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TAc-6 Photoconductivity and Electronic Structure of Ferromagnetic Semiconductor $CdCr_2Se_4$

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Photoconduction measurements have been made with a view to getting information on the energy band structure of the ferromagnetic semiconductor $CdCr_2Se_4$. The spectrum of the photoconduction shows peaks at the energies 1.25 and 1.9 eV in the spectral region 1.0 to 2.5 eV. Below the Curie temperature, the peak of 1.25 eV moves toward lower energy as the temperature is decreased (red shift). The photoresponse at 1.25 eV is enhanced with magnetic field near the Curie temperature. From these results, it is postulated that the absorption edge for the band to band transition is about 1.9 eV and the transition associated with magnetic ions occurs at 1.25 eV.

INTRODUCTION

Several models concerning the electronic structure of $CdCr_2Se_4$ have been proposed and there is an interesting problem whether the observed optical absorption edge is associated with the "band to band" transition or with the "charge transfer" transition.

According to Goodenough,[1] the excited state of Cr^{2+} is placed below the bottom of the conduction band and the optical absorption edge is determined by the transfer of electrons from the valence band to the vacant d-levels of Cr^{2+}. The fact, reported by Harbeke *et al.*,[2] that the absorption edge is shifted toward lower energy as the temperature is decreased at temperatures below the Curie point is interpreted as a change of the energy of the electrons in the valence band induced by the spin ordering in Cr ions. This model is also consistent with the smaller mobility of electrons compared with that of holes.[3] On the other hand, Haas[4] has supposed that the level of Cr^{2+} lies above the bottom of the conduction band and the absorption edge is corresponding to the transition of electrons from valence band to conduction band. In his model the red shift arises from the splitting of conduction band due to the spin ordering and the small mobility of electron is related to scattering of electrons by spin-disorder.

Recently Berger, *et al.*[5] and Wittekoek, *et al.*[6] have reported that the absorption edge is not the semiconductor band edge but rather consisting of several types of excitation such as those due to charge transfer and crystal field transitions within the d-shell.

In the present work, photoconduction measurements were carried out with a view to getting further information on the above-mentioned problem.

EXPERIMENTAL

The samples used were undoped p-type single crystals with resistivity of the order of 10^3 ohm-cm at room temperature grown by the chemical transport reaction method reported by Wehmeier.[7] Evaporated gold provided electrodes with good ohmic contact over the temperature range 77° to 300°K. Monochromatic light with the energies from 1.0 to 4 eV was chopped at 480 Hz and the photocurrent was detected by a phase sensitive detector after narrow band amplification.

Figure 1 is the spectral response curve which shows two prominent peaks in the measured spectral region, one lies at 1.25 eV (peak-A) and the other at 1.9 eV (peak-B) at room temperature. Peak-A is narrower and weaker than peak-B. Below the Curie temperature (about 130°K), as the temperature is decreased, our peak-A moves remarkably toward lower energy (red shift), as shown in Fig. 2. On the contrary, the peak-B moves slightly toward higher energy with decreasing temperature (blue shift). This behaviour is summarized in Fig. 3.

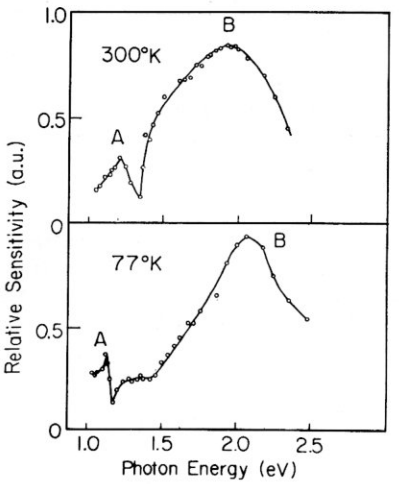

FIG. 1. Photoconduction spectra.

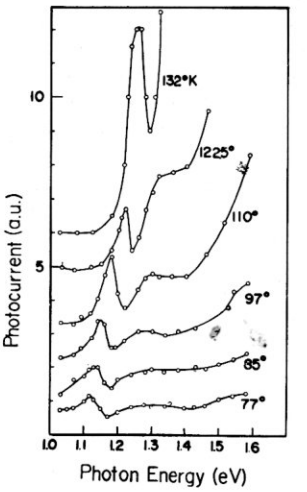

FIG. 2. Detailed spectra around peak-A. The ordinate for each curve has been shifted arbitrarily for easiness to see.

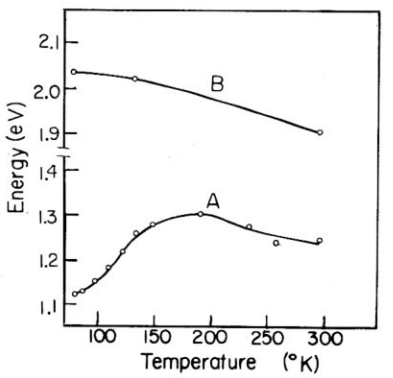

FIG. 3. Temperature dependence of peak-A and peak-B.

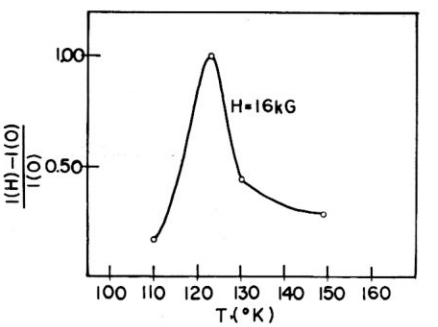

FIG. 4. Temperature dependence of the magneto-photoconduction of peak-A. I(H) and I(O) are the photocurrent with and without external magnetic field, respectively.

Negative magneto-resistance was not observed in the dark, because the samples used were of p-type, as pointed out by Lehmann.[3] When the samples were illuminated, however, the negative magneto-resistance was observed, i.e., the height of the photocurrent peak-A was enhanced with application of magnetic field near the Curie temperature. Figure 4 represents temperature dependence of this "magneto-photoconduction."

DISCUSSION AND CONCLUSION

The photoconduction peak-A is located at the same photon energy as the absorption edge reported by Harbeke, *et al.*[2] and its red shift is similar to their data, too. Therefore, it may be concluded that peak-A corresponds to the transition associated with the

absorption edge. Peak-A is weaker and much narrower than peak-B and shows negative magneto-resistance. Peak-B shows a slight blue shift with decreasing temperature as in ordinary semiconductors. From these results, we have concluded that the absorption edge should be associated with an exciton-like localized transition involving a d-electron level of the chromium ion which contributes to the photocurrent through some ionization mechanism, and that peak-B originates from so-called band-to-band transitions. The photocurrent is presumably of electrons because the negative magneto-resistance is not observed in hole conduction in the dark.

As for the excitation involving a d-electron level and concerning the absorption edge, two schemes might be considered. One is the transition producing holes in the valence band and excited electrons in unfilled localized d-levels. The other is a combination of d-holes in filled d-levels and excited electrons in the conduction band. From the preliminary measurements of photoemission, we, at present, tentatively suppose that the latter scheme is preferable.

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