

Photoluminescent Determination of the Fundamental Gap for the Ferromagnetic Semiconductor CdCr_2Se_4

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Photoluminescence has been used to elucidate the electronic structure of the ferromagnetic semiconductor CdCr_2Se_4 . Luminescence spectra and decay have been measured and analyzed as a function of temperature and the quantum efficiency has been determined at 77 K. The data indicate that the observed emission results from conduction-band to valence-band transitions and place the fundamental gap at 1.8 eV.

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Chromium chalcogenide spinels have generated considerable interest because they present the opportunity to study magnetic interactions in systems where the itinerant-electron population is accessible to experimental control.^{1,2} We report here the first photoluminescence decay and quantum efficiency measurements for any of these materials. In addition, we have obtained, for the first time, emission under cw excitation and have demonstrated that luminescence is observed for all pump wavelengths shorter than that of the emission. As a result of these measurements, we have determined that the fundamental gap E_g of CdCr_2Se_4 is 1.8 eV.

CdCr_2Se_4 orders ferromagnetically at 130 K and has attracted special attention because it displays optically induced permeability changes³ and possibly magnetization changes as well.⁴ Although this material has been extensively studied by a wide variety of optical and transport techniques, its electronic structure has remained controversial. Recently, two band-structure calculations have appeared which differ both in the size of the fundamental gap and in the position of the narrow d bands relative to the valence and conduction bands.^{5,6} To clarify experimentally the electronic structure of this material, we have measured quantum efficiency at 77 K as well as luminescence decay, line shape, and line position as a function of temperature. Although 1.8-eV luminescence had previously been reported by Veselago *et al.*⁷ for CdCr_2Se_4 , these authors attributed it to transitions between crystal-field-split states of Cr^{3+} rather than band-gap emission. This luminescence is difficult to assign because the absorption edge lies at lower energy (1.2 eV at 77 K⁸). The analysis of our data, however, indi-

cates that this emission is not due to an intra- Cr^{3+} transition but rather results from a parity allowed, conduction-band to valence-band transition (possibly involving a shallow donor or acceptor). Accordingly, we have been able to determine that the size of the fundamental gap is 1.8 eV.

The experiments were performed with use of cw, nanosecond-pulse, and picosecond-pulse excitation. For line-shape analysis, low power (≤ 10 mW) cw excitation was provided by the 488-nm line of an argon-ion laser. A nitrogen-laser-dye-laser system was used to probe the effect of varying the exciting wavelength over the interval 560–685 nm. With both these excitation sources the emission was analyzed with spectrometers and detected with conventional photomultipliers. In the decay measurements, picosecond excitation was provided by a frequency doubled (530 nm), mode-locked Nd:glass laser (pulse width ≈ 6 ps) with detection by a 10-ps-resolution streak camera used in combination with band-pass filters. Single crystals of CdCr_2Se_4 approximately 1 mm on a side were mounted in optical cryostats and cooled by flowing N_2 gas.

The samples were grown with use of the flux method⁹ and the lattice parameter was verified by an x-ray powder pattern. Spectrochemical analysis revealed only trace impurities.

Several samples were subjected to electron microprobe analysis which revealed no significant variations in composition across the 1-mm faces.

Figure 1 illustrates the results of the luminescence decay measurements at temperatures from 77 to 250 K. The decays are exponential at all temperatures. The large uncertainties in the

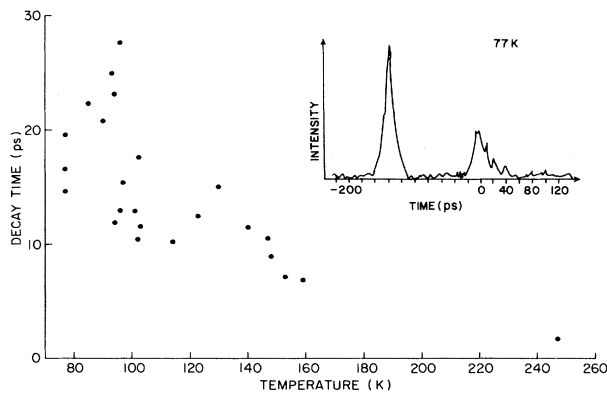


FIG. 1. Lifetime of CdCr_2Se_4 luminescence as a function of temperature. Decays are exponential at all temperatures and were measured at the emission peak (1.8 eV at 77 K). The inset shows a typical decay measurement.

shorter lifetimes are caused by the need to deconvolve the pulse width and streak tube response. The data show a clear pattern of an ~ 25 ps lifetime at 77 K falling to just a few picoseconds at room temperature. These very short lifetimes indicate that the relaxation of the excited state is dominated by nonradiative decay or transitions to intermediate states. This conclusion is confirmed by quantum efficiency measurements in which the emission intensity was compared to that of Rhodamine-6G under identical excitation and collection conditions. If we assume unit efficiency for Rhodamine-6G, the quantum efficiency of the 1.8-eV emission of CdCr_2Se_4 is 10^{-4} at 77 K. This value is probably an underestimate because of the strong self-absorption at this energy.

Taken together, these measurements reveal important information about the states involved in this transition. The quantum efficiency measurement indicates that at 77 K the radiative decay rate is $\geq 10^{-4}$ of the total decay rate, yielding a minimum value of $4 \times 10^6 \text{ sec}^{-1}$ for the radiative transition rate. This is too large for a parity forbidden transition and precludes the possibility of the transition being between crystal-field-split $3d^3$ states of Cr. In this material the Cr sites have octahedral symmetry¹⁰ and in the many-electron representation the ground state of Cr^{3+} has ${}^4A_{2g}$ symmetry while the first excited state is either 2E_g or ${}^4T_{2g}$.¹¹ In the high-crystal-field limit the former is lower making the transition to the ground state both spin and parity forbidden with typical radiative transition rates of $\approx 10^2 \text{ sec}^{-1}$. In the low-field limit the ${}^4T_{2g}$ is the low-

est excited state making the transition spin allowed with radiative rates $\approx 10^3 \text{ sec}^{-1}$, still three orders of magnitude smaller than in CdCr_2Se_4 . In the context of the more appropriate energy-band scheme, the $4 \times 10^6 \text{ sec}^{-1}$ rate for this material requires that the emission result from transitions between bands of opposite parity.

The decay measurements also clarify the ambiguities in electronic structure resulting from the absorption edge being at lower energy than the luminescence. As is the case for CdSe, one expects the band states and resonances to be strongly coupled to polar optical modes¹² and, therefore, to relax via intraband phonon-assisted processes on a time scale of less than a picosecond.¹³ The observed decay time of 25 ps at 77 K requires a gap between the levels involved in the radiative transition and the lower-lying ones involved in the 1.2-eV absorption edge. The simplest interpretation of the optical data requires a 1.8-eV valence-band to conduction-band gap with d bands in the gap. The octahedral symmetry splits the Cr $3d^3$ states into two components with the Fermi level between them and one⁶ or both⁵ components in the gap. The absorption edge results from transitions between either occupied d bands in the gap and the conduction band or unoccupied d bands in the gap and the valence band. Emission results from conduction-band to valence-band transition. Both published calculations show some variation of this structure.^{5,6}

To verify that we are observing fundamental-gap recombination we performed several additional tests, including line-shape analysis. Under moderate excitation nondegenerate free carriers in the conduction or valence band are described by a Maxwell-Boltzmann distribution.¹² For these conditions, interband recombination radiation reflects the Boltzmann factor, and the carrier temperature can be ascertained from an exponential fit to the high-energy edge of the line. This was done for spectra obtained under low-power cw excitation over the temperature interval from 90 to 200 K. The high-energy edges are exponential to within the accuracies of the measurements and Fig. 2 shows the calculated carrier temperature plotted as a function of the measured sample temperature. The good agreement indicates that free carriers thermalized to the lattice temperature are involved in this transition. At these high sample temperatures and low excitation levels the carrier temperature is expected to deviate little from that of the lattice.

The quadratic temperature dependence of E_g

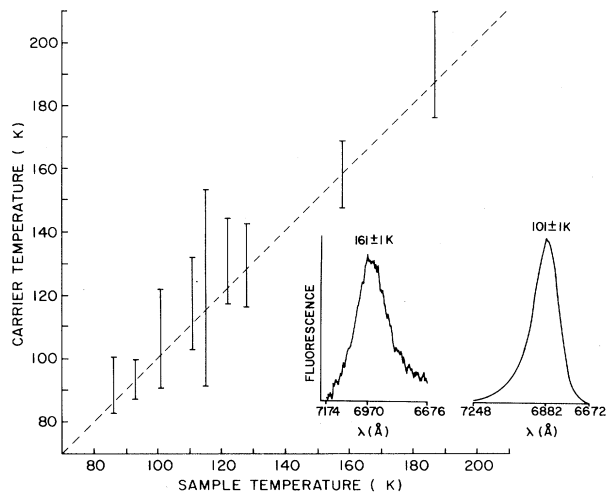


FIG. 2. Carrier temperature as a function of sample temperature. The carrier temperature T_c was obtained by fitting $\exp[-(E - E_g)/kT_c]$ to the high-energy edge of the recombination luminescence line. The dashed line corresponds to a carrier temperature equal to the sample temperature. The inset shows a typical emission spectrum.

for semiconductors at low temperature¹⁴ has been used to further test our assignment of the 1.8-eV luminescence as band-gap emission. Figure 3 shows position versus temperature for the photoluminescence peak which demonstrates the expected behavior for E_g by shifting to lower energy as the temperature is increased. In contrast, the absorption edge shifts to higher energy with increasing temperature.⁸ For allowed, interband recombination of noninteracting carriers the emission peak lies $\frac{1}{2}kT$ higher in energy than E_g for a direct transition and $2kT$ higher for an indirect transition. For both direct and indirect cases the electron-hole interaction will introduce an additive constant to the offset, while for the indirect transition it will in addition modify the offset so that it has no simple functional form but lies in the range from $\frac{1}{2}kT$ to $2kT$.¹⁵ If either $\frac{1}{2}kT$ or $2kT$ is subtracted from the data of Fig. 3, the resulting values of E_g have a quadratic dependence on T . The peak position calculated by fitting E_g to a quadratic function is indicated for the $\frac{1}{2}kT$ and $2kT$ extreme cases by the lines in Fig. 3. The good agreement verifies that the temperature dependence of the luminescence is completely explained by a temperature dependence of the energy gap typical of nonmagnetic semiconductors. Unfortunately, the fits are not sensitive enough to determine where in

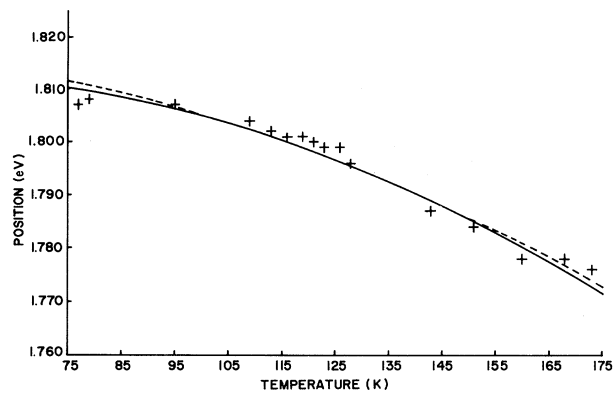


FIG. 3. Energy of the luminescence peak as a function of temperature. The lines are peak positions resulting from least-squares fits of E_g to a quadratic expression. The extreme values of the offset between emission peak and E_g are represented: the solid line is for a peak $2kT$ above E_g and the dashed line is for a peak $\frac{1}{2}kT$ above E_g .

the range from $\frac{1}{2}kT$ to $2kT$ the offset lies and give no information as to whether the transition is direct or indirect.

The above analyses, although establishing that a band must be involved in this emission, do not eliminate the possibility that the other state may be a deep level associated with an impurity or native defect. This situation would require the threshold for excitation to be a significant fraction of E_g larger than the emission energy. However, luminescence was excited with a dye laser tuned continuously over the range from 40 meV to 0.4 eV above the transition. The near-resonance excitation indicates that deep levels are not involved. Equipment limitations prevented a closer approach to resonance excitation, and so it is possible that the band gap is indirect or that shallow donors or acceptors are involved in the transition.

Our results are in qualitative agreement with the two recent theoretical band structures published for CdCr_2Se_4 , and extended Hückel calculation by Kambara, Oguchi, and Gondaira⁵ and a self-consistent $X\alpha$ calculation by Oguchi, Kambara, and Gondaira.⁶ Kambara, Oguchi, and Gondaira predict a direct 1.7-eV fundamental gap for the ferromagnetic phase which is consistent with the value of 1.8 eV which we observe. Oguchi, Kambara, and Gondaira find a larger, slightly indirect gap of 2.3 eV. Although the emission energy is close to the separation at the

Γ point between the top of the valence band and the lowest antibonding d bands in the Oguchi calculation, the latter states have negative dispersion. Thus one would not expect to see emission from the bands at Γ but rather from the indirect minimum at X , a transition of only 0.7 eV. In addition to this quantitative discrepancy between our measurements and the $X\alpha$ calculation, another unresolved problem is the short carrier lifetime of this material. Nonradiative recombination or transitions to intermediate levels, possibly the d bands, are the dominant relaxation processes in CdCr_2Se_4 . Like the deep levels in semi-insulating GaAs:Cr , the d bands in the gap may have the effect of shortening carrier lifetimes but to a much greater extent in this stoichiometric material.

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Two-Photon Absorption as a New Test of the Judd-Ofelt Theory

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Observation by fluorescence detection of direct two-photon absorption within the $4f$ configuration of the Gd^{3+} ion following excitation with a continuous-wave laser is reported. Quantitative intensity measurements test assumptions behind the Judd-Ofelt theory of lanthanide transition intensities in a new way, and significant discrepancies are found. The discrepancies indicate that the radial integrals $\langle 4f|r|5d \rangle$ vary markedly for different J multiplets, and that ligands significantly influence two-photon intensities.

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Kaiser and Garrett¹ observed direct two-photon absorption for the first time by exciting a $4f^n \rightarrow 4f^{n-1}5d$ transition in a lanthanide ion with a pulsed ruby laser. Few subsequent studies of

two-photon absorption, however, have explored the parity-allowed transitions within the $4f^n$ configuration of lanthanides.^{2,3} In the present work we report observation of direct two-photon $f \rightarrow f$