Evidence from Photoluminescence for the Splitting of the s-Conduction Band of the Ferromagnetic Semiconductor $CdCr_2Se_4$

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Photoluminescence spectra from $CdCr_2Se_4$ have been measured at low temperatures. When the temperature was lowered below 70 K, an extra peak was observed on the higher-energy side of the band-to-band luminescence transition. The energy difference between the two peaks was measured to be 3.5 meV. The emission was attributed to the transitions from the split s-conduction bands.

Ferromagnetic semiconductors are well known for their anomalous optical and electrical properties. The absorption edges[1] shift to the red as the temperature is lowered below the Curie temperature, and the critical scattering effects[2] at the Curie temperature cause very large electrical resistivity and negative magnetoresistance. The most widely studied ferromagnetic semiconductors are europium oxide, europium chalcogenides,[3] and chromium spinels.[4] Many theories have been proposed to explain these phenomena. Rys, Helman, and Battensperger[5] and Haas[6] claimed that the red shift is proportional to the exchange energy between the carriers and the local magnetic moments. In addition, Haas believes that the conduction band is split into two spin-polarized components below the Curie temperature for weak exchange interactions. Kubo[7] and Aldea and Teleman[8] derived different conduction-band energy diagrams for stronger exchange interactions in the ferromagnetic region. Recently, Nolting and Olés[9] proposed that the conduction band is composed of complex mixed-spin states at all temperatures and the red shift is caused by a broadening of the lowest spin-up quasiparticle subband with decreasing temperature.

A most interesting ferromagnetic semiconductor is $CdCr_2Se_4$ with a Curie temperature at 130 K.[2] Recently, we have determined[10] the fundamental energy gap between the s-conduction band and the p-valence band is located at 1.8 eV. Miniscalco *et al.*[11] have determined that the filled d band (t_{2g}) is at 1.45 eV below the top of the p-valence band using photoemission spectroscopy. The anomalous absorption edge is probably caused by transitions[4,12] between the p-valence band and the unfilled d band (e_g). Up to now, little is known experimentally about the exchange effect

on the s-conduction band from the local magnetic moments of Cr in $CdCr_2Se_4$. In this Letter, experimental data are reported on the photoluminescence spectra of band-to-band transitions at liquid-helium temperature. Direct information is presented for the first time on the splitting of s-conduction band in a semiconductor. The spectra contain two peaks which are ascribed to the emission from conduction bands split by the exchange interaction between the s-conduction electrons and the magnetic moments in filled d band (t_{2g}). Using Nolting and Olés's theory,[9] the exchange constant is estimated from the spectra to be 2.3 meV.

In the experiment, an argon laser beam at 488 nm with 10 to 100 mW power was used to excite the $CdCr_2Se_4$ sample. The sample was located in an optical helium dewar. The luminescence from both linear and circular polarized excitations were measured. The luminescence was collected and imaged into a double Spex $\frac{1}{2}$-m spectrometer, detected by a RCA 7265 photomultiplier, and analyzed by a PAR lock-in amplifier-recorder combination. Circular polarized emission was measured with a $\lambda/4$ plate, a linear polarizer, and a depolarizer plate. The sample temperature was measured using a silicon diode.

Typical emission spectra from $CdCr_2Se_4$ at 10 to 70 K are shown in Fig. 1. The salient feature of the spectra is an extra peak on the high-energy side of the band-to-band emission peak for each spectrum. The electronic temperature T_e obtained from the high-energy tail of the higher-energy peak is 13.5 K which is larger than T_s. The sample heating caused by the laser is estimated[13] to be less than 1 K. The higher electron temperature than the sample temperature is due to the reduced interaction between electrons and phonons at very low temperatures.[14] When the sam-
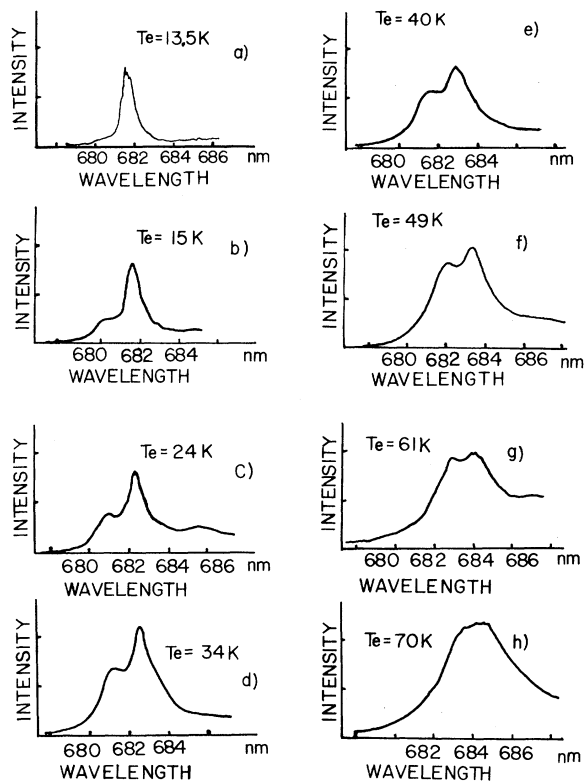
FIG. 1. Emission spectra of $CdCr_2Se_4$ excited by argon laser of 10-mW power at different temperatures. (a) T_s = 4.4 K, T_e = 13.5 K; (b) T_s = 4.9 K, T_e = 15 K; (c) $T_s = T_e$ = 24 K; (d) $T_s = T_e$ = 34 K; (e) $T_s = T_e$ = 40 K; (f) $T_s = T_e$ = 49 K; (g) $T_s = T_e$ = 61 K; (h) $T_s = T_e$ = 70 K.
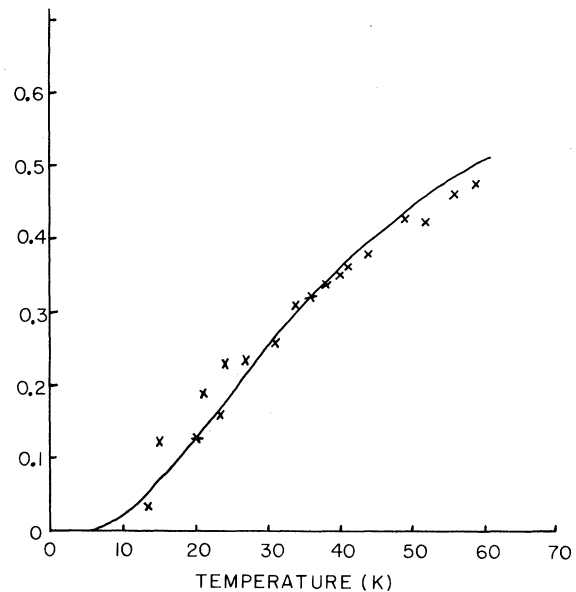

FIG. 2. Ratio of half intensity of the higher-energy peak to the intensity of the lower-energy peak vs the electronic temperature T_e (crosses). The solid line is proportional to $\exp(-\Delta E/KT_e)$ with ΔE = 3.5 meV.

ple temperature is above 20 K, the electronic temperature T_e is the same as the sample temperature T_s. For temperatures above 70 K, the two peaks are not resolved. The spectral resolution for the data displayed in Fig. 1 is ±1 meV. The energy differences between these two emission bands are ~ 3.5 meV from 4 to 70 K.

The location of the energy peak of the band-to-band transition of $CdCr_2Se_4$ from 170 to 4 K of sample temperature was measured. The spectral resolution in this case is larger than 4 meV; therefore the two peaks are not resolved. The peak energy shifts to blue by 40 meV over the whole temperature range. In Fig. 2, the ratio of one half of the higher-energy-peak intensity to the lower-energy-peak intensity is plotted versus the electronic temperature T_e from 10 to 70 K. The solid line is $\exp(-\Delta E/KT_e)$ with ΔE = 3.5 meV.

From the spectra displayed in Fig. 1, the two photoluminescence bands have been observed. The exchange effect on the p-valence band can be

neglected compared with that on the s electrons because the valence electrons are located on the selenium ions which are about 3 Å away from the Cr ions, and the s electrons are mainly located on the Cr $4s$ orbitals.[4] It is important to know whether the main peak shown in Fig. 1(a) is a band-to-band transition in order to conclude that these two emission bands are from two split s-conduction bands. The photoluminescence intensity from $CdCr_2Se_4$ at 77 K was measured to increase quadratically with the excitation intensity.[15] This excludes the possibility that these two emission bands are both exciton states or impurity states because both exciton emission and impurity emission increase linearly with excitation intensity.[16,17] It may be argued that the lower-energy emission band is exciton or impurity emission and the higher-energy emission band is electron-hole recombination; however, this can be excluded because the intensity ratio between the two bands remains the same value at a fixed temperature over a wide range of excitation intensity. Furthermore, excitons would be dissociated when the temperature is above 41 K (~ 3.5 meV) which is the energy difference between the two emission bands.

The high-energy sides of both emission bands at various temperatures were analyzed. Both bands can be fitted approximately to $\exp[-(h\nu$

$-E_{gi})/KT_e]$, $i=1,2$, where $h\nu$ is the emission energy. This indicates that the density of states is close to constant values within certain energy ranges ($\leqslant 20$ meV) from the band edges. From the above analysis, we conclude that the two emission bands arise from electron-hole recombination. Hence, the split in the photoluminescence spectra is due to the split of s-conduction band by the magnetic exchange effect.

From the data displayed in Fig. 2, the half intensity of the higher-energy peak increases relative to the lower-energy peak by $\exp(-\Delta E/KT_e)$ with $\Delta E = 3.5$ meV. This means the two s-conduction bands are in thermal equilibrium and separated by 3.5 meV. The density of states at the bottom of the higher split band is assumed to be the same as that at 3.5 meV above the bottom in the lower split band. Both theories developed by Haas[6] and Nolting and Olés[9] predicted a ratio of $\exp(-\Delta E/KT_e)$ between the two bands because the two bands have a common chemical potential and the distribution of carriers is a Maxwellian distribution for nondegenerate semiconductors at low temperatures. If the two split s bands are purely spin polarized, the right- and left-circular-polarized emission spectra from $CdCr_2Se_4$ at very low temperatures should be different for the two bands. This is because the transition probabilities from spin-up and spin-down conduction band to valence band by emitting right- and left-circular-polarized light are different.[18] However, the measured right- and left-circular-polarized emission spectra from $CdCr_2Se_4$ at $T_e = 25$ K with or without 4-kG external magnetic field applied on the sample are the same within experimental accuracy. The ratio of two bands remained the same for linear and circular excitations. Furthermore, the energy difference between two emission bands remains ~ 3.5 meV over a wide range of temperatures (10 to 70 K). This contradicts the Haas theory which states that the splitting is proportional to the magnetization which decreases with increased temperatures. Therefore, we conclude that the s bands are not purely spin polarized and are probably mixed-spin bands.

According to the theory developed by Nolting and Olés,[9] the conduction band of a ferromagnetic semiconductor is composed of multiquasiparticle spin bands. The center of gravities for conduction bands are located at $-\frac{1}{2}g\langle S_z\rangle$ and $\frac{1}{2}g\langle S_z\rangle$, where g is the exchange interaction constant between the conduction electrons and the local Cr magnetic moments. For $CdCr_2Se_4$, $\langle S_z\rangle = \frac{3}{2}$. The

above result is true when the conduction band is very weakly occupied and the exchange constant g should be larger than that between the local magnetic moments J. The value of J is ~ 1.2 meV for nearest-neighbor coupling.[19] The steady-state carrier density n generated by a 10-mW argon laser equals P/RV, where $P=10$ mW, R is the decay rate of the s electrons (~ 50 ps at 10 K), and V is the volume where the photogenerated carriers occupy (10^{-5} to 10^{-4} cm^{-3}). Since n $\sim 10^{10}$ to 10^{11} cm^{-3} is very small compared with the ion density ($\sim 10^{22}$ cm^{-3}), the conduction band of $CdCr_2Se_4$ is very weakly occupied using a 10-mW argon laser excitation. From the data displayed in Fig. 1, the energy difference between the two split bands is 3.5 meV. If the difference between the two lower band edges is close to the difference between two centers of gravity, the theory of Nolting and Olés can be used to estimate the exchange constant g. In this case ΔE is equal to $\frac{1}{2}g\langle S_z\rangle - (-\frac{1}{2}g\langle S_z\rangle) = g\langle S_z\rangle = \frac{3}{2}g$, yielding the exchange constant g to be 2.3 meV. Since $g \geqslant J$, the present theory should be extended to yield an accurate value of g.

Yanase and Kasuya[20] have found the exchange constants of an s-f model for EuSe to be 7 meV at center ion, 2 meV at nearest neighbors, and 9 meV at all sites except the center ion and the nearest neighbors, with a model of magnetic impurity state in doped europium selenide. In $CdCr_2Se_4$, the s-d bands do not overlap and the exchange constant for the s-d model should be in the millielectronvolt range. The value measured from the photoluminescence splitting is 2.3 meV which is the correct order of magnitude for non-overlapping bands. In addition, the energy difference between the filled d band (t_{2g}) of Cr ions and the s band is $1.8 + 1.45 = 3.25$ eV which is much larger than the energy difference 1.78 eV of EuSe.[21] Therefore the exchange constant g in $CdCr_2Se_4$ should be smaller than the s-f exchange constant in EuSe because of lack of overlapping and larger energy difference.

The reason why the splitting of the s-conduction band is observable in $CdCr_2Se_4$ at low temperatures arises because the thermal distribution energy KT is smaller than the energy difference between the two bands. This is illustrated in Fig. 1. The two bands can not be clearly differentiated at 70 K because $KT_s \sim 6$ meV and the higher-energy peak intensity is close to the lower-energy peak intensity. Above 70 K, the split conduction bands can no longer be observed. For europium oxide and chalcogenides, the red shifts of the

absorption edges are the same order of magnitude[9] as the exchange constant between the conduction electrons and the local magnetic moments. In $CdCr_2Se_4$, the red shift is not observed in the photoluminescence spectra because the exchange constant is very small compared with the total blue shift of the fundamental gap.

Evidence is presented from the photoluminescence spectra for the splitting of s-conduction band in the ferromagnetic semiconductor $CdCr_2Se_4$. The recent theory developed by Nolting and Olés was used to obtain the exchange energy constant of 2.3 meV between the s-conduction electrons and the Cr ions spins.

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Spin and Energy Analyzed Secondary Electron Emission from a Ferromagnet

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Measurements are presented of the energy dependence of the spin polarization of low-energy (0.5–25 eV) secondary electrons when a 500-eV primary beam is incident on an iron-based ferromagnetic glass. The polarization of the lowest-energy electrons is found to correspond to the net valence-band spin density. Possible causes for the observed decrease in polarization with increasing secondary energy are discussed. The results demonstrate a mechanism for measuring surface magnetic structure with the very high spatial resolution of scanning electron microscopy.

We have measured the polarization of secondary electrons emitted from a ferromagnetic Fe glass target as a function of the emitted electron energy. The aim of these first measurements of spin- and energy-analyzed secondary emission from a ferromagnet was to test the hypothesis that the spin polarization of the secondary cascade is closely related to the net spin density near the surface of the material. The results have significant implications for the study of microscopic magnetic structures including spin distributions within a domain or domain wall through the use of polarization analysis of secondary electrons in scanning electron microscopy.

When energetic primary electrons are incident on a solid, they lose energy and cause valence