# ESR saturation and exciton luminescence in $Cd_{1-x}Mn_xSe$

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During strong saturation of ESR it is possible to substantially increase the spin temperature in a magnetic-impurity system in a semimagnetic semiconductor. As a result, the magnetooptical effects associated with the giant spin splitting are weakened. An optical detection method has been used to measure the spin-lattice relaxation time of a magnetic-impurity system.

In semiconductors doped heavily with a magnetic impurity, or "semimagnetic semiconductors," one observes magnetooptical effects because of a giant spin splitting in a magnetic field.[1–3] This splitting results from an exchange interaction of electrons from the conduction and valence bands with magnetic ions which are spin-polarized in the external magnetic field. The magnitude of this splitting is proportional to the magnetization of the magnetic impurity system, and at liquid-helium temperatures it is tens of times the Zeeman splitting. The luminescence of $Cd_{0.99}Mn_{0.01}Se$ in a magnetic field was studied in Ref. 3, where it was observed that an exciton-impurity complex decays at a neutral donor under conditions of giant spin splitting. If the magnitude of the giant spin splitting for an electron exceeds the binding energy of an exciton with a neutral donor, the bound-exciton state becomes energetically unfavorable with respect to decay accompanied by electron spin flip, because two electrons in a complex form a spin singlet. As a result of saturation of the ESR of $Mn^{++}$, the magnetization of the $Mn^{++}$ ions, which determines the magnitude of the giant spin splitting, decreases. This process causes the lines to shift in the luminescence spectrum. These effects underlie the method for optical detection of ESR in semimagnetic semiconductors.[4]

In the present experiments we use $Cd_{1-x}Mn_xSe$ samples with dimensions of about (1mm)·(1mm)·(30 $\mu$m) and a manganese concentration $x = 0.01$. The **c** hexagonal axis runs perpendicular to the plane of the sample, along the static magnetic field. The luminescence measurements are carried out in the Faraday geometry. The luminescence is excited by the line $\lambda = 5145$ Å from an argon laser with a power of about 10 mW. The sample is placed at the center of a cylindrical copper resonator with a quality factor $Q \sim 2000$, in which the $H_{011}$ mode is excited. The 5-W microwave source can produce a magnetic field with an amplitude on the order of 1 Oe at a frequency of 35.1 GHz in the resonator. To measure the magnetization relaxation kinetics, we work in a regime of 100% modulation of the microwave power by square pulses at a frequency from 1 to 4 kHz; the rise time is less than 1 $\mu$s. Analysis of the luminescence spectrum with the help of a strobe integrator synchronized with the square pulses makes it possible to observe the kinetics of the luminescence lines after the microwave field is turned off.

Figure 1 shows luminescence spectra of $Cd_{0.99}Mn_{0.01}Se$ without a magnetic field (dashed line) and in a 12.5-kOe magnetic field for various amplitudes of the resonant microwave field. The giant spin splitting causes a major shift of the line of an exciton

  

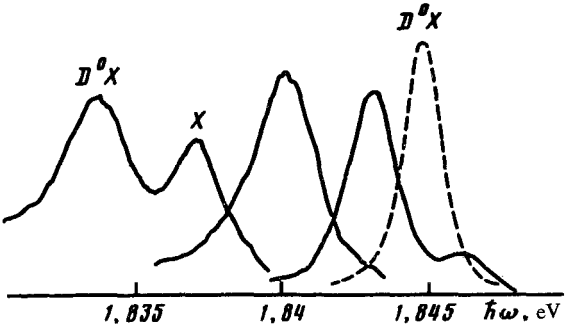


FIG. 1. Luminescence spectrum of $Cd_{0.99}Mn_{0.01}Se$ in a 12.5-kOe magnetic field at various degrees of saturation of the ESR. The dashed line is the luminescence spectrum in the absence of a magnetic field.

bound to a neutral donor ($D^0X$), and it gives rise to a free-exciton line ($X$) by virtue of the decay of exciton-impurity complexes. At the power levels of the optical pumping in these experiments, the sample is heated slightly. Knowing the values of the exchange integrals,[5] we can work from the position of a line in the magnetic field to determine the magnetization of $Mn^{++}$ and the lattice temperature; the latter turns out to be 3.5 K. The resonant microwave field raises the spin temperature of the $Mn^{++}$ ions, reducing the magnetization and the magnitude of the giant spin splitting. It also shifts the $D^0X$ line to a higher energy. The maximum spin temperature reached in these experiments was about 80 K; a further increase in the amplitude of the microwave field resulted in impact ionization of bound shallow states and a pronounced heating of the sample due to microwave absorption by free carriers. Judging from the shape of the luminescence spectrum, the heating of the sample by the microwave field is no more than a few degrees below the ionization threshold.

Figure 2 shows the shape of the ESR line of the $Mn^{++}$ ions. In general, the ESR spectrum of $Mn^{++}$ in II–VI semiconductors with the wurtzite structure consists of 30 lines. The splitting into these lines is caused by the hyperfine interaction with the $Mn^{55}$ nucleus and with the crystal field.[6] At an Mn concentration $x = 0.01$ the hyperfine structure and the fine structure of the ESR spectrum are not resolved,[7] and we observe a single structureless line about 200 Oe wide. Although inhomogeneous broadening affects the shape of the ESR line, the magnetic impurity system is demagnetized essentially completely at ESR saturation at the center of the resonant line. This result is evidence that the cross relaxation in the magnetic impurity system occurs quite rapidly

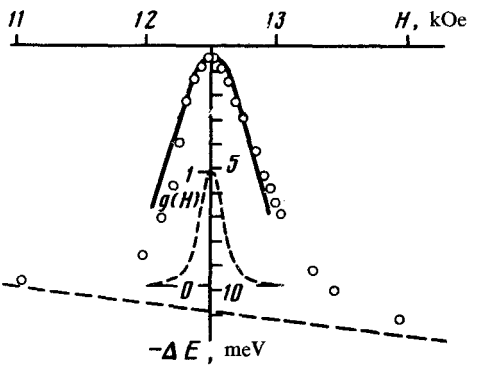


FIG. 2. Shift of the peak of the $D^0X$ line versus the magnetic field in the case of strong saturation of the ESR near resonance. Circles—Experimental points; dashed line—line shift in the absence of a microwave field; solid line—prediction of the Bloembergen-Purcell-Pound theory; dashed curve—shape of the unsaturated ESR line, $g(H)$.

and can be described by a single spin temperature. It also shows that the ESR line may be regarded as homogeneous.[8]

In time-resolved measurements in the modulation regime, after the microwave field is turned off, we observed a relaxation of the spectrum to its equilibrium form in a magnetic field. The maximum of the $D^0X$ line returns in an exponential fashion to its equilibrium position, with a time constant of 60 $\mu$s. This time is equal to the longitudinal relaxation time ($T_1$) of the magnetization at a lattice temperature of 3.5 K. The spin-lattice relaxation of ions of the iron group is caused by an orbit-lattice interaction, which affects the spin through the spin-orbit interaction.[9] The spin-lattice relaxation of $Mn^{++}$ ions in samples with a concentration $x \sim 10^{-5}$ occurs rather slowly,[10,11] $\tau \sim 10^{-1}$ s, because the $Mn^{++}$ ion has a zero orbital angular momentum in its ground state, and the spin-orbit interaction is manifested as the result of a crystal-field-induced mixing of states with a nonzero orbital angular momentum. The high rate of the spin-lattice relaxation in samples with a manganese concentration $x \sim 0.01$ is probably due to the local crystal fields, which cause a more pronounced mixing.

For a spin system with a cross-relaxation time shorter than the longitudinal relaxation time we take a thermodynamic approach. We introduce a Zeeman energy reservoir to correspond to the interaction with the external magnetic field, and a local-field reservoir, each with its own temperature.[8,12] When the ESR is observed in the steady-state regime, the second reservoir affects the lineshape. In contrast with the theory of Bloembergen, Purcell, and Pound,[13] in which the line becomes infinitely broad with increasing degree of saturation of the ESR, the lineshape in this case tends toward a Lorentzian function with a width $H_L(T_1/T_1')^{1/2}$, where $H_L$ is the average local field, and $T_1'$ is the spin-lattice relaxation time for the local-field reservoir. Since the shift of the $D^0X$ luminescence line in a magnetic field is proportional to the magnetization of the $Mn^{++}$ ions, we have attempted to describe the shift $\Delta E$ as a function of $H$ with intense microwave pumping (Fig. 2). The solid line in Fig. 2 corresponds to the expression $\Delta E = \Delta E_0/(1 + Kg(H))$, which follows from the Bloembergen-Purcell-Pound theory; here $\Delta E_0$ is the shift in the absence of a microwave field, $K$ is the saturation factor at the center of the resonance, and $g(H)$ is the shape of the unsaturated ESR line, normalized to a unit maximum. The experimental points do not indicate a contraction of the experimental curve in comparison with that predicted by the Bloembergen-Purcell-Pound theory. This result implies $T_1' \ll T_1$, i.e., that the local-field reservoir transfers energy to the lattice very rapidly and has no appreciable effect on the lineshape.

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[1]A. V. Komarov, S. M. Ryabchenko, I. I. Zheru, and R. D. Ivanchuk, Zh. Eksp. Teor. Fiz. **73**, 608 (1977) [Sov. Phys. JETP **46**, 318 (1977)].
[2]R. R. Galazka, Proceedings of the Fourteenth International Conference on Physics of Semiconductors (ed. V. L. H. Wilson), Edinbourgh, 1978, p. 138.
[3]S. I. Gubarev and B. N. Shepel', Pis'ma Zh. Eksp. Teor. Fiz. **37**, 528 (1983) [JETP Lett. **37**, 628 (1983)].
[4]A. V. Malyavkin, Phys. Status Solidi **115**, 353 (1983).
[5]R. L. Agarwal, S. N. Jasperson, I. Stankiewicz, Y. Shapira, S. Foner, B. Khazai, and A. Wold, Phys. Rev. B **28**, 6907 (1983).
[6]J. Lambe and C. Kikuchi, Phys. Rev. **119**, 1256 (1960).

[7]S. B. Oseroff, Phys. Rev. B **25**, 6584 (1982).
[8]S. Clough and C. A. Scott, J. Phys. C **1**, 919 (1968).
[9]M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).
[10]G. R. Wagner, J. Murphy, and J. G. Castle, Jr., Phys. Rev. B **8**, 3103 (1973).
[11]V. Ya. Bratus', I. M. Zaritskiĭ, A. A. Konchits, G. S. Pekar, and B. D. Shanina, Fiz. Tverd. Tela (Leningrad) **18**, 2311 (1976) [Sov. Phys. Solid State **18**, 1348 (1976)].
[12]V. A. Atsarkin and M. I. Rodak, Usp. Fiz. Nauk **107**, 3 (1972) [Sov. Phys. Usp. **15**, 251 (1972)].
[13]N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

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