Exchange-Induced Spin-Flip Raman Scattering in a Semimagnetic Semiconductor

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A magnetic-field– and temperature–dependent line is observed in the Raman spectra of a n-type semimagnetic semiconductor: $Cd_{0.95}Mn_{0.05}Se$. It is attributed to spin-flip Raman scattering, with "giant" Stokes shift: 75 cm^{-1} in 1 T at 1.6 K. A small zero-field Stokes shift is observed, which is attributed to an exchange-induced magnetic molecule under the electronic orbit of neutral donors.

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The so-called "semimagnetic semiconductors"[1] such as $Cd_{1-x}Mn_xTe$ have been revealed as most interesting recently, because of the ability to gradually incorporate localized magnetic moments of Mn^{++} ions in a classical semiconductor matrix. Under external magnetic field, the exchange interaction between the electron band states and the Mn^{++} d states mainly results in a huge enhancement of spin splittings of the former ones (several millielectronvolts per tesla at low temperature). This explains several magneto-optical properties unusual from the semiconductor point of view: giant Faraday rotation,[2] giant Zeeman-like splittings of exciton lines [3,4] autoionization of bound exciton.[5]

This Letter deals with a line appearing in the Raman spectra of a semimagnetic compound, with Stokes energy strongly dependent on magnetic field and temperature.

The experiment we report was performed on the new material $Cd_{0.95}Mn_{0.05}Se$. Single crystals of $Cd_{1-x}Mn_xSe$ alloys were grown in the Institute of the Polish Academy of Sciences (Warsaw), with use of a modified Bridgman method. The crystals obtained may be reasonably large and nice looking. Contrary to $Cd_{1-x}Mn_xTe$ alloys, they grow as n type and have the wurtzite-type structure, as in the case of CdSe. An extensive study of the free-exciton Zeeman-like splittings in $Cd_{1-x}Mn_xSe$ alloys is in progress and will be published later.[6] Preliminary results indicate a physical situation similar to that of $Cd_{1-x}Mn_xTe$: The exchange integrals, parameters of interaction of band electrons with the Mn^{++} ions, are of comparable magnitude in both types of alloys; the Mn^{++}-ion system exhibits a paramagnetic behavior at liquid-helium temperature, in the magnetic field range of interest (from 0.01 to 6T), at least for Mn concentration up to 15%.

The n-type conductivity of our samples is 2.78 Ω^{-1} cm^{-1} at room temperature and 1.1×10^{-4} Ω^{-1} cm^{-1} at 4.2 K. In addition, the luminescence spectrum at 4.2 K exhibits a strong line situated some 80 cm^{-1} below the free A-exciton absorption energy (15 230 cm^{-1}); by continuity to the case of CdSe,[7] this line may be attributed to the recombination of excitons bound to neutral shallow donors. These two experimental facts indicate the presence of neutral isolated donors in the crystals.

The crystals were sawed in the form of a parallelepiped, allowing right-angle, as well as back-scattering, studies, then polished and etched. The sample was fixed on a small superconducting coil, immersed in a liquid-helium vessel: The magnetic field is limited to 2 T, and the temperature to the range 1.5–4.2 K. The excitation could be provided by the various lines of a 1-W all-lines Kr^+ laser. Collection optics focuses the sample image, four times magnified, on the entrance slit of a double spectrometer that gives a linear dispersion of 8 Å/mm; it is followed by a conventional photon counting system.

We have observed Raman spectra with exciting energies 14 783 cm^{-1} (6764 Å) and 13 288 cm^{-1} (7525 Å), both being situated in the transparent region of the semiconductor. The former energy is situated close to resonances of the scattering process; thus, the scattering efficiencies are

high. However, as the external field is swept up to 1.5 T at 1.6 K, luminescent levels come down in resonance with the exciting energy, somewhat complicating the secondary emission spectra.

For the sake of clarity, in the following we deal only with data obtained at lower exciting energy (13 288 cm^{-1}). Although weaker, the Raman spectra is relieved of any additional phenomena. In the energy range 0–120 cm^{-1}, one Raman line is observed with fair intensity: a few thousand counts per second, with reasonable resolution (1.5 cm^{-1}) and incident power (100 mW). The associated Stokes energy $\Delta\nu$ is strongly dependent on magnetic field H and temperature T. Typical spectra are presented in Fig. 1, together with an example of $\Delta\nu$ variation as a function of H. Except in the low-field range, that is for 0.1 T $< H <$ 2 T, $\Delta\nu(H,T)$ follows a Brillouin-type law, which suggests that the magnetic field influence is mediated by exchange interaction with the Mn^{++} magnetization.

In fact, it is now well established that, in wide-gap semimagnetic semiconductors, under given H and T conditions, the spin splitting of the conduction band, as given by Gaj, Planel, and Fishman,[3] is

$$\Delta E_c(H,T) = N_0\alpha x\langle S_z\rangle,$$

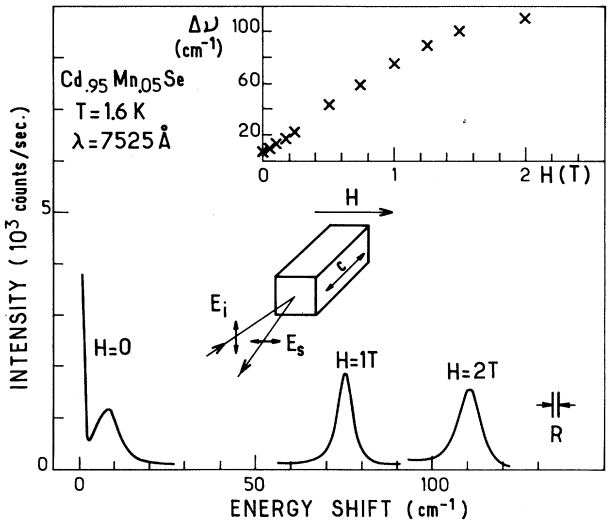

FIG. 1. Some typical SFRS spectra, in the scattering configuration $[(z,xy,\bar{z})$, $z \| c$, $H \| g]$, for three values of the magnetic field H, and at temperature T = 1.6 K. The elastic diffusion peak (energy 13 288 cm^{-1}) is centered on the energy scale origin. Inset: the Stokes shift $\Delta\nu$ as a function of H in the same experimental conditions.

where $N_0\alpha$ is the exchange parameter between conduction S and Mn^{++} d states, x is the mole fraction of Mn, and $\langle S_z\rangle$ is the mean spin component along H of the Mn^{++}-ion system. At low temperatures, $\langle S_z\rangle$ may be described by a Brillouin function:

$$\langle S_z\rangle \sim \tfrac{5}{2}B_{5/2}(\tfrac{5}{2}g\mu_B H/k(T+T_{AF})),$$

where $\frac{5}{2}g\mu_B = 5\mu_B$ is the magnetic moment of Mn^{++} ions, and T_{AF} is a positive effective temperature describing interactions between Mn^{++} spins.

In $Cd_{0.95}Mn_{0.05}Se$, values such as $N_0\alpha \sim 0.2$ eV and $T_{AF} \sim 2$ K may be estimated.[3,6] More precisely, in the magnetic field range of interest, $\Delta\nu(H,T)$ is equal, within a few percent, to the conduction-band spin splitting which we deduce from Zeeman analysis of the absorption spectra; for example, $\Delta\nu$(1 T, 1.6 K) = 75 cm^{-1}, and ΔE_c(1 T, 1.6 K) = 76 cm^{-1}.

As a consequence, the scattering is suggested to occur from exchange-split levels close to the conduction band, namely from electrons bound to donors; the Stokes energy being transferred, by spin flip, to unpaired electrons in the exchange field of the Mn^{++} ions. This spin-flip Raman scattering (SFRS) presents specific aspects with respect to analogous experiments in classical non-magnetic semiconductors such as CdS[8]: The Stokes shifts are much greater, by one or two orders of magnitude at low temperature, and they follow a Brillouin-type law. These are two consequences of the huge exchange perturbation, which dominates the direct magnetic field spin splitting. As we show below, the exchange interaction may also explain another peculiarity of our results: the existence of a "zero-field" SFRS, which clearly appears on Fig. 1.

It is worth pointing out that within a 5% uncertainty due to crystal inhomogeneities,[9] the Stokes shifts only depend on magnetic field and temperature, and not on the relative directions of the field, c axis of the crystal, light propagation, and polarization vectors. The most reasonable conclusion which is to be drawn is that both Mn^{++} magnetization and exchange integral of interest are isotropic. (The situation should be very different for valence states in this wurtzite-type material.)

An extensive study of the relative scattering intensities depending on the various possible magnetic field H, c axis, and light beam geometries is beyond the scope of this paper. Let us simply note that such a study is complicated, from both experimental and theoretical points of view, by

several causes specific to semimagnetic semiconductors: For example, giant Faraday rotations inside the crystal, so that beam polarizations may be unknown; giant shifts of virtual intermediate states, so that classical group-theory analysis becomes inadequate. Generally speaking, the physical problems involved require a more detailed analysis and could provide, in the future, interesting physical information.

We are now led to discuss the "anomalous" behavior of SFRS in the low-field range ($H < 0.1$ T): Actually, $\Delta\nu$ does not tend towards zero with H, as seen in Fig. 2, with magnified scales, for different temperatures. Let us emphasize that in the same typical (H,T) conditions, no zero-field splitting is noticeable on free-exciton absorption.

In this latter case, we deal with intrinsic electronic states, with delocalized wave function.[10] It has been shown, in the case of $Cd_{1-x}Mn_xTe$ alloys,[3] that the spin splitting of such states provides an accurate optical access to the *bulk* magnetization. In SFRS at low temperature, bound electrons are concerned with spatially localized wave function. When compared to free-exciton states, the impurity states present two important differences for this problem: (i) The wave function of the bound electron reaches noticeable values on each Mn^{++} site lying in its orbit. (ii) The state is populated, without any illumination, by one unpaired electron, which forms a paramagnetic center.

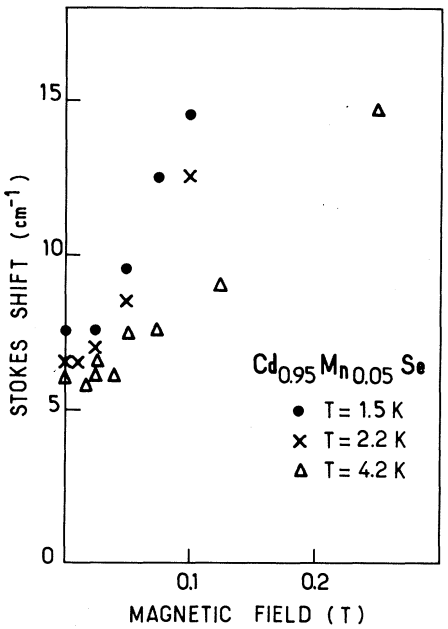

FIG. 2. The Stokes shift as a function of the magnetic field, in the low-field region, and for different temperatures T.

As a consequence of these two points, the Mn^{++} d states are submitted to a noticeable exchange field from the bound electron, even in zero external field. In return, the bound electron experiences only the local magnetization surrounding the donor, and this exchange-induced magnetization is detected on its spin splitting.

Actually, such a partial alignment of Mn^{++} ions around a neutral impurity site has been recently observed in the case of acceptors in $Cd_{1-x}Mn_xTe$, by luminescence experiments, and described in terms of magnetic molecule.[11] To some extent, it may be compared to the bound magnetic polarons that have been proposed to explain transport properties of ferromagnetic semiconductors such as EuO.[12] To our knowledge, such complexes, which may carry a large magnetic moment, had never been directly observed by spectroscopy.

To get an experimental estimation of the electronic field intensity experienced by the Mn^{++} ions, we proceed in the following way: As we are reminded above, the low-field bulk magnetization is proportional to $H/(T+T_{AF})$, with $T_{AF} \sim 2$ K. On the other hand, the variation of the Stokes shift $\Delta\nu$ as a function of H (see Fig. 2) presents a linear region, in the field range $0.05 < H < 0.2$ T; this linear part is properly described by equations $\Delta\nu \propto (H+H_e)/(T+T_{AF})$, where $H_e \sim 0.05$ T and $T_{AF} \sim 2$ K for the three different experimental temperatures. This allows us to describe the partial alignment of the Mn^{++} ions surrounding the donors in terms of an additional exchange field $H_e \sim 0.05$ T.

As a matter of additional evidence, the spatial extension of the bound-electron wave function may be estimated from the experimental value of H_e: By using exchange parameter values such as 0.2 eV, and remembering that we get two atoms per unit cell, we deduce a Bohr radius of 10 unit cells, which is quite reasonable for donor in CdSe; some 400 Mn^{++} ions are involved in the "magnetic molecule" with average spin value along H_e of $\langle S_z \rangle \sim 0.05$.

As a consequence, a giant spin value of about 20 may be associated to the whole molecule; this is some eight times larger than an isolated Mn^{++} spin value ($\frac{5}{2}$). Let us notice that the small-field behavior of the Stokes shift ($\Delta\nu$) may be understood as alignment of this "giant spin" along the external field. This alignment is completed when $\Delta\nu$ varies linearly with the external field H. For

smaller H values ($H<H_e$), the effective field experienced by the Mn^{++} ions is a vectorial sum of H and H_e, the mean spin direction of the magnetic molecule being no longer aligned along H.

To conclude, SFRS in semimagnetic semiconductors is a new giant magneto-optic effect, which could be expected. But it also reveals a powerful tool to study magnetic molecules through a direct process (spin flip), which is simply related to the magnetic moment of these complexes.

The authors acknowledge fruitful discussions with C. Benoît à la Guillaume, D. Paquet, and R. Romestain.

[1]See the review by R. Galazka, in *Proceedings of the Fourteenth International Conference on Semiconductors, Edinburg, Scotland, 1978,* edited by B. L. H. Wilson (Institute of Physics, London, 1979), p. 133.

[2]J. Gaj, R. Galazka, and M. Nawrocki, Solid State Commun. 25, 193 (1978).

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[6]M. Nawroki, to be published.

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[8]D. G. Thomas and J. J. Hopfield, Phys. Rev. 175, 1021 (1968); on SFRS, see also the review by Y. Yafet, in *New Developments in Semiconductors*, edited by P. R. Wallace, R. Harris, and M. J. Zuckerman (Noordhoff, Leyden, 1973).

[9]In addition, microscopic inhomogeneities are likely responsible for a part of the linewidth of SFRS. In the case of impurities, they are enhanced by the spatial localization (~50 Å) of the magnetization inducing the bound-electron spin splitting.

[10]Actually, the free electrons experience a magnetization averaged over their mean free path, of the order of 1000 Å.

[11]A. Golnik, J. Gaj, M. Nawrocki, R. Planel, and C. Benoît à la Guillaume, to be published.

[12]See, for example, P. Leroux-Hugon, J. Magn. Magn. Mater. 3, 165 (1976).

Fractionally Charged Excitations in Charge-Density-Wave Systems with Commensurability 3

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A theoretical study of topological excitations (kinks) in a one-dimensional one-third-filled Peierls system is presented. The charges associated with the kinks are found to be fractional $Q=\pm\frac{1}{3}e, \pm\frac{2}{3}e$. Calculations of the spatial widths and electronic structure of different types of kinks are carried out numerically. Possible applications to tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) are mentioned.

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Recently, some novel physics have emerged from studying the nonlinear topological excitations in a simple one-dimensional coupled electron-phonon system.[1] It is known that in this model for the half-filled-band case (one electron per site), the lattice will undergo a commensurate Peierls distortion, i.e., dimerize, thereby opening a gap in the electronic spectrum at the Fermi surface, $k_F=\pm\pi/2a$, where a is the mean lattice spacing. The dimerization is due to the energy lowering of the occupied electronic states being initially larger than the lattice strain energy, with the total energy reaching a minimum for two displacements $\pm u_0$. These two degenerate dimerization patterns are termed the A $(+u_0)$ and B $(-u_0)$ phases. B is simply a translation of A by one lattice spacing.

A topological soliton excitation or kink is formed by a domain wall separating regions of A and B phase material. Associated with each kink is a localized electronic state φ_0 located at the center of the gap. This state results from the removal of one-half of a state from the valence band and one-half from the conduction band in the vicinity of the kink. Since for topological reasons a soliton S and an antisoliton $\bar{S}$ must be formed at the same time, an integral number of states is removed from either band, as required for a Her-