

PHOTOLUMINESCENT SPECTRA AND KINETICS OF CdCr_2Se_4
AND CdCr_2S_4

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Photoluminescence at the fundamental gap has been used to clarify the electronic structure of the ferromagnetic semiconductors CdCr_2Se_4 and CdCr_2S_4 . For the latter this is the first report of band gap emission. For 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. Implications of these results for recent band structure calculations and photoemission measurements are considered.

Chromium chalcogenide spinel magnetic semiconductors have attracted considerable interest because of the interaction between their electronic and magnetic systems. Despite the large amount of effort directed toward these materials, their electronic structure has remained controversial. We report photoluminescence measurements which identify the fundamental gap for the two most extensively studied Cr spinels, CdCr_2Se_4 and CdCr_2S_4 . In combination with a recent photoemission investigation,¹ these measurements determine the qualitative electronic structure of these two compounds.

CdCr_2Se_4 and CdCr_2S_4 are ferromagnetic semiconductors which order at 130 K and 84 K, respectively. These materials have attracted special attention because of the strong interaction between their carriers and spins, typified for CdCr_2Se_4 by an absorption edge which shifts to the red with decreasing temperature² and unusual transport properties in the vicinity of the Curie temperature.³ In addition, CdCr_2Se_4 displays optically induced permeability changes⁴ which may result from magnetization changes.⁵ Attempts to explain these effects have been handicapped by the poor understanding of the electronic structure of chromium chalcogenide spinels which has persisted despite extensive study by a wide variety of optical and transport techniques. Photoluminescence was first observed for CdCr_2Se_4 by Veselago et al.⁶ who attributed it to transitions between crystal field split states of Cr^{3+} (R-line emission). This luminescence is difficult to assign because it lies at higher energy than the absorption edge (1.8 eV vs. 1.2 eV at 77 K). Recent photoluminescence measurements by Yao et al.⁷ have reinterpreted this as band gap emission. Using photoconductivity, Larsen and Wittekoek⁸ found a band gap of 2.5 eV for CdCr_2S_4 but did not observe luminescence at this energy. New insight into the electronic structure of these materials has been added by

band structure calculations performed using the extended Hückel⁹ and discrete variational X α ¹⁰ (DV-X α) methods.

The octahedral symmetry of the Cr site splits the free ion d-levels into a three-fold orbitally degenerate t_{2g} lower state and a two-fold orbitally degenerate e_g upper state. Intra-Cr exchange should introduce a large splitting between the spin components of these states. With regard to the electronic structure, the most important questions concern the locations of these d-bands with respect to the p-like valence band and s-like conduction band. To experimentally clarify the electronic structure of CdCr₂S₄, we have measured quantum efficiency at 77 K as well as luminescence decay, line shape, and line position as a function of temperature. In addition, we report the first observations of fundamental gap luminescence for CdCr₂S₄.

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-pumped dye laser system was used to excite CdCr₂S₄. 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 bandpass filters. Single crystal samples typically 1 mm on a side were mounted in optical cryostats and cooled by flowing N₂ gas.

The CdCr₂Se₄ crystals were grown by the flux method¹¹ and the CdCr₂S₄ samples were grown by vapor transport.¹² The lattice parameters were verified by X-ray powder patterns and spectrochemical analysis revealed only trace impurities. As an additional test, samples were subjected to scanning electron microprobe analysis and no variations in composition were found across the faces.

The luminescence decay measurements for CdCr₂Se₄ revealed a lifetime of 25 ps at 77 K which decreases to a few picoseconds at 250 K. 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 made by comparing the 1.8 eV emission to that of Rhodamine 6G. An efficiency of 10^{-4} was found in this way. This value is probably an underestimate because of the strong self-absorption at this energy. Combining the decay and quantum efficiency measurements produces a lower limit for the radiative transition rate of $4 \times 10^6 \text{ sec}^{-1}$. This is too large a value for a parity forbidden transition and precludes the possibility that the transition is between crystal field $3d^3$ states of Cr for which the transition rates are at least three orders of magnitude smaller.

The decay measurements are also useful in explaining why the absorption edge is at lower energy than the luminescence in these materials. For compound semiconductors, one expects the band states to be strongly coupled to polar optical modes¹³ and relax via intraband, phonon-emitting processes on a

subpicosecond time scale.¹⁴ The 25 ps decay time at 77 K requires a gap or bottleneck between the levels involved in the radiative transition and the lower-lying ones involved in the 1.2 eV absorption edge. The simplest electronic structure consistent with this requirement has a 1.8 eV fundamental gap, E_g , with d-bands in this gap responsible for the absorption edge. From absorption and photoluminescence data alone it is not possible to determine whether the d-bands in the gap are the filled t_{2g} , unfilled e_g , or both.

As a further test of the nature of the CdCr_2Se_4 emission, the temperature dependence of the peak was measured. This shifts to the blue with decreasing temperature in contrast to the absorption edge which shifts to the red. For interband transitions the luminescence peak lies from $\frac{1}{2}kT$ to $2kT$ higher in energy than E_g depending on whether the transition is direct or indirect.¹⁵ Using this relationship between E_g and the luminescence peak yields a band gap with the quadratic temperature dependence typical of non-magnetic semiconductors.¹⁶ The line shape analysis also indicates that the emission involves band states. Under moderate excitation conditions free carriers are described by a Maxwell-Boltzmann distribution.¹⁷ The Boltzmann factor will accordingly appear in the line shape of the recombination radiation. By fitting exponentials to the high energy edge of lines measured at low excitation levels, we deduced carrier temperatures which fell within experimental uncertainty of the sample temperatures over the range 80 to 200 K. The carrier temperature is expected to deviate little from that of the lattice at these high sample temperatures and low excitation levels.

In contrast to the single line observed at 1.8 eV for CdCr_2Se_4 , the fundamental gap photoluminescence of CdCr_2S_4 consists of several rather weak lines extending from 2.5 eV down to 2.3 eV. These were observed under pulsed excitation at 450 nm and a temperature of 77 K. Although lifetime and temperature-dependence measurements are not yet available, it is possible to conclude that the fundamental gap of CdCr_2S_4 is ≈ 2.5 eV. This is in agreement with the value obtained by photoconductivity.⁸ The emission lines at lower energy are likely due to traps.

Recent photoemission measurements by Miniscalco et al.¹ have determined that the occupied t_{2g} d-bands lie below the top of the valence band for both CdCr_2Se_4 and CdCr_2S_4 . By combining the photoemission and photoluminescence results it is possible to ascertain that it is only the unfilled e_g band which occupies the fundamental gap. The experimentally determined electronic structure qualitatively supports the band structure calculations. The extended Hückel calculation gives 1.7 eV for the band gap of CdCr_2Se_4 and the 2.5 eV for CdCr_2S_4 .⁹ The corresponding values from photoluminescence are 1.8 eV and 2.5 eV. However, the Hückel calculation places both the t_{2g} and the e_g bands in the fundamental gap in contradiction with the photoemission measurements. The DV-X α calculation gives larger values for E_g than photoluminescence, 2.3 eV for CdCr_2Se_4 and 2.6 eV for CdCr_2S_4 .¹⁰ For CdCr_2Se_4 it places the t_{2g} band below the top of the valence band in agreement with the photoemission results. For CdCr_2S_4 , however it disagrees and shows the t_{2g} band extending above the top of the valence band. These discrepancies remain to be resolved.

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- [1] W.J. Miniscalco, B.C. McCollum, N.G. Stoffel, and G. Margaritondo, to be published.
- [2] B. Busch, B. Magyar, and P. Wachter, *Physics Lett.* 23 (1966) 438; G. Harbeke and H. Pinch, *Phys. Rev. Lett.* 17 (1966) 1090.
- [3] H.W. Lehmann, *Phys. Rev.* 163 (1967) 488; C. Haas, A.M.J.G. van Run, P.F. Bongers and W. Alber, *Solid State Commun.* 5 (1967) 657; A. Amith and G.L. Gunsalus, *J. Appl. Phys.* 40 (1969) 1020.
- [4] W. Lems, P.J. Rijnierse, P.F. Bongers, and U. Enz, *Phys. Rev. Lett.* 21 (1968) 1643.
- [5] N.M. Salanskii and N.A. Drokin, *Fiz. Tverd. Tela (Leningrad)* 17 (1975) 331 [*Sov. Phys. Solid State* 17 (1975) 205].
- [6] V.G. Veselago, I.A. Damaskin, S.L. Pyshkin, S.I. Radautsan, and V.E. Tezlevan, *Pis'ma Zh. Eksp. Teor. Fiz.* 20 (1974) 335 [*JETP Lett.* 20 (1974) 149]; V.G. Veselago, *Colloq. Int. C.N.R.S.* 242 (1974) 295.
- [7] S.S. Yao, F. Pellegrino, R.R. Alfano, W.J. Miniscalco, and A. Lempicki, *Phys. Rev. Lett.* 46 (1981) 558.
- [8] P.K. Larsen and S. Wittekoek, *Phys. Rev. Lett.* 29 (1972) 1597.
- [9] T. Kambara, T. Oguchi, and K.I. Gondaira, *J. Phys. C* 13 (1980) 1493.
- [10] T. Oguchi, T. Kambara, and K.I. Gondaira, *Phys. Rev. B* 22 (1980) 872.
- [11] G.H. Larsen and A.W. Sleight, *Phys. Lett.* 28A (1968) 203.
- [12] H.L. Pinch and S.B. Berger, *J. Phys. Chem. Solids* 29 (1968) 2091.
- [13] J. Shah, *Phys. Rev. B* 9 (1974) 562.
- [14] C.V. Shank, R.L. Fork, R.F. Leheny, and J. Shah, *Phys. Rev. Lett.* 42 (1979) 112.
- [15] R.J. Elliott, *Phys. Rev.* 108 (1957) 1384.
- [16] G.D. Mahan, *J. Phys. Chem. Solids* 26 (1965) 751.