Reflectance Magnetocircular-Dichroism Spectra and Electronic Structures of CdCr$_2$Se$_4$ (*)

K. Sato and T. Teranishi

Broadcasting Science Research Laboratories of Nippon Hoso Kyokai (Japan Broadcasting Corporation) - Kinuta, Setagaya-ku, Tokyo 157, Japan

(ricvuto il 14 Settembre 1982)

Summary. — Reflectance magnetocircular-dichroism spectra of a ferromagnetic semiconductor CdCr$_2$Se$_4$ were measured for temperatures between 4.2 K and 157 K. Off-diagonal elements of the dielectric tensor were calculated from the measured spectra. A number of fine structures was resolved, the energy position of which was plotted against temperature. It is found that there are two red-shifting structures: one at 1.1 eV (the well-known absorption edge) and the other at 1.9 eV. Other structures show slight blue-shift. These energy positions were compared with the band structure calculated by means of the self-consistent DV-Xz technique.

PACS. 78.20. — Optical properties and materials.

1. — Introduction.

CdCr$_2$Se$_4$ is one of the most extensively studied magnetic semiconductors. Despite the long history of investigations, the electronic structures of this material have not been fully understood. However, it seems that researches on this magnetic semiconductor have entered into a new stage in these few years, as there has been much progress in both experimental and theoretical fields, e.g. absorption edge shift (1), photoluminescence (PL) (2), photoemis-

(*) Paper presented at the s V International Conference on Ternary and Multinary Compounds s, held in Cagliari, September 14-16, 1982.
sion (\textsuperscript{3}), wave-length modulation (WM) (\textsuperscript{4}) and theoretical calculations (\textsuperscript{5,6}).

It may be significant to present detailed information of the magneto-optical (MO) spectrum of CdCr\textsubscript{2}Se\textsubscript{4}, since such a spectrum has been known to offer plenty of information on the electronic structures of magnetic materials. We, therefore, present in this paper the MO spectra of this material for various temperatures and give a brief discussion on the electronic structure based on the experimental results.

2. – Experiments.

The single crystal of CdCr\textsubscript{2}Se\textsubscript{4} used in this study was prepared by the chemical vapour transport technique with CdCl\textsubscript{2} as a transporting agent and with a Se excess atmosphere. Magnetic measurements on crystals of the same lot revealed that $T_c$ is $\left(130 \pm 1\right)$ K and $\theta_{p}$ is $\left(154 \pm 3\right)$ K.

Reflectance magneto-circular-dichroism spectra were measured by means of the polarization modulation technique, details of which have been published elsewhere (\textsuperscript{5}). The temperature was varied between 4.2 K and 157 K. The maximum applied field was 4 kOe, which was sufficient to saturate the sample. Spurious CD and MCD signals introduced by a window material of a cryostat have been carefully removed with the aid of a microcomputer.

3. – Results and discussions.

The observed RMCD, $\Delta R/R = (R^{+} - R^{-})/(R^{+} + R^{-})/2$; as well as those of $\Delta \theta = \theta^{+} - \theta^{-}$ calculated from the RMCD by the dispersion relation derived by Smith (\textsuperscript{6}) are plotted in fig. 1a) and b), $R^{\pm}$ and $\theta^{\pm}$ being the reflectivity and the phase shift for RCP$(\pm)$ and LCP$(-)$.

From the experimental RMCD data, the spectra of the real and imaginary parts of the off-diagonal element of the dielectric tensor $\varepsilon$ were calculated ac-

\begin{itemize}
\end{itemize}
Fig. 1. - Spectra of RMCD (a)) and $\Delta \theta$ (b)) for temperatures between 4.2 K and 157 K.

cording to the procedure described previously in ref. (9), where $\hat{\varepsilon}$ is defined by

$$
\hat{\varepsilon} = \begin{pmatrix}
\varepsilon_0 & -i\varepsilon_1 & 0 \\
i\varepsilon_1 & \varepsilon_0 & 0 \\
0 & 0 & \varepsilon_2
\end{pmatrix},
$$

in which $\varepsilon_0 = \varepsilon_0' + i\varepsilon_0''$ and $\varepsilon_1 = \varepsilon_1' + i\varepsilon_1''$.

In fig. 2a) and b) the spectra of $\varepsilon_1'$ and $\varepsilon_1''$ so obtained by the calculation are shown. There are a doublet structure around 1.1 eV (named $A$), a shoulder around 1.6 eV (B), a strong dispersive structure at 1.9 eV (C), dispersive shapes around 2.2 eV (D) and 2.5 eV (E) and a shoulder at 2.8 eV (F). According to the theory of the magneto-optical effect, the spectrum of $\varepsilon_1$ can be decomposed into a superposition of Lorentzian oscillators. The energy positions of the Lorentzian oscillators fitted to the experimental spectra are plotted against temperature in fig. 3. In this plot small structures are neglected for the sake of simplicity.

The energy positions are then compared with the reported band structure calculated by means of the self-consistent DV-Xα method (5,6). As shown in table I, most of the observed MO lines can be associated with transitions across the gap at some symmetry point T, X, K or L in the Brillouin zone.

The structure A consists of two peaks A₁ and A₂ with an energy separation of 0.1 eV and shows a shift toward lower energy by decreasing the temperature (red-shift). The energy position of A₁ as well as its temperature shift is in good agreement with that of the carefully measured absorption edge (1). The doublet-shaped fine structure at the absorption edge has also been reported in photoconductivity (19) and polarized absorption (11) spectra. We can associate the structure with the transitions $L₁(d_{ε}) \rightarrow L₁(d_{γ\cdot}p)$ at 0.96 eV and $L₄(HV) \rightarrow L₁(d_{γ\cdot}p)$ at 1.07 eV found in the calculated band structure.

Another red-shifting structure C, the most prominent one, is observed at 1.9 eV, which can be decomposed into two peaks C₁ and C₂ with opposite

Fig. 3. – Plot of peak positions of $\varepsilon_1$ spectra against temperature. Open circle: positive peak; closed circle: negative peak. The symbol $\times$ denotes the data of Zvára et al. (4), $\times$ represents the photoconductivity peak (19) and + the absorption edge reported by Balberg and Maman (4).

Table I. – Comparison of transition energies determined by the present experiment with those given by the theoretical band calculation (6).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Experimental energy position (eV) [polarity]</th>
<th>Shift</th>
<th>Corresponding transition energy from band calculation (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>1.1, 1.2 [-] [-]</td>
<td>red</td>
<td>0.96 ($d\varepsilon \rightarrow d\gamma$-p) at $L$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.07 ($HV \rightarrow d\gamma$-p) at $L$</td>
</tr>
<tr>
<td>$B$</td>
<td>1.53, 1.65 [+][+]</td>
<td>no</td>
<td>1.53 ($HV \rightarrow d\gamma$-p) at $X$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.55 ($HV \rightarrow d\gamma$-p) at $L$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.60 ($HV \rightarrow d\gamma$-p) at $K$</td>
</tr>
<tr>
<td>$C$</td>
<td>1.83, 1.91 [+][-]</td>
<td>red</td>
<td>1.74 ($HV \rightarrow d\gamma$-p) at $\Gamma$</td>
</tr>
<tr>
<td>$D$</td>
<td>2.10, 2.26 [-][+]</td>
<td>blue</td>
<td>2.14 ($d\varepsilon \rightarrow d\gamma$-p) at $\Gamma$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.20 ($HV \rightarrow d\gamma$-p) at $\Gamma$</td>
</tr>
<tr>
<td>$E$</td>
<td>2.46, 2.63 [-][+]</td>
<td>blue</td>
<td>2.30 ($HV \rightarrow d\gamma$-p) at $\Gamma$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.34 ($HV \rightarrow LC$) at $\Gamma$</td>
</tr>
<tr>
<td>$F$</td>
<td>2.80</td>
<td>blue</td>
<td>2.78 ($HV \rightarrow d\gamma$-p) at $X$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HV: highest valence band.
LC: lowest conduction band.
polarity, the separation of which is about 0.1 eV and can be related to the spin-orbit splitting. A PL peak has been observed in the vicinity of C (1.8 eV) (2) and has been attributed to the HV $\rightarrow$ LC transition. Since the PL peak shows a slight blue-shift, we consider that this does not correspond to the C-structure. ZVÁRA et al. also reported a similar red-shifting structure at 1.9 eV in their WM spectrum (3). We associate the structure C to the charge-transfer-type transition $I_{15}^{a}(HV) \rightarrow I_{25}^{a}(\gamma-p)$ in the band diagram. Peaks associated with D, E and F can also be related to the same type of transitions. However, these exhibit blue-shift, which poses the problem why the same type of transition causes a red-shift for A and C and a blue-shift for the other.

A detailed analysis of MO line shapes would give more definite assignments of transitions. This study is now in progress.

***

The authors are very grateful to Prof. T. KAMBARA for helpful discussions.

• RIASSUNTO (*)

Gli spettri di riflettanza del dierismo magnetocircolare di un semiconduttore ferromagnetico CdCr$_2$Se$_4$ sono stati misurati per temperature tra 4.2 K e 157 K. Gli elementi fuori dalla diagonale del tensore dielettrico sono stati calcolati dagli spettri misurati. Si è determinato un certo numero di strutture fini, la cui posizione energetica è stata rappresentata in un grafico rispetto alla temperatura. Si è trovato che ci sono due strutture che si spostano nel rosso: una a 1.1 eV (il ben noto picco di assorbimento) e l'altra a 1.9 eV. Altre strutture mostrano un leggero spostamento nel blu. Queste posizioni di energia sono state confrontate con la struttura di banda calcolata mediante la tecnica autoconsistente $DV$-$Xz$.

(*) Traduzione a cura della Redazione.

Спектры отражательной способности и электронная структура CdCr$_2$Se$_4$.

Резюме (*). — В области температур от 4.2 K до 157 K измеряются спектры отражательной способности ферромагнитного полупроводника CdCr$_2$Se$_4$. Для измеренных спектров вычисляются ненагональные элементы диэлектрического тензора. Разрешается ряд тонких структур, энергетическое положение которых вычисляется в зависимости от температуры. Обнаружено, что существуют две структуры, обладающие красным смещением; одна при 1.1 эВ (хорошо известный край поглощения) и другая при 1.9 эВ. Другие структуры обладают голубым смещением. Энергетические положения этих структур сравниваются с зонной структурой, вычисленной с помощью $DV$-$Xz$ метода.

(*) Переведено редакцией.