THERMOREFLECTANCE, PHOTOCONDUCTANCE AND RAMAN SCATTERING OF FERROMAGNETIC SPINELS MCr 2X4 (M=Cd, Hg; X=S, Se) NEAR THE MAGNETIC PHASE TRANSITION

Milko Iliev

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Résumé.- Le compte rendu présent a pour but d'étudier certains résultats des expériences faites récemment sur la thermoréflexion, la photoconductibilité et la diffusion Raman de résonance des spinelles ferromagnétiques (CdCr$_2$Se$_4$, CdCr$_2$S$_4$, HgCr$_2$Se$_4$) près et au-dessus du seuil d'absorption. Le comportement critique près de la transition de phase magnétique des éléments particuliers du spectre de la thermoréflexibilité associés aux bandes des électrons itinérants met en évidence l'existence d'un fort couplage entre les sous-systèmes des électrons et des spins. Ceci est confirmé aussi par les variations en température du spectre de photoconductibilité et la section efficace de la diffusion Raman. Le mécanisme réel des processus électroniques dépendants du spin paraît donc plus compliqué que celui prévu par les modèles les plus simples. Les Raman spectres eux-mêmes aussi bien que leur dépendance de la température et de l'énergie des photons incidents mettent en cause le concept actuel sur la diffusion Raman dépendant du spin dans les spinelles ferromagnétiques. Les résultats prouvent que les intensités des phonons Raman actifs sont déterminées par les formes des courbes de résonance et leur variation avec la température.

Abstract.- The results of recent experiments on thermoreflectance, photoconductance and resonant Raman scattering of CdCr$_2$Se$_4$, CdCr$_2$S$_4$ and HgCr$_2$Se$_4$ at photon energies near and above the absorption edge are reviewed. The critical behaviour near the magnetic phase transition of the thermoreflectance (TR) spectral features associated with the bands of itinerant electrons provide evidence of a strong coupling between electrons and spins. The latter is supported by the temperature variation of both the photoconductivity spectra and the resonance of the Raman scattering cross section. The actual mechanism of spin-dependent electronic processes seems to be more complex than predicted by the simplest models. The Raman spectra and their dependence on temperature and incident photon energy show that the concept of spin-dependent Raman scattering in the ferromagnetic spinels has to be revised. The results allow to conclude that the intensities of the Raman-active phonons are determined mainly by the line shapes of the resonance curves and their changes with temperature.

1. Introduction.- The ferromagnetic chromium chalcogenide spinels are often used as a model for investigation of those specific features which characterize a material as a ferromagnetic semiconductor. The coexistence of two electronic subsystems and their interaction, results in a complicated electronic structure and an anomalous behaviour (in comparison with classical semiconductors) of their electrical, optical and transport properties near the magnetic phase transition at $T_c$.

Until recently the effect of magnetic ordering on the optical properties of the Cd- and Hg- ferromagnetic spinels has been inferred from the existence of a "red shifting" absorption band, its position being related to the magnetization. The explanation of spin-dependent absorption has been the starting point in all theoretical models accounting for the dependence of the electronic states on temperature or external magnetic field /1-7/. As the realistic description of magnetic-ordering-effects is of fundamental interest, it is quite important how the validity of these models can be verified by further optical experiments, in particular, in the highly absorbing region.

Another phenomenon related to the spin ordering is the unusual temperature dependence of the scattering cross section observed for some of the Raman-active modes in CdCr$_2$S$_4$ and CdCr$_2$Se$_4$ /8/. Although several models for spin-dependent Raman scattering have been proposed /8-10/ none of them accounts for the changes of the intermediate electronic state in the
scattering process. The results of recent experiments /11-13/ show, however, that the resonant Raman scattering and its temperature dependence play an important role for variations of the scattering cross section and may be the dominating mechanism which governs the Raman line intensities.

We will review further the results of thermoreflectance (TR), photoconductance and Raman scattering experiments related to magnetic-ordering-effects and how they correlate to the existing models which describe the interactions between electrons, spins and phonons.

2. Thermoreflectance. - In TR experiments one measures the relative changes of reflectance $R_R$ as the temperature $T$ is modulated by $\Delta T$. The thermomodulation and the employment of lock-in-techniques for detection of the signals have the general advantage of modulation spectroscopy, namely, the weak spectral features are enhanced while the temperature-independent background is suppressed. Furthermore, in the case of magnetic semiconductors it is reasonable to expect that the TR spectra will be dominated by structures related to optical transitions with higher differential temperature coefficients, i.e. to transitions involving band states rather than to intrionic d-d transitions. The situation is opposite to that of polar magneto-optical Kerr spectra where the main contribution comes from transitions involving localized magnetic states. Finally, due to its derivative nature the amplitude of TR signal should be very sensitive to the magnetic phase transition. In view of the above, the TR studies can be quite informative, especially if one is concerned with the effect of magnetic ordering on the optical transitions.

TR spectra and their variations with temperature near $T_C$ have been measured for CdCr$_2$Se$_4$ /14,15/ and quite recently also for CdCr$_2$S$_4$ /16/ and HgCr$_2$Se$_4$ /17/. The results are shown in figures 1, 2 and 3, respectively.

By inspecting the experimental curves of figures 1, 2 and 3 and comparing with other available optical spectra for these materials in the same photon energy regions one easily concludes that the TR spectra exhibit much richer structures.

Weak peaks (shoulders) are seen for CdCr$_2$Se$_4$ (peak B) and CdCr$_2$S$_4$ with positions which correspond to the energies of d-d transitions of Cr$^{3+}$ ions. The main TR peaks however, are obviously related to optical transitions involving band states. The origin of the peak I for CdCr$_2$S$_4$ is discussed in ref. /16/.

The thermal variations of the TR spectral line shapes for all three materials exhibit the following common features : (a) The TR spectra change drastically between $T_{CW}$ (Curie-Weiss point) and $T_C$ (Curie point). Away from this region the spectral line shape remains nearly unchanged in both the ferromagnetic and the paramagnetic regions. (b) The TR signal as function of temperature exhibits a sharp lambda-shape maximum centered at $T_C$ (see for instance figure 4 for HgCr$_2$Se$_4$). This happens for any photon energy which corresponds to optical transitions involving band states.

The fact that the TR spectra are strongly influenced by the magnetic phase.
transition both, near the absorption edge and in the highly absorbing region, is a strong argument that the concept of magnetic-order-sensitive defects, or "magnetic" excitons adopted for explanation of the spin-dependent absorption of CdCr$_2$Se$_4$ and CdCr$_2$S$_4$ [18,19], has to be reconsidered.

Fig. 2: TR spectrum of CdCr$_2$S$_4$ at various temperatures near $T_C$ /16/.

An alternative explanation for the "red shift" of the absorption edge has also been presented, based on the model of spin-polarized bands /1,2/. According to this model the exchange interaction between localized and band electrons results in a spin-splitting of the conduction and valence bands. In first approximation, the corresponding energy changes are given by

$$\Delta E_{bk}^{\pm} = \mp \frac{1}{2} S J_{bkm} M(T),$$

where $S$ is the localized spin, $J_{bkm}$ - the exchange parameter, $M(T)$ - the magnetization, and $b$ - the band index.

The concept of band splitting is strongly supported by the temperature variations of TR spectra of CdCr$_2$Se$_4$ /14/(Fig.1).

Fig. 3: TR spectrum of HgCr$_2$Se$_4$ at various temperatures near $T_C$ /17/. A chopped laser beam ($h\nu = 2.54$ eV, $f = 2.5$ Hz) has been used to modulate the temperature. The region between 2.4 and 2.7 eV has been omitted from the curves as a spurious signal due to the scattered laser light has been superimposed on the TR signal.

Thus, the TR peaks A and C split into "red" and "blue" shifting components below the Curie-Weiss temperature $T_{CW} = 204$ K, i.e. at $M(T) \neq 0$, in agreement with eq. (1). The position of the $A(A_1)$ peak corresponds to the absorption edge, whereas that of $C(C_1^-$ to $C_2^+)$ to the main reflectance peak. On the other hand, the splitting is rather asymmetric, in disagreement with eq. (1). The latter is not surprising as the treatment of the exchange interaction as a perturbation is only rough approximation. The asymmetry could be formally accounted for in eq. (1) by introducing two different exchange parameters $J^+$ and $J^-$. The $A_1$-$A_2$ splitting has also been observed in the photoconductance spectrum /20/. The above results give the first direct evidence for magnetic-order-induced band splitting in...
ferromagnetic spinels.

Fig. 4: Temperature dependence of the TR signal for HgCr$_2$Se$_4$ at three different photon energies /17/. Similar splitting of TR peaks had been observed earlier for the ferromagnetic Eu-chalcogenides in the photon energy range corresponding to the direct band-to-band gap, by Mitani and Koda /21/. Preliminary measurements for CdCr$_2$Se$_4$ show that the TR peaks at higher energies split in a manner similar to that of the A and C peaks (Fig. 5). Furthermore, the splitting increases linearly with photon energy.

A splitting TR structure is also observed in the case of CdCr$_2$S$_4$ /16/ in the same photon energy range where the "red shifting" absorption band occurs. Instead of "red shifting" and "blue shifting" components, one finds "strongly" and "weakly" red shifting components, respectively (Fig. 6). Two red-shifting absorption bands with different magnetic circular polarisation properties were reported for CdCr$_2$S$_4$ at $T < T_c$ by Koshizuka et al. /22/. Since it is not possible to follow the changes of the energy position of these bands near and above $T_c$, no final conclusion can be made whether they arise from the same band in the paramagnetic region.

Fig. 5: TR spectrum of CdCr$_2$Se$_4$ between 1 and 4.5 eV.

Fig. 6: Variation with temperature of the energies of characteristic points of the TR spectrum of CdCr$_2$Se$_4$ /16/.

Besides the splitting A'-A" a new TR oscillation M-K appears below $T_{cw}$ for CdCr$_2$S$_4$ in the energy region above the direct absorption edge (Figs. 2 and 6). This oscillation exhibits a "red shift". Similar oscillation related to magnetic ordering appears also in the case of HgCr$_2$Se$_4$ (Fig. 3). No splitting of the TR structures has been observed for the latter material.
We should note, however, that the TR measurements for HgCr$_2$Se$_4$ do not cover the absorption edge region which is placed at lower energies.

The absence of splittings in the TR spectra does not indicate absence of electronic band splitting. The temperature induced changes near a reflectance spectral feature characterized by its energy $E_C$, broadening parameter $\Gamma$ and oscillator strength $f$, may be written as:

$$\Delta R = \frac{1}{R} \left( \frac{2R}{\alpha E_C} \frac{d\alpha}{dT} + \frac{3R}{\alpha^2} \frac{d\rho}{dT} + \frac{2R}{\alpha^3} \frac{df}{dT} \right) \Delta T,$$

or (in the case of splitting) by a superposition of two such expressions. Depending on the actual line shape of $R$ near $E_C$ and on the relative weight of the different terms in eq.(2), a variety of line shapes corresponding to the spin splitting effect can be observed.

3. Photoconductance.- It is reasonable to expect that most unambiguous information on the optical transitions in the highly absorbing region and the way in which they are influenced by magnetic ordering, would be obtained by direct absorption measurements. Unfortunately, the difficulties of preparation of good stoichiometric thin samples limit such measurements to the lowest absorption edge region. These difficulties can be partly overcome in photoconductance studies.

There exist several works on the photoconductance spectra of CdCr$_2$S$_4$ /23/ and CdCr$_2$Se$_4$ /20,24,25/. It was found in these measurements that the intraionic d-d transitions also contribute to the photoconductance. Thus, it was concluded that a charge transfer must occur between the crystal field levels and band levels. The tentative electronic band schemes proposed on the basis of these results and other available information assume either indirect transitions or transitions between impurities and band states for the low energy absorption. Such an assumption is consistent with the low values of absorption coefficient in this region. The direct gap which must correspond to the strongest photoconductance peak is placed at 0.7 eV towards higher energies, i.e. at energies corresponding to the direct absorption edge of related binary compounds CdS and CdSe.

It is remarkable that a split band which has the same energy position and temperature behaviour as those of the $A(A_1-A_2)$ TR structure of CdCr$_2$Se$_4$ is also observed in the photoconductance spectrum /20/. The latter is illustrated in figure 7.

![Fig. 7: Spectral dependence of the photoconductance of CdCr$_2$Se$_4$ at various temperatures near $T_C$ /20/](image)
five Raman-active phonon lines predicted by group theory. The assignment of the Raman lines to certain ionic vibrations was further discussed by Brüesch and D'Ambrogio /9/ and was confirmed by measurement of the Raman spectrum of HgCr$_2$Se$_4$ /12/. Typical Raman spectra of CdCr$_2$Se$_4$ and HgCr$_2$Se$_4$ are shown in figure 8.

![Raman Spectra](image)

**Fig. 8:** Raman spectra of CdCr$_2$Se$_4$ and HgCr$_2$Se$_4$ at 80 K /12,13/.

The most striking feature found in the early experiments on CdCr$_2$Se$_4$ and CdCr$_2$S$_4$ was the strong dependence on temperature of the scattering cross section for some of the Raman lines. In particular, it was observed that the intensity of the D-line ($F_{2g}$) follows the spin-correlation function whereas the intensity of the C-line ($E_g$) remains almost unchanged. In an attempt to explain this behaviour, several models for spin-dependent scattering have been proposed. Either magnon scattering /8/ or coupling between the phonon and the spin subsystems /8-10/ have been assumed in these models.

More recent experimental findings have posed the question whether the latter mechanisms actually determine the temperature variations of the scattering cross section. These finding are as follows:

(a) The Raman line intensities for the non-magnetic compound CdIn$_2$S$_4$ also depend strongly on temperature provided the excitation laser line is close to the absorption edge of this material /26/;
(b) The relative and absolute scattering intensities strongly depend on the excitation photon energy /11-13/;
(c) The IR-active phonon line intensities do not show any significant dependence on the magnetic ordering /27/.

Shepherd /28/ was the first who pointed out that the thermal dependence of the Raman line intensities for CdCr$_2$Se$_4$ may be related to resonant Raman scattering. Koshizuka et al. /11,26/ later observed for CdCr$_2$S$_4$ different types of variations with temperature for the $D$ and $E$ integrated intensity ratios. They also observed a breakdown of the polarization selection rules for the E- and F-lines. In these studies, different laser lines were used in the energy range which contains the absorption edge and the d-d transitions. Similar experiments on HgCr$_2$Se$_4$ and CdCr$_2$Se$_4$ were performed by Iliev et al. /12,13/.

Figures 9 a and 9b show the resonant Raman scattering for the lines C and D of CdCr$_2$Se$_4$ ($T_c$ = 130 K) at 340 and 110 K, respectively.

![Resonant Raman Spectra](image)

**Fig. 9:** Resonant Raman scattering for C and D phonons of CdCr$_2$Se$_4$ at 340 K(a) and 110 K (b) /13/. The arrows indicate the prominent structure in the TR at 2.03 eV for 340 K, which undergoes a splitting for $T<T_{cw}$.

A strong resonance peak is seen between 1.9 and 2.1 eV as there is only one experimental point in this region, it is difficult to determine the exact peak position and
line shape. Nevertheless, the tendency of broadening at low temperature is obvious and correlate to the prominent structure of thermoreflectance which undergoes a splitting for $T < T_c$ (indicated by arrows). The halfwidth of the resonance peak increases from nearly 0.2 eV at 340 K to 0.5 eV at 110 K. It is reasonable to ascribe this broadening to the magnetic-order-induced exchange splitting. As the values of the band splitting and the halfwidth of the resonance peak are comparable, one should expect stronger or weaker changes of the scattering cross section near $T_c$ depending on the choice of excitation photon energy. In particular, the changes will be quite strong with the 1.96 eV laser line used in the experiments of ref. [8].

The dependence of the temperature variation of the scattering intensity on the excitation photon energy and on the particular phonon studied, is illustrated in figure 10 for the case of HgCr$_2$Se$_4$ [12].

In particular, the changes will be quite strong with the 1.96 eV laser line used in the experiments of ref. [8].

The dependence of the temperature variation of the scattering intensity on the excitation photon energy and on the particular phonon studied, is illustrated in figure 10 for the case of HgCr$_2$Se$_4$ [12].

Within the experimental conditions used in these measurements the temperature dependences could be fitted by neither the spin-correlation function alone, nor by a sum of a spin-independent term and the spin-correlation function as suggested in various models for spin-dependent Raman scattering [8-10].

It should be pointed out that in several experimental studies the assumption has been made that the intensity of the C-line does not change significantly with either temperature or excitation photon energy. Thus, the relative intensity of the other lines with respect to that of the C-line has been used as a measure of their intensity. The results of figures 9 and 10 as well as the resonance curves for the C- and D-lines of HgCr$_2$Se$_4$ [12] demonstrate that such an assumption is not correct, at least for CdCr$_2$Se$_4$ and HgCr$_2$Se$_4$. Figure 11 shows the dependence of the $D/C$ ratio for CdCr$_2$Se$_4$ on photon energy. These curves are quite different from those for the C- and D-lines.

**Fig.10**: Thermal variation of the integrated Raman line intensities using 6471 Å (1.83 eV) and 5145 Å (2.41 eV) laser lines. The spin-correlation function for HgCr$_2$Se$_4$ [12] is also shown in the third figure.

**Fig.11**: Dependence of the D-line to C-line integrated intensity ratio on the photon energy for CdCr$_2$Se$_4$ [13].

5. **Conclusions.**—From the experimental results presented on thermoreflectance photoconductance and resonant Raman scattering it follows that the interaction between localized magnetic electrons and delocalized band electrons affects significantly the electronic band states of ferromagnetic Cd- and Hg-spinels near the magnetic phase transition. The observed band splitting is in a qualitative agreement with the theory of spin-polarized bands and explains the anomalous temperature shift of the absorption edge. However, such experimental facts as the asymmetry of the
splitting and its energy dependence can not be accounted for by a simple exchange-splitting model. As to the spin-dependent Raman scattering, it is plausible to conclude that the temperature changes of the Raman intensities are mainly governed by the temperature shift of the intermediate electronic state with consequent change of the resonance conditions. Additional combined studies of optical spectra and resonant Raman scattering using cw dye lasers would provide a good basis for elucidating the nature and the assignment of electronic transitions in these materials.

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