S. Wittekoek
P. F. Bongers

Magneto-optical Investigation of the Band Edge of $CdCr_2S_4$ and Related Absorption Measurements on Cr-doped $CdIn_2S_4$

Abstract: The $^4T_1$ and $^4T_2$ crystal-field transitions of Cr^{3+} have been observed in the absorption spectrum of $CdIn_2S_4(Cr)$. From the similarity between the temperature dependence of the $^4T_2$ band and the reported blue shift of the absorption edge of $CdCr_2S_4$ it is concluded that in $CdCr_2S_4$ this edge is caused by the $^4T_2$ absorption band of the Cr^{3+} ions. The polar magneto-optic Kerr effect between 560 and 700 nm and the Faraday rotation between 800 and 8000 nm are reported for $CdCr_2S_4$. The Kerr effect spectrum indicates that the intrinsic band edge of $CdCr_2S_4$ is at 1.91 eV at 60°K and shifts to lower energies with decreasing temperature.

The absorption edge of several magnetic semiconductors, e.g. EuX (X = O, S, Se),[1] $HgCr_2S_4$,[2] $HgCr_2Se_4$ [3] and $CdCr_2Se_4$ [4,5] shifts to lower energies (red shift) when the temperature is decreased below the Curie temperature, T_c. $CdCr_2S_4$ forms an exception to this behavior.[4,5] In this compound the absorption edge, found at 1.57 eV at room temperature, exhibits a structure and a shift to higher energies (blue shift) at lower temperatures. This blue shift persists down to temperatures far below T_c = 86°K.

In order to elucidate the exceptional behavior of $CdCr_2S_4$ we have studied the wavelength region around the absorption edge by means of the polar magneto-optic Kerr effect and the Faraday rotation. Furthermore, in order to obtain insight on the possible Cr^{3+} absorption bands in this type of compound, we measured the absorption spectrum of $CdIn_2S_4$, doped with Cr^{3+}. A detailed account of these measurements on $CdIn_2S_4(Cr)$ will be published elsewhere;[6] the results relevant to the present investigation are given here briefly.

Figure 1 shows the absorption spectrum of single crystals of $CdIn_2S_4$ and of $CdIn_2S_4$ with 0.7% of the In replaced by Cr. The maximum at 675 nm (14,800 cm^{-1}) and the shoulder at 540 nm (18,500 cm^{-1}) in the 5°K spectrum can be attributed[6] to the $^4T_2$ and $^4T_1$ crystal-field transitions of Cr^{3+}.

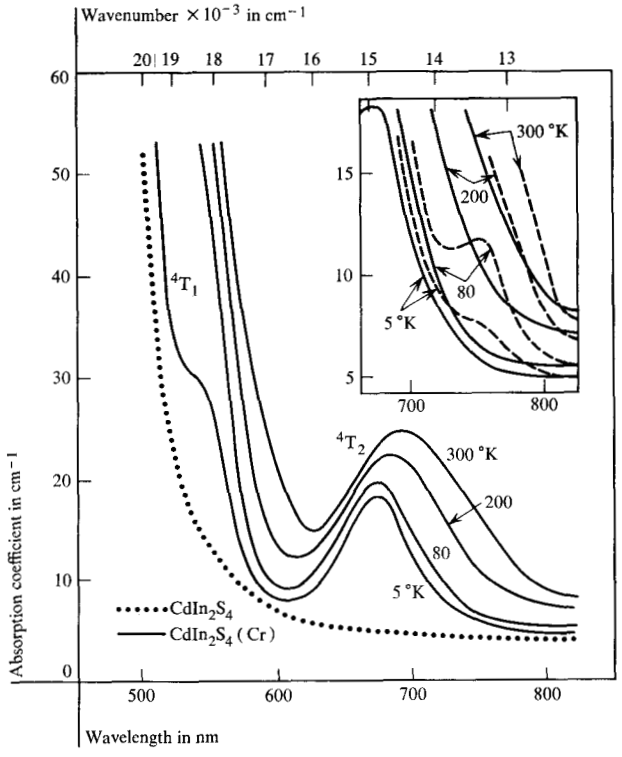

Figure 1 Absorption spectrum of $CdIn_2S_4$ at 5°K and of $CdIn_2S_4(Cr)$ at 5, 80, 200 and 300°K. In the insert the long wavelength parts of the curves are compared with the absorption spectra of $CdCr_2S_4$ (dashed lines) at the same temperatures. The $CdCr_2S_4$ data are taken from Ref. 4 (see text).

The authors are located in the Philips Research Laboratories, N. V. Philips Gloeilampenfabrieken, Eindhoven, The Netherlands.

The low-energy wing of the $^4T_2$ band is found in the same wavelength region and has the same temperature dependence as the steep absorption edge of $CdCr_2S_4$.[4] The magnitude of the absorption coefficient is similar too, as is shown in the insert of Fig. 1, where the spectra of $CdCr_2S_4$ and of $CdIn_2S_4$(Cr) are compared. The data for the $CdCr_2S_4$ spectrum are taken from Ref. 4 and normalized to the same Cr^{3+} concentration as in $CdIn_{1.986}Cr_{0.014}S_4$, assuming the absorption coefficient to be proportional to the Cr^{3+} concentration.

From the similarity between the two spectra it is concluded that the absorption edge of $CdCr_2S_4$ is not the semiconductor band edge but rather the wing of the $^4T_2$ transition of the Cr^{3+} ions.

The origin of the apparent "blue shift" of the absorption edge is a narrowing of the long wavelength wing of the $^4T_2$ band. This narrowing has been observed earlier[7] for Cr^{3+} bands in Cr-doped oxy-spinels and has been attributed to the temperature dependence of vibration-induced electric-dipole transitions.

To locate the real semiconductor bandgap of $CdCr_2S_4$ we have measured the polar magneto-optic Kerr effect in the wavelength region between 560 and 700 nm. Figure 2(a) gives the Kerr rotation ψ at different temperatures between 60°K and 5°K and the Kerr ellipticity ϵ at 5°K. The experiments were performed on a polished and etched surface of a hot-pressed, polycrystalline sample (porosity $< 1\%$). At 60°K two strong disperions of ψ and corresponding maxima of ϵ are found at 650 nm (15,400cm^{-1}) and 590 nm (17,000cm^{-1}), which are attributed to two magneto-optical transitions I and II. Transition II, at 590 nm, does not shift with temperature between 60°K and 5°K. Transition I shifts from 650 nm (15,400 cm^{-1}) at 60°K to 675 nm (14,800 cm^{-1}) at 5°K [see Fig. 2(b)]. This Kerr spectrum and its temperature dependence are quite analogous to that of $CdCr_2Se_4$,[8] where a temperature independent transition (II) is found at 17,200 cm^{-1} and a temperature dependent one (I) at about 11,000 cm^{-1}. The latter shows a red shift with decreasing temperature and is attributed to the semiconductor bandgap transition, i.e., from valence to conduction band. By analogy we interprete transition I in $CdCr_2S_4$ as the semiconductor bandgap transition. According to this interpretation the bandgap of $CdCr_2S_4$ decreases by an amount of 700 cm^{-1} (0.09 eV) between 0.7 T_c and 0°K, compared with 0.07 eV for $CdCr_2Se_4$. According to this interpretation the semiconductor band edge shows a red shift with decreasing temperature, while the absorption edge due to the $^4T_2$ transition shows a blue shift. At low temperatures (5°K) the two transitions are practically degenerate at 680 nm. Therefore a detailed analysis of the Kerr rotation peak I, associated with the band edge, should take into account a possible contribution from the $^4T_2$ band.

From the strong similarity between the Kerr rotation

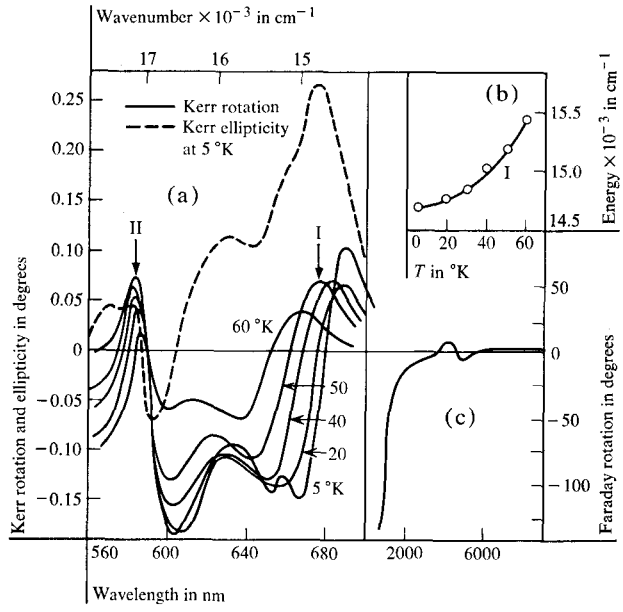

Figure 2 (a) Kerr effect spectrum of $CdCr_2S_4$ at various temperatures, showing a temperature independent (II) and a temperature dependent (I) transition. (b) Temperature dependence of the center of transition (I) from Fig. 2(a). (c) Faraday rotation of a $CdCr_2S_4$ single crystal of 200 μm thickness at $T = 80$°K and $H = 7650$ Oe.

peaks I in $CdCr_2S_4$ and in $CdCr_2Se_4$, where no crystal-field transition is nearby and peak I can be assigned unambiguously to the interband transition, we conclude that this contribution from the $^4T_2$ transition is small. This is not surprising since the parity forbidden $^4T_2$ band is expected to produce considerably smaller rotations than the allowed band-band transition. A more detailed analysis must await accurate calculations of the magnetic rotations caused by the different type of transitions involved.

Finally, Fig. 2(c) shows the wavelength dependence of the Faraday rotation of a $CdCr_2S_4$ single crystal of 200 μm thickness at 80°K. At 800 nm, the shortest wavelength where rotation measurements could be performed, the specific rotation amounts to 7000 deg-cm^{-1}.

The specific rotation θ_F is the sum of a wavelength independent contribution θ_M from magnetic resonance and a strongly dispersive contribution θ_D from electronic transitions at short wavelengths. Since the Cr^{3+} ions are in a $^4A_2$ ground state with $g_\parallel = 1.995 \pm 0.005$ and $g_\perp = 2.000 \pm 0.005$,[9] the contribution to θ_D arising from an electronic transition at λ_0, will have a wavelength dependence[10] given by $\lambda^2/(\lambda^2 - \lambda_0^2)^2$.

Under the assumption that θ_D originates from a single transition at λ_0, θ_F should obey the relation

$$\theta_F = \theta_M + \frac{A\lambda^2}{(\lambda^2 - \lambda_0^2)^2}. \qquad (1)$$

We find that, apart from a dispersion-like singularity at 4000 nm, the origin of which is not clear, the experimental results can be described accurately by Eq. (1), with $\theta_M = 75$ deg/cm, $A = -2.8 \times 10^{-5}$ deg-cm and $\lambda_0 = (400 \pm 5)$ nm. The values of θ_M and A refer to the experimental conditions $T = 80°K$ and $H = 7650$ Oe.

This result indicates that the major contribution to the rotation is not due to the valence band to conduction band transition which is situated at $\lambda \approx 670$ nm, but originates from electric-dipole transition(s) at much shorter wavelength ($\lambda \approx 400$ nm). A similar result has been found in $CdCr_2Se_4$.[11]

In summary, we have found from a comparison of the absorption spectra of $CdIn_2S_4(Cr)$ and $CdCr_2S_4$ that the absorption edge of $CdCr_2S_4$ is caused by the wing of the $^4T_2$ band of the Cr^{3+} ions rather than by the semiconductor band edge. The Kerr effect spectrum indicates that the transition from valence band to conduction band occurs at 15,400 cm^{-1} at 60°K and shifts to lower energy with decreasing temperature, similar to the behavior of $CdCr_2Se_4$. Consequently, there is no longer reason to accept the argument that the shift of the $CdCr_2S_4$ band edge is anomalous with respect to other magnetic semiconductors. The major contribution to the Faraday rotation of $CdCr_2S_4$ is not a consequence of the semiconductor bandgap transition but, rather, the electric-dipole transitions at considerably higher energies.

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