Photoconductivity and Luminescence Caused by Band-Band and by Cr^{3+} Crystal Field Absorptions in $CdCr_2S_4$

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By photoconductivity measurements the direct band edge has been located at 2.5 eV. With decreasing temperature this edge shows a blue shift, also below T_C. Irradiation at the energies of Cr^{3+} crystal field transitions causes both luminescence and photoconduction. The latter shows a strong magnetic field dependence near T_C. An energy-level model for $CdCr_2S_4$ is proposed. In the model the energy difference between conduction- and valence-band extrema is considerably smaller (about 1.6 eV) than the optical band gap.

Various optical methods have been used to determine the energy-level scheme of the ferromagnetic semiconductor $CdCr_2S_4$.[1-10] The energy levels of the Cr^{3+} ion in the octahedral crystal field of the sulfur ions have been located relative to the Cr^{3+} ground state $^4A_2$.[4,7] The transitions between these levels, however, impede the observation of other optical transitions like those between the valence and the conduction bands. To locate the latter type of transitions we have recently performed photoconductive measurements. In this Letter we report a successful attempt to locate the direct transitions between valence and conduction bands in $CdCr_2S_4$ by this method. Furthermore we observe that the optical transitions between the Cr^{3+} crystal field levels give rise to a noticeable photoconduction as well as to luminescence. To our knowledge it is the first time that such "crystal-field-induced" photoconductivity and luminescence have been observed in magnetic semiconductors.[11] These measurements are useful in locating the relative positions of the Cr^{3+} crystal fields levels and the semiconductor energy bands.

Figures 1(a) and 1(b) show the spectral dependence of the photoconductivity of n-type, undoped polycrystalline platelets of $CdCr_2S_4$. The photoconductivity is found to be proportional to the light intensity. We identify the sharp rise of the photoconductivity at 0.52 μm [Fig. 1(a)] with the onset of direct transitions between the valence and the conduction bands. This value is in fair agreement with the value obtained by a more indirect method from reflection measurements.[7] The band edge shifts to higher energy with decreasing temperature as shown in Fig. 1(a). We find no magnetic red shift of the direct edge below the Curie temperature T_C (85°K for $CdCr_2S_4$) as predicted by models of exchange splitting of the energy bands.[12]

At temperatures near T_C the photoconductivity at the band edge is enhanced when a magnetic field is applied. This enhancement is much larger than that of the thermally activated dark conductivity of electrons in n-type undoped $CdCr_2S_4$.[13] At $T \sim 80$°K the dark conductivity increases by about 2% after applying a field of 7 kOe, whereas the photoconductivity for chopped irradiation at 434 Hz increases by 17%. The photoconductivity itself and its field dependence are frequency dependent, and a study of the time dependence shows that there are two contributions to the photoconductivity with different relaxation times. We find that the contribution with the shorter relaxation time ($\tau < 5$ msec) has by far the strong-

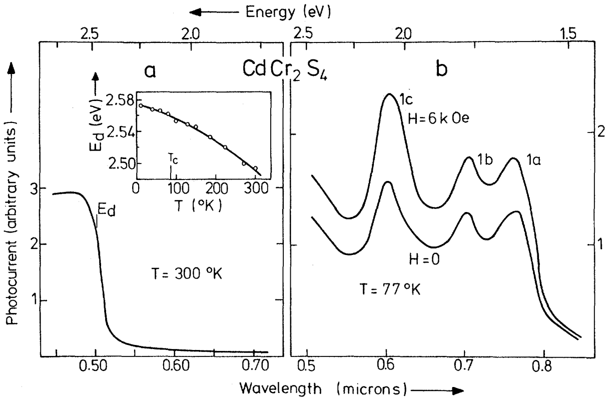

FIG. 1. Spectral dependence of the photoconductivity for polycrystalline undoped n-type $CdCr_2S_4$. (a) Sample resistivity 6×10^4 Ω cm at room temperature and activation energy of 0.22 eV. The inset shows the temperature variation of the direct edge E_d. (b) Sample resistivity 6×10^{10} Ω cm at room temperature and an activation energy of 0.43 eV. The photoconductivity is shown in zero magnetic field and in a transverse magnetic field of 6 kOe.

er field dependence. These observations can be explained by assuming that the "fast" contribution to the photoconductivity is due to photoexcited holes with a relatively large magnetic field dependence.

At photon energies below the band edge we can distinguish clearly three peaks 1*a*, 1*b*, and 1*c* [see Fig. 1(b)] for not too high temperatures ($T \lesssim 150°K$). The peaks are observed in all our samples, which were *n* type with activation energies between 0.1 and 0.7 eV. The peak positions are temperature independent and occur at the energy positions of internal Cr^{3+} *d-d* transitions as identified by absorption[3,4] and Kerr-effect measurements.[7] The energies of the peaks and the corresponding crystal field transitions are 1.61 eV ($^4A_2 \rightarrow {}^2T_1, {}^2E$), 1.76 eV ($^4A_2 \rightarrow {}^4T_2$), and 2.1 eV ($^4A_2 \rightarrow {}^2T_2$). The photoconductivity in the region of these peaks varies linearly with the excitation intensity and shows a large magnetic field dependence (up to 50%) as shown in Fig. 1(b). Referring to the discussion of the field dependence of the direct-edge photoconductivity, we conclude from this that the crystal-field-induced photoconductivity is largely due to holes. The enhancement shows a maximum at T_C and can be attributed to an increase in the hole mobility due to spin-disorder scattering.[12]

The luminescence and excitation spectra of the luminescence of $CdCr_2S_4$ are shown in Fig. 2. The weak luminescence peak at 1.6 eV observed only at liquid-helium temperatures is attributed to the transition $^2T_1, {}^2E \rightarrow {}^4A_2$, known as the Cr^{3+} *R* line. A strong luminescence peak is found at 0.9 eV. This peak is easily observed at temperatures below 100°K and was in some specimens still observable at room temperature. The decay time of the luminescence was of the order of 1 msec. No influence of the presence of a magnetic field on the luminescence was observed. The excitation spectrum for the 0.9-eV luminescence peak (see Fig. 2) shows maxima at the energies of the Cr^{3+} crystal field transitions just as in the photoconductivity spectrum.

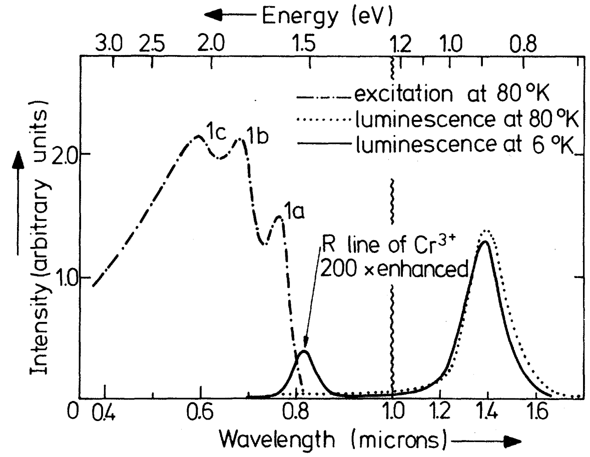

FIG. 2. Luminescence and excitation spectrum of undoped $CdCr_2S_4$ powders. The excitation spectrum is for luminescence at wavelengths between 1.0 and 2.5 μm. The peaks 1*a*, 1*b*, and 1*c* in this spectrum are interpreted as Cr^{3+} crystal field transitions. Note the low intensity of the *R* line compared with the 1.4-μm luminescence.

The similarity between the luminescence excitation spectrum and the photoconductive spectrum, and the observation of a decay time for the luminescence of the same order as the relaxation time of the hole term in the photoconductivity, indicate that the luminescence is due to a recombination of holes. This means that recombination levels (presumably acceptors) are situated 0.9 eV above the valence band. Results of conduction measurements are in agreement with the presence of deep-lying acceptors in $CdCr_2S_4$.[14] Both Cd vacancies and impurities (Cu) could form the acceptor levels.

The results of the two types of experiments show that after the Cr^{3+} ion has been excited in one of its crystal field levels a charge transfer must occur in which a charge carrier is created so that conduction and luminescence can occur. We consider in the following model the transfer of an electron from the excited Cr^{3+} ion. As we will discuss later, a transfer of a hole from the excited Cr^{3+} ion is highly unlikely.

As basis for our model we adopt the proposal by Lotgering and van Stapele[15] that in chromium sulfospinels the Cr^{3+} band is situated at about the same energy as the top of the valence band. For convenience we take this energy to be zero on the energy scale. The conduction-band minimum of the direct edge is then situated at 2.5 eV. If this minimum is the lowest conduction-band minimum, it is not possible to have an electron transfer from the lowest excited Cr^{3+} state ($^2T_1$, ^2E at 1.61 eV) to the conduction band since this Cr^{3+} state is then 0.9 eV below the conduction band. It is also impossible that the electron is transferred to an empty donor level since for some *n*-type samples all levels up to about 0.1 eV below the conduction band are filled.

We therefore propose that another, lower conduction-band minimum exists at or below 1.6 eV. This minimum can be an indirect minimum or a direct minimum to which optical transitions from

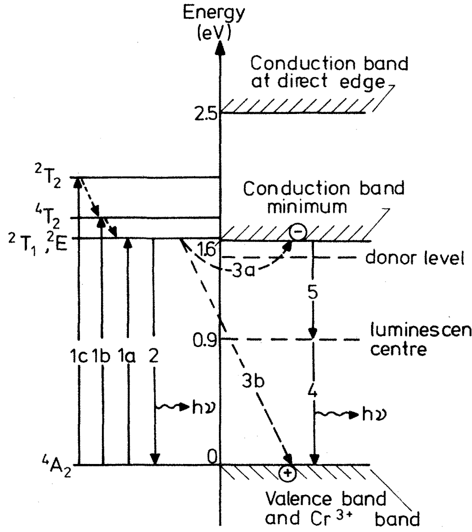

FIG. 3. Energy-level model for $CdCr_2S_4$. The various transitions are identified in the text.

the valence band are forbidden.

With this assumption we will explain the experimental data with the aid of Fig. 3. By virtue of the Cr^{3+} crystal field transitions $1a$, $1b$, and $1c$, the Cr^{3+} ion can be excited in the various excited states ($^2T_1$, ^2E, $^4T_2$, and $^2T_2$). Apart from possible radiationless relaxation to the $^4A_2$ ground state, these excited states can relax back to the state $^2T_1$, ^2E. From there the luminescent transition (2) $^2T_1, {}^2E \rightarrow {}^4A_2$ (the Cr^{3+} R line) can occur, or an electron from the excited Cr^{3+} ion can be transferred to a nonchromium state—specifically to the conduction-band minimum at 1.6 eV ($3a$). This transfer means that a hole is formed in the Cr^{3+} band ($3b$). This hole can move in either the Cr^{3+} band or the valence band, giving rise to the observed photoconductivity. Furthermore this hole can recombine with an electron in the acceptor level at 0.9 eV and lead to luminescence (4). The return to the original charge state is completed by transfer of an electron from the conduction band to the acceptor level (5). A variation of this explanation could be that the electron of the Cr^{3+} ion is transferred to an empty donor level (e.g., an S vacancy). In this explanation a low-lying conduction-band minimum is still necessary.

We have also considered an explanation of the experimental results by assuming the transfer of a hole from the Cr^{3+} ion. We find this highly unlikely since then a Cr^{2+} state would be formed. According to Kerr-effect measurements the lowest Cr^{2+} state is situated at 3.4 eV above the valence band, which is much too high to allow a hole transfer from the Cr^{3+} states at about 1.6–1.9 eV.

Some arguments for an indirect edge have been given by Harbeke and Lehmann,[6] but from absorption data this edge is difficult to deduce because of the strong $^4A_2 \rightarrow {}^4T_2$ crystal field transition which has a broad wing. It may also be noted that pseudopotential calculations by Meloni and Mula for the related sulfospinel[16] $CdIn_2S_4$ predict an indirect edge.

More detailed measurements at various temperatures on samples prepared under different sulfurizing conditions are in progress and will be reported in a later article.

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