Temperature Dependence of the Ultrafast Photoluminescence Kinetics from the Magnetic Semiconductors CdCr$_2$Se$_4$ Excited by Femtosecond Laser Pulse

PING-PEI HO, W. LAM, A. KATZ, SHING-SHWANG YAO, AND ROBERT R. ALFANO

Abstract—The recombination time of photogenerated carriers in CdCr$_2$Se$_4$ has been directly measured as a function of temperature. The relaxation kinetics of carriers has been observed to change above and below the Curie temperature 130 K. A deviation from a monotonic increase in the recombination time is measured as the temperature is lowered toward the Curie temperature. This complex behavior is attributed to the interaction between the short-range spin critical fluctuation of the magnetic ions and the spins of the carriers. The fastest measured recombination time at room temperature is 3.8 ps.

CdCr$_2$Se$_4$ is a ferromagnetic semiconductor [1] with interesting optical and transport properties [2], [3]. Below its Curie temperature, $T_C = 130$ K, it displays optically induced permeability and magnetization changes [5]. Our previous research on the photoluminescence kinetics of CdCr$_2$Se$_4$ has implicitly determined that the recombination time could be as short as 2 ps at room temperature [3]. The dominant mechanism for the ultrafast carrier lifetime most likely arises from the nonradiative recombination transitions to the Cr intermediate levels, possibly the d bands [2]. It is technologically important to determine the relaxation time at room temperature since the nonradiative decay in semiconductors is dominant by the Auger effect, surface recombination, defects, and multiphonon emission. The presence of magnetic imperfections in a magnetic semiconductor may exercise an appreciable carrier scattering, especially near the critical transition temperature. The conduction electron owing to the c-1 exchange interaction is scattered by spin fluctuations [6]. CdCr$_2$Se$_4$ could be used as an ultrafast optical switch at room temperature.

In this paper, the time resolved photoluminescence decay of single crystals CdCr$_2$Se$_4$ has been directly studied by using a femtosecond laser system as the excitation light source and a 2 ps resolution streak camera. The nonradiative relaxation process due to the addition of the critical scattering [7] through the Curie transition temperature has
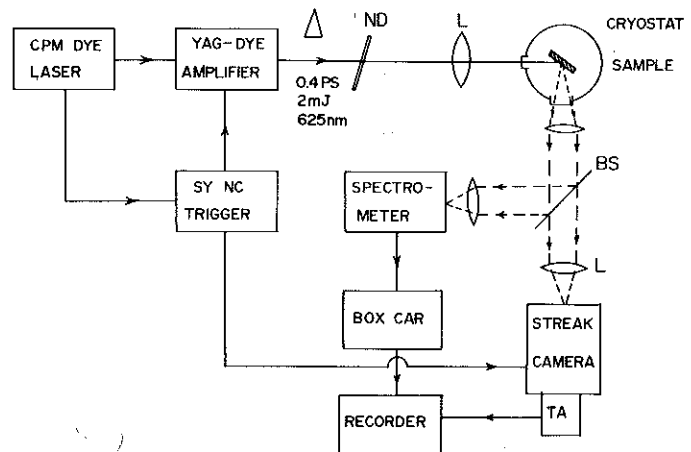
Fig. 1. The experimental setup of the measurements of the photoluminescence spectra and decay time of CdCr$_2$Se$_4$ at different temperatures. *L*: lenses, *ND*: neutral density filters, *F*: color filters and narrow-band filters.

been first directly determined from the photoluminescence recombination time measurements.

The experimental setup is shown in Fig. 1. A laser pulse of 0.4 ps duration at 625 nm was generated from a CPM ring dye laser and a four-stage amplifier system. A similar laser system was described by Shank [8]. The output laser pulse energy was about 1 mJ and was operated at repetition rate of 1–10 Hz. Single crystals of CdCr$_2$Se$_4$ approximately 1 mm on a side were mounted in an optical cryostat and heated from 77 K to room temperature by controlling the flow rate of cooled N$_2$ gas. The lattice parameter was verified by an X-ray powder pattern and only trace impurities had been revealed by spectrochemical analysis [2].

The laser pulse was weakly focused at the simple site. The power density was varied from 10^8 W/cm^2 to 10^{11} W/cm^2 by calibrated neutral density filters. A McPherson spectrometer was used to record the photoluminescence spectra under the intense short pulse excitation. The wavelength resolution of this system was 2 nm. A typical emission spectrum of CdCr$_2$Se$_4$ at 80 K is displayed in Fig. 2. There was no evidence of stimulated emission over the intensity range used to excite the sample. The photo-
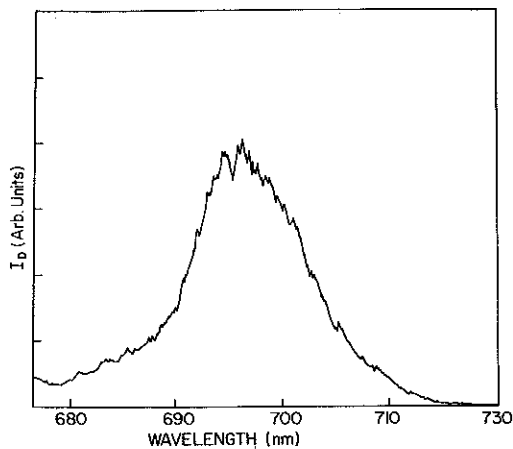
Fig. 2. The emission spectrum of a single crystal $CdCr_2Se_4$ time integrated measurement under 10^{10} W/cm^2 625 nm laser pulse excitation.
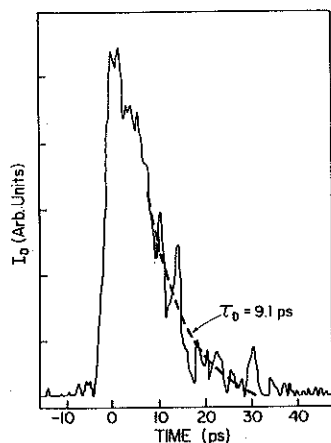

Fig. 3. A typical 700 nm wavelength emission curve of $CdCr_2Se_4$ at 95 K measured by a 2 ps resolution streak camera. The rise time (10–90 percent I_F, peak) is about 2.8 ps and the decay time ($I(t + \tau_D) = 1/e\ I(t)$) is about 9.1 ps. The dashed line is a theoretical fit of 9.1 ps single exponential decay.

Fig. 4. The photoluminescence decay time of a single crystal $CdCr_2Se_4$ at different temperatures directly measured by a 2 ps time resolved system. (a) The steady-state spectral integrated intensity of the photoluminescence from $CdCr_2Se_4$ as a function of temperature. (b) Electrical conductivity of n-type $CdCr_2Se_4$ as a function of temperature from [1].

luminescence recombination time was measured by a Hamamatsu model HTV 1370 streak camera with a time resolution of 2.5 ps (FWHM) [9]. The input slit width of the streak camera was set at 50 μm. The wavelength selection of the streak camera was obtained by using a Ditric 700 nm 3C narrow-band filter and Hoya R66 color filter to select the peak photoluminescence wavelength and to remove the scattered laser light. A typical photoluminescence intensity profile versus time at 95 K is shown in Fig. 3. The decay profile is fitted by a single exponential decay of 9.1 ps. The photoluminescence decay time of $CdCr_2Se_4$ was also measured as a function of the input laser excitation intensity from 10^8 W/cm^2 to 10^{11} W/cm^2. Over this intensity range, there was no significant difference in the measured recombination time. The rise time (10–90 percent of peak intensity) from the time resolved photoluminescence curves is measured to be about 2.8 $\pm$ 0.3 ps.

The carrier recombination time extracted from the photoluminescence decay profiles from 4 to 300 K is shown in Fig. 4. Each datum point corresponds to an average of about four to six measurements. The recombination time from 4 to 90 K from [3] is included to complete the tem-
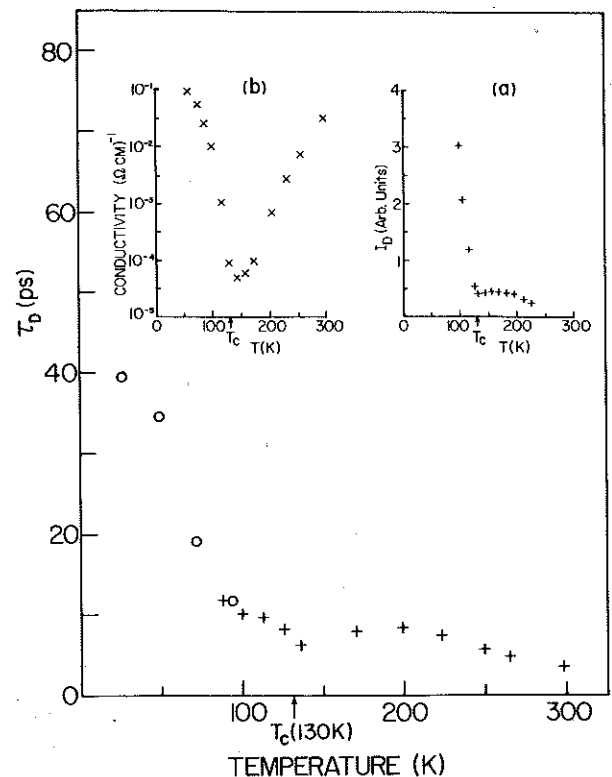
perature dependent study. The measured recombination time from both the femtosecond and the previous picosecond laser pulse report are in good agreement in the overlap temperature region of around 100 K. The measured recombination time at 298 K is 3.8 ps $\pm$ 0.3 ps.

The salient feature of the curve in Fig. 4 indicates that the carrier recombination time increases from 298 K as the temperature is lowered. However, when the temperature approaches the Curie temperature, the decay time decreases slightly and forms a plateau region. Below the Curie temperature, the recombination time monotonically increases as the temperature is lowered further. The steady-state spectra integrated photoluminescence intensity I_D as a function of temperature is shown in the inset (a) in Fig. 4. These data also show a similar plateau and dip near the Curie temperature. This is to be expected since I_D is proportional to τ_D^2 (3).

The complex behavior of carrier recombination time versus temperaure (in Fig. 4) can be described by a model which assumes an additional nonradiative rate arising from the spin interaction, especially from the short-range magnetic critical fluctuation effect near the Curie temperature [7]. From the analysis of Fisher and Langer [7], deGennes and Friedel [10], and Hayes and Loudon [11], the resistivity φ due to the spin scattering can be related to the scattering relaxation time through the conventional equation

$$\varphi = \frac{m}{ne^2\tau} \tag{1}$$

where n is the density of conduction electrons, m is the effective mass of the conduction electrons at the Fermi surface, and τ is the scattering relaxation time associated with the interaction of electrons with spin fluctuations. The enhancement of the resistivity near the Curie temperature is related to a shortening in τ due to the scattering of carriers with spin fluctuations. A temperature dependent conductivity measurement of an n-type $CdCr_2Se_4$ from [1] is displayed in the inset (b) in Fig. 4. The scattering rate of carriers to different $\overline{K}$ states of the conduction band and to the localized d band increases. The spin scattering component of the resistivity versus temperature seems to follow the photogenerated carrier recombination rate. This is due to the scattering of carriers to the d band which arises from the magnetic interactions near the critical phase transition temperature.

The resistivity due to the magnetic critical interaction above and below the Curie temperature can be expressed to be proportional to [7], [10]–[13]

$$\rho \propto (T - T_C)^{-\alpha} \quad \text{for } T > T_C \tag{2}$$

$$\rho \propto (T - T_C)^{-\beta} \quad \text{for } T < T_C \tag{3}$$

where T_C is the Curie temperature and α, β are two constants. For $T > T_c$, φ behaves like the specific heat with $\alpha = 1$. For $T < T_c$, the experimental result of the resistivity measurement (1) and the theoretical prediction [7], [10], [14] gives values of β between 1 and 2. This is a probable mechanism to explain the plateau and dip near the curve temperature of Fig. 4.

In the low temperature region, the resistivity [7] below the Curie temperature is proportional to the square of the spontaneous magnetization M_s. From the Kubo argument [12], the spontaneous magnetization can be approximated by

$$\frac{M_s}{M_o} = 1 - \frac{1}{s} \exp\left(-\frac{q\mu_B}{KT} g M_0\right) \tag{4}$$

where M_0 is the spontaneous magnetization at 0 K and s is the spin number. $q\mu_B$ is the spin magnetic moment, and g is the molecular field coefficient.

In our model to describe the carrier recombination time, a contribution from the electron-Cr spin scattering rate was added to the nonradiative rate of photogenerated carrier. This rate is assumed to have a similar temperature dependence as the resistivity or the spin–spin correlation function. The magnetic interaction causes the carriers to scatter to different states of the d band. This is an empirical assumption to explain the data obtained. The carrier recombination rate K for the photogenerated carriers is defined to be

$$K = K_{radiative} + K_{nonradiative} \tag{5}$$

where

$$K_{nonradiative} = K_{critical\ scattering} + K_{spontaneous\ magnetization}$$

$$+ K_{nonmagnetization} + K_{others}. \tag{6}$$

The temperature dependent nonradiative $K_{nonmagnetization}$ decay rate can be assumed to follow a simple expontential function, $\exp(-A/KT)$. The plateau and dip of decay time near the Curie temperature in Fig. 4 indicates an additional nonradiative decay process which may arise from the magnetic critical scattering as we discussed in (2) and (3). The leveling of the decay time at lower temperature ($T < 50$ K) may account for the spontaneous magnetization interaction discussed in (4). Because of the rapid recombination time observed in this sample, $K_{nonradiative} \gg K_{radiative}$. Therefore, $K \approx K_{nonradiative}$.

In conclusion, the ultrafast photoluminescence recombination time of photogenerated electrons in $CdCr_2Se_4$ has been determined as a function of temperature. The complex behavior of τ versus temperature is attributed to the carrier-magnetic interaction. Near the Curie temperature, the short-range spin scattering causes an additional scattering of carriers which is exhibited in the measured carrier recombination time of the photoluminescence decay. The magnetic interaction plays an important role in the nonradiative decay time of carriers in magnetic semiconductors. The measured carrier recombination time in $CdCr_2Se_4$ at room temperature is 3.8 ± 0.3 ps. This will be ideal for an ultrafast optoelectromagnetoplasmon switch.

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Ping P. Ho, for a photograph and biography, see this issue, p. 204.

W. Lam was born in Hong Kong, China, on March 15, 1964. He came to the United States in 1969.

He entered the City College of New York, New York, in 1981 and joined the Institute for Ultrafast Spectroscopy and Lasers in 1982. He has worked in steady-state laser spectroscopy and is currently working in time-resolved spectroscopy of semiconductors and dyes.

A. Katz was born in New York, NY. He received the B.S. degree in physics from City College of New York and is currently completing the Ph.D. in physics at the Institute for Ultrafast Spectroscopy and Lasers at the City University of New York.

Mr. Katz is a recipient of the Newport Research Award of the Optical Society of America. He is a member of the American Physical Society and the Optical Society of America.

Shing-Shwang Yao was born in Taiwan, China, on December 24, 1952. He graduated from the National Central University, Taiwan, with the B.S. degree in physics in 1974. In 1976 he graduated from the National Taiwan University with the M.S. degree in physics. In 1980 he graduated from Polytechnic Institute of New York with the M.S. degree in electrical engineering. He graduated from the City University of New York with the Ph.D. degree in physics in 1982.

Since then he worked as a Postdoctor in the CUNY and the Optical Sciences Center, University of Arizona. In 1985 he joined IBM at Tucson, AZ, where he is a Staff Engineer. His main interest is in the optical computing and optical data storage.

Robert R. Alfano, for a photograph and biography, see this issue, p. 204.