fig. 6(a). The error bar for $\widetilde{E}_g$ is ±4 meV. In Fig. 6(b), $E_g - \widetilde{E}_g$ is plotted as a function $n^{1/3}$, where E_g is the gap energy of $CdCr_2Se_4$ at 80 K and is equal[1,7] to 1.804 ±0.002 eV. $E_g - \widetilde{E}_g$ increases linearly with $n^{1/3}$. The reduced gap $\widetilde{E}_g$ is $\widetilde{E}_g = E_g - (48\pm4)\times10^{-6}$
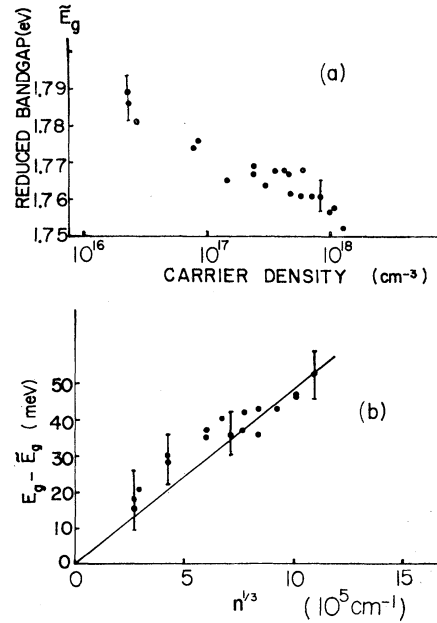

FIG. 6. (a) Reduced band gap $\widetilde{E}_g$ as a function of the carrier density n of $CdCr_2Se_4$ at 80 K and (b) $E_g - \widetilde{E}_g$ as a function of $n^{1/3}$. E_g (1.804$\pm$0.004 eV) is the band-gap energy of $CdCr_2Se_4$ at 80 K. $\widetilde{E}_g$ is the reduced band-gap energy at the carrier concentration n.

(meV cm) $n^{1/3}$ (cm^{-1}).

The many-body Coulomb effect[8-10] among photogenerated free carriers causes the red shifts of the luminescence from $CdCr_2Se_4$. According to the theory of Rice,[11] the lowering of the band gap is equal to (in units of $\mu e^4/2\kappa^2\hbar^2$)

$$E_{\text{exc}} + E_{\text{corr}} + n\frac{\delta}{\delta n}(E_{\text{exc}} + E_{\text{corr}}) .$$

For an ideal parabolic band shape, the reduction of band gap is $E_g - \widetilde{E}_g \simeq -1.6(e^2/\kappa)n^{1/3}$ $\simeq -(21.8/\kappa)\times10^{-5}$ (meV cm) $n^{1/3}$ (cm^{-1}), where κ is the static dielectric constant of the semiconductor, $E_{\text{exc}} = -1.832/r_s$ and $E_{\text{corr}} = 0.497 \ln r_s - 0.33$ for equal masses of electrons and holes, $n = 3/(4\pi r_s^3 a_x^3)$, a_x is the exciton Bohr radius (equal to $\kappa\hbar^2/\mu e^2$), and μ is the reduced mass. If $CdCr_2Se_4$ has an ideal parabolic band, then $\kappa = 4.8\pm0.4$ from data in Fig. 6. This value is about 2 times smaller than the calculation by Itoh et al.[12] of the real part ϵ_1 (~9) of dielectric constant at 1.8 eV. This difference may be due to the assumption of $m_e = m_h = 0.5m_0$. When the values of m_e and m_h change, the carrier density will change and the κ value will be adjusted. The correlation energy $E_{\text{correlation}}$ can be different from the above value and can affect the result of $E_g - \widetilde{E}_g$, this also may account for the difference in κ. As

discussed by Rice,[11] the temperature dependence of the reduced band-gap energy can be neglected as long as the thermal energy is small compared with the plasmon energy. The thermal energy is ~ 7 meV at 80 K, which is much smaller than the plasmon energy (~ 20 meV) at $\sim 10^{18}$ cm^{-3} for $m_e = m_h = 0.5 m_0$. Therefore, the temperature effect on the reduced band gap is small for the carrier temperature (~ 80 K) and the carrier concentration ($\sim 10^{18}$ cm^{-3}). However, the thermal effect on the reduced band gap could be finite at low carrier concentration ($\leq 3 \times 10^{17}$ cm^{-3}) and $\widetilde{E}_g$ becomes smaller compared with that at lower temperature than 80 K.

The Brinkman and Rice theory[13] and Shah et al.[14] theory for the electron-hole plasma in GaAs estimated the reduced band-gap energy $\widetilde{E}_g$ as $\widetilde{E}_g = E_g - 21 \times 10^{-6}$ (meV cm) $n^{1/3}$ (cm^{-1}) for $n \geq 5 \times 10^{16}$ cm^{-3}. Comparing our result on CdCr$_2$Se$_4$ with GaAs, we conclude that CdCr$_2$Se$_4$ gives similar experimental renormalization results to those of GaAs. From the above analysis, it is obvious that the reduction of the band gap is related to the optically generated electron-hole plasma.

In conclusion, we found that electron-hole plasma can be generated in CdCr$_2$Se$_4$ under high-power picosecond-laser excitations which affect the band structures. The band gap renormalizes as a function of the photogenerated carrier density. The good fitting of the photoluminescence spectral shape by a theoretical expression for electron-hole plasma indicates that CdCr$_2$Se$_4$ is a direct-gap semiconductor.

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[6]Since $I(h\nu) \propto (h\nu - \widetilde{E}_g)^{1/2} f_e f_h$, $dI(h\nu)/d(h\nu) = 0$, and $m_e = m_h = 0.5 m_0$ implies that $1 + e^{(1/2)x - \mu} - 2x e^{1/2x - \mu} = 0$, where $x \equiv (h\nu - \widetilde{E}_g)/kT_{\text{carrier}}$ and $\mu \equiv \mu_e /kT_{\text{carrier}} = \mu_h /kT_{\text{carrier}}$, μ_e and μ_h are the chemical potentials of electrons and holes, respectively. At highest density $n = 1.25 \times 10^{18}$ cm^{-3}, $\mu = 0.4$, and $x = 0.9$. At lower density $\leq 10^{18}$ cm^{-3}, x is close to 0.5. Therefore, the carrier density will change the value of chemical potential which reduces the band gap from $0.5 kT_{\text{carrier}}$ to $0.9 kT_{\text{carrier}}$ lower than the peak energy of the emission spectrum. (When $n < 2.5 \times 10^{16}$ cm^{-3}, the high-energy side can be fitted approximately by $\exp[-(h\nu - \widetilde{E}_g)/kT_c]$, and the peak energy equals $\widetilde{E}_g$, i.e., $x = 0$.)

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