

GIANT STOKES SHIFT OF SPIN FLIP RAMAN SCATTERING
IN THE SEMIMAGNETIC SEMICONDUCTOR $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$

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We report the first observation of Spin Flip Raman Scattering in a "semimagnetic" semiconductor ternary alloy : the experiment is done in n-type $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$. The Stokes shifts are unusually large : some 75 cm^{-1} in 1 Tesla at 1.6 K. In addition, zero field spin flip scattering is observed, which is attributed to the formation of "magnetic molecules" under the electronic orbit of the donors.

I. Introduction

The ability to gradually incorporate Mn^{++} ions in a non-magnetic semiconductor explains the recent attention devoted to semimagnetic compounds [1] : in the framework of a well-known classical semiconductor, the exchange interaction characteristic of magnetic phenomena is progressively taken into account, between band electrons and Mn^{++} -d-shells. Its influence appears to be two-fold :

i) in external magnetic field, the magnetization of the Mn^{++} system induces giant spin-splittings of the electron states of the semiconductor ; this has been evidenced up to now by Zeeman analysis of free-exciton absorption lines [2,3] and by other related phenomena (for example, Faraday rotation [4]) ;

ii) more recently, the reverse influence of the semiconductor electron states on the magnetization has been evidenced on acceptor states in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ alloys, through luminescence experiments ; it gives rise to the formation a "magnetic molecule" of "bound magnetic polaron" [5].

The interest of spin-flip Raman scattering (SFRS) in semimagnetic compounds raises from these two types of regards. In a SFRS experiment, under external magnetic field, the energy difference (Stokes shift) between the exciting and scattered light energies is transferred to the semiconductor by spin-flip of unpaired electrons which are present in the crystal [6]. As a consequence, the Stokes-shift is a straightforward and accurate measurement of the spin-splitting of a single type electron (for example conduction states in a n-type material). As giant Stokes-shifts are expected, the feasibility of producing SFRS lasers, tunable over a wide energy range by magnetic field or temperature, has been suggested.

On the other hand, at low temperature, the scattering is likely due to states bound to shallow impurities. In such conditions, SFRS is a selective measurement of the Mn^{++} magnetization surrounding such impurities, hence a powerful tool to study magnetic molecules.

II. Material

The experiment we report was performed on the new material $Cd_{0.95}Mn_{0.05}Se$. Single crystals were grown in the Institute of the Polish Academy of Sciences (Warsaw), by modified Bridgman method. Similarly to CdSe, these crystals grow in wurzite type structure and reveal a n-type conductivity ($2.78 \Omega^{-1}cm^{-1}$ at room temperature, $1.1 \times 10^{-4} \Omega^{-1}cm^{-1}$ at 4.2 K). Excepting these two peculiarities, preliminary Zeeman analysis of absorption lines [7] exhibits phenomena quite comparable to the case of $Cd_{1-x}Mn_xTe$ alloys :

i) the crystal is paramagnetic at Helium temperature : the Mn^{++} mean spin component along an external magnetic field follows a law :

$$\langle S_z \rangle \propto B_{5/2} \quad (5/2 g \mu_B H / (T + T_{AF}))$$

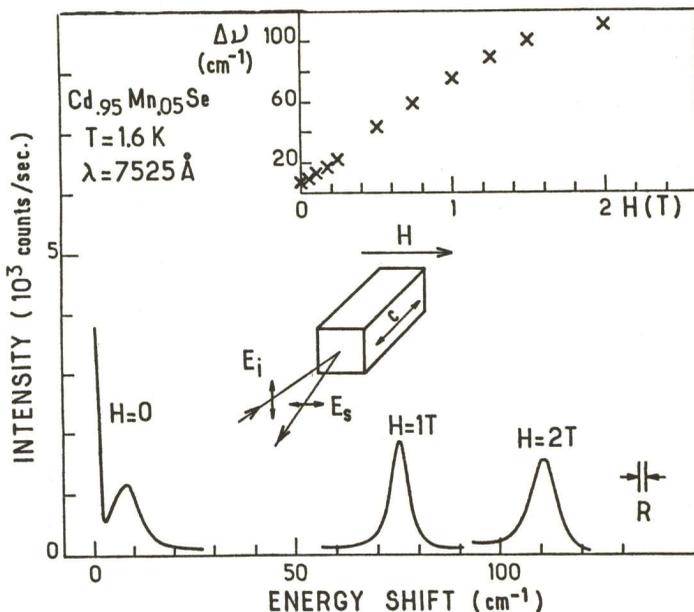
where $B_{5/2}$ is the Brillouin-function for 5/2 spin, H is the external field, T the temperature, and T_{AF} a phenomenological parameter which describes the negative interaction between Mn^{++} spins. This departure from an isolated spin behaviour is growing with Mn concentration x, and $T_{AF} \sim 2$ K for $x = 0.05$ materials [3]. Let us emphasize that, in the low field region, the magnetization is proportional to the external field.

ii) This magnetization induces giant Zeeman like splittings of exciton states ; the parameters for the conduction and valence bands exchange interaction with $Mn^{++}d$ -states are of comparable magnitude in $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xTe$ alloys ($N_0\alpha \sim 0.2$ eV for conduction band, $N_0\beta \sim 0.9$ eV for valence bands ; in notations of ref. 5).

III. Experiment

We used a typical experimental setup for Raman spectroscopy with excitation provided by 1 watt-all-lines Kr^+ laser. The sample was immersed in a liquid helium vessel, together with a small superconducting coil providing magnetic fields up to 2 Teslas. This setup allows the sample temperature to be adjusted in the range 1.5 K to 4.2 K.

Figure 1
Some typical SFRS spectra, in the scattering configuration $z(x,y)\bar{z}$, $z//c$, $H \perp c$, for three values of the magnetic field H, and at temperature $T = 1.6$ K. The elastic diffusion peak (energy $13\ 288\ cm^{-1}$) is centered on the energy scale origin. Insert : the Stokes shift as a function of H in the same experimental conditions.



The SFRS was observed with two different exciting energies situated in the transparent region of the semiconductor : $14\,783\text{ cm}^{-1}$ ($6\,764\text{ \AA}$) and $13\,288\text{ cm}^{-1}$ ($7\,525\text{ \AA}$). As may be expected for a Raman scattering process, the efficiency is higher in the former case, due to the energy vicinity of the virtual intermediate states of the transition. However, for the same reasons, the Raman scattering appears superimposed on luminescence. For the lower energy excitation, SFRS appears weaker, but free from any parasitic phenomena.

Representative spectra are shown in Fig. 1, for different magnetic field values. A comparison with SFRS in non-magnetic semiconductor brings out two main differences which we shall discuss.

i) The Stokes-shifts are unusually large, temperature dependent and tend to saturate in the high field range (see Fig. 1 insert) ;

ii) in zero-magnetic field, a comparatively small Stokes-shift remains noticeable (6 to 8 cm^{-1} , depending on temperature).

IV. Discussion

1) At 1.6 K , the Stokes-shift reaches 75 cm^{-1} (9.3 meV) in $H = 1\text{ T}$; this is two orders of magnitude larger than in a non-magnetic wide gap semiconductor [6]. As H is swept from 0.2 T to 2 T , the Stokes-shift follows the Brillouin-type law of the Mn^{++} magnetization.

Such values are quite comparable with the exchange induced spin splitting of the conduction band which we deduce from Zeeman analysis in the same material (76 cm^{-1} in 1 T at 1.6 K) [7]. Thus the scattering is thought to be due to electron states close to the conduction band, which is not surprising in a n-type semiconductor.

Essentially due to crystal inhomogeneities, the experimental accuracy on Stokes-energies is estimated to 5% . Let us point out that, within this precision, the experimental spin splittings are independent from the relative directions of the magnetic field and c-axis, as well as from the light propagation and polarization vectors. We deduce the exchange integrals of interest are isotropic. The situation should be very different for valence band states, in this wurtzite type structure.

Let us notice that, due to large Stokes energy, no anti-Stokes line is observed for temperatures below 4.2 K .

2) We now discuss the existence of a zero-field SFRS, which clearly appears in Fig. 1. This behaviour contrasts with previous magnetization measurements or Zeeman analysis of absorption lines in semimagnetic compounds [2,3]. In this latter case, the bulk magnetization is measured, since the free exciton experiences a magnetization averaged over their mean free path, typically several 10^3 \AA . In the experiment we are describing here, the Stokes energy is transferred, by spin-flip, to electrons

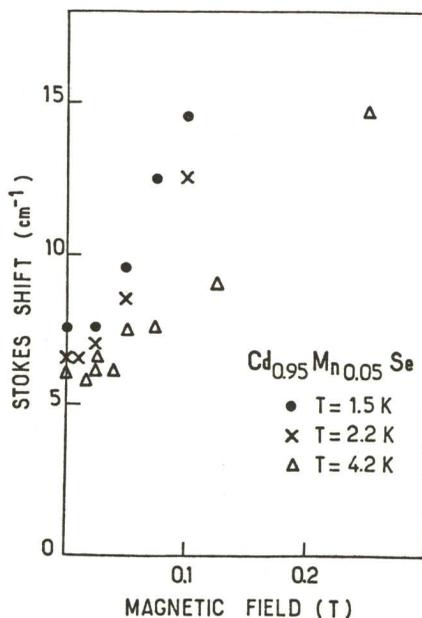


Figure 2
The Stokes shift as a function of the magnetic field, in the low field region, and for different temperatures T

bound to donors. Their wave function is localized around impurities within, typically, 50 Å ; thus, these electrons experience the magnetization surrounding impurities.

In addition, the conditions for the formation of a "magnetic molecule" [5] are fulfilled : the electronic wave function reaches noticeable values on each Mn^{++} site, due to its spatial localization ; and the state is populated by one unpaired electron, with free spin. As a consequence, the $Mn^{++}d$ -states are submitted to a noticeable exchange field from the bound electron. This explains the departure from the Brillouin law evidenced in the variation of the Stokes-shift $\Delta(H)$ in low field (see Fig. 2).

The zero-field Stokes-shift is a measure of the electron spin-splitting due to the mean spontaneous magnetization in the "magnetic molecule". On the other hand, as H is increased, this mean magnetization direction tends to align along H, so that the Mn^{++} ions experience the electronic exchange field plus the external field. Actually, in the field range $0.05 \text{ T} < H < 0.2 \text{ T}$, the experimental variation of Δ with external field H and temperature T is accounted for by equation : $\Delta(H,T) \propto (H + H_e)/(T + T_{AF})$, where $H_e \sim 0.05 \text{ T}$ and $T_{AF} \sim 2 \text{ K}$. This allows to describe the partial alignment of Mn^{++} ions surrounding the donors in terms of a mean electronic field $H_e \sim 0.05 \text{ T}$ (500 gauss).

The spatial extension of the electronic wave function of interest may be estimated from this value of H_e , or from the zero-field splittings. Using exchange integral value for the conduction band $N_0\alpha = 0.2 \text{ eV}$, one gets a typical radius of 50 Å, which is the typical Bohr radius for donors in CdSe. We deduce that some 400 Mn^{++} ions are involved in the "magnetic molecule", with average spin value along H_e , in zero external field : $\langle S_z \rangle \sim 0.05$ at 1.6 K.

Thus, a giant spin value of about 20 may be associated to the whole molecule, at 1.6 K. In return, the alignment of the molecule along H is performed within 0.1 T at 1.6 K (that is, in Fig. 2, $\Delta(H)$ is linear for $H > 0.1 \text{ T}$). This alignment may be, to some extent, regarded as the "superparamagnetic" behaviour of this giant spin under external field.

V. Conclusion

The SFRS in semimagnetic compounds exhibits, as expected, giant Stokes-shift. It also appears to be an accurate tool for the study of magnetic molecules, since a direct access to the absolute value of the magnetization is, for the first time, provided. In the case of $Cd_{0.95}Mn_{0.05}Se$, it evidences the formation of large, loosely bound complexes of this type. This contrasts with the situation in $Cd_{1-x}Mn_xTe$, where these molecules have been found, up to now, on neutral acceptors with more localized wave function [5] : the number of Mn^{++} ions involved in the molecule is, typically, two orders of magnitude larger around donors than around acceptors, and, as a consequence, the electronic density on each Mn^{++} site is two orders of magnitude smaller. However, for a given Mn concentration, the associated giant spin values are comparable in both cases.

- 1) See for example the review by J. Gaj, this conference .
- 2) A. Twardowski, M. Nawrocki and J. Ginter: Phys. Stat. Sol. (b) 96 (1979) 497.
- 3) J. Gaj, R. Planel and G. Fishman: Solid State Comm. 29 (1979) 435.
- 4) J. Gaj, R. Galazka and M. Nawrocki: Solid State Comm. 25 (1978) 193
- 5) A. Golnik, J. Gaj, M. Nawrocki, R. Planel and C. Benoit à la Guillaume: this conference .
- 6) On SFRS, see for example the review by Y. Yafet, in New Developments in Semiconductors, ed. Wallace et al, Nordhoff Int. Pub., Leyden .
- 7) M. Nawrocki: to be published.