Fial Report to the Department of Energy

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Science, Technology, and Public Policy Program
Belfer Center for Science and International Affairs
Kennedy School of Government
Harvard University

"Energy R&D Expenditures: Assessment and Analysis of the Last 20 Years"

This award was for work conducted in the Science, Technology, and Public Policy Program (STPP), Belfer Center for Science and International Affairs, Kennedy School of Government (KSG), Harvard University, in support of the DOE-funded study on "Federal Energy Research and Development for the Challenges of the Twenty-First Century" carried out at the request of President Clinton by his Committee of Advisors on Science and Technology (PCAST). This PCAST study, which was requested by President Clinton in January 1997 and delivered in final form in November 1997, was chaired by Harvard professor and STPP Director John P. Holdren, who also served as Principal Investigator on the indicated DOE award to KSG.

The principal focus of the work conducted under the award was to develop a quantitative understanding of the pattern of public and private expenditures on energy-technology research and development in the twenty-year period leading up to the study, to serve as the starting point of an exploration of the adequacy of current U.S. federal energy research and development programs in relation to the challenges facing the U.S. and world energy systems and in the context of current and likely future energy R&D spending by the private sector and by other countries. Within this overall scope, primary attention was given to developing a detailed picture of U.S. federal energy R&D spending in this period, secondary attention to U.S. private-sector spending, and tertiary attention to spending in other countries (with emphasis on the G-7). Included, in addition to development of the relevant data from a wide variety of sources and the presentation of these data in an accessible format lending itself to the illumination of trends and comparisons, was analysis of the causative factors underlying the trends, the public-private allocation of effort, and national differences in these patterns.

The conduct of the work entailed acquisition and analysis of data on R&D spending; participation of and presentations by the STPP researchers in the meetings of the PCAST panel conducting the parent ("Federal Energy R&D for the Challenges of the 21st Century") study; interactions with DOE, RAND, and national-lab personnel with expertise in the history of energy R&D spending; and an intensive series of research meetings at KSG in which the researchers on this project presented preliminary findings for discussion and refinement with a larger set of Harvard faculty, senior researchers, and postdoctoral fellows engaged in related efforts on energy-technology innovation. The principal "deliverable" from this effort was a chapter entitled "The Role of R&D and the Changing R&D Paradigm", which was Chapter 2 in the final report of the PCAST study (delivered to DOE and the President in November 1997). The principal authors of this chapter were the two STPP postdoctoral fellows working under this award, Dr. Paul de Sa and Dr. Ambuj Sagar, who worked on this task under the supervision of Prof. Holdren and PCAST Energy R&D Panel member Dr. Richard Balzhiser of the Electric Power Research Institute. (A copy of that chapter is appended to this report.)

Work under this award also supported the preparation of additional tabular information and briefing materials for use in presentations to the Council of Economic Advisors, Office of Management and Budget, DOE, and members and staff of key Congressional committees, in the months immediately following completion of the report, in support of the recommendations of the PCAST study. The part of the work that followed the November 1997 delivery of the final PCAST report also laid the groundwork for the chapter on international patterns of energy R&D in the subsequent PCAST study for the President (on international cooperation in energy research, development, demonstration, and deployment), which was completed in June 1999.
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Abstract

We present experiments in the 60 Tesla Long-Pulse magnet at the Los Alamos National High Magnetic Field Lab (NHMFL) focusing on the high-field, low temperature photoluminescence (PL) from modulation-doped ZnSe/Zn(Cd,Mn)Se single quantum wells. High-speed charge-coupled array detectors and the long (2 second) duration of the magnet pulse permit continuous acquisition of optical spectra throughout a single magnet shot. High-field PL studies of the magnetic 2D electron gases at temperatures down to 350mK reveal clear intensity oscillations corresponding to integer quantum Hall filling factors, from which we determine the density of the electron gas. At very high magnetic fields, steps in the PL energy are observed which correspond to the partial unlocking of antiferromagnetically bound pairs of Mn$^{2+}$ spins.
Among the collection of experimental probes of the physics in semiconductor 2D electron gases (2DEGs), photoluminescence (PL) spectroscopy has proven particularly useful in unraveling energy-dependent carrier behavior. Oscillations in PL energy, intensity, and linewidth are used to identify both integer and fractional quantum Hall states, and spectral features are associated with many-body shakeup processes, spin textures (skyrmions), and Fermi-edge singularities at high magnetic fields and low temperatures. [1] Recently developed magnetic doped 2DEGs, in which local magnetic moments (typically Mn$^{2+}$ ions) are incorporated directly into a sea of mobile electrons [2], lend themselves naturally to an investigation of their spin-dependent high-field PL properties. In particular, we might anticipate qualitatively new physical phenomena as a result of the interplay between many-body effects and the ferromagnetic s-d electron-ion exchange. We also note that this exchange interaction yields a large spin-splitting of the electron subbands, resulting in a highly spin-polarized electron gas in which adjacent Landau levels can be separated purely by a cyclotron gap rather than a spin gap as in traditional non-magnetic 2DEGs. Magneto-transport experiments in these systems clearly reveal quantum Hall states at both even and odd integer filling factors, as well a distinctive magneto-resistance related to the exchange-enhanced spin-splitting. [3,4]

Here we present field-dependent PL data from a series of n-type modulation-doped ZnSe/Zn(Cd,Mn)Se single quantum wells at fields up to 60 Tesla and temperatures down to 350mK. These large magnetic fields drive the embedded Mn$^{2+}$ moments into nearly complete alignment, where the data reveal a large Zeeman shift and eventual saturation of the of the fundamental PL peak as the electron and hole bands track the sample magnetization. Oscillations in the PL intensity show clear evidence of integer
quantum Hall filling factors down to $v=1$ (~20 Tesla), permitting computation of the carrier density which can be compared with that obtained from transport data. At higher fields, steps are observed in the PL energy, corresponding to discrete jumps in the sample magnetization arising from the partial unbinding of antiferromagnetically-locked Mn$^{2+}$-Mn$^{2+}$ pairs.

PL spectroscopy of semiconductor systems in traditional capacitor-driven 50T and 60T pulsed magnets is typically hindered by the fast risetime ($dB/dt \sim 10$ T/ms) and short duration (~10 ms) of the magnet pulse, thereby making it difficult to obtain PL spectra with the desired signal-to-noise. To reconstruct the PL response as a function of field, experiments have therefore either relied on taking a single spectra at the ~1ms “flat top” of many individual magnet pulses (with ~1 hour cooldown between pulses), or on taking multiple exposures of microsecond duration during a single shot, which often requires large excitation powers to generate sufficiently bright PL.

The newly-commissioned 60 Tesla Long-Pulse magnet at the Los Alamos National High Magnetic Field Laboratory (NHMFL) has demonstrated its ability to facilitate the continuous collection of high-resolution PL spectra from 250nm to 900nm. The two-second duration of the magnet pulse represents a hundred-fold increase in time “at field” as compared with traditional “short-pulse” capacitor-driven magnets, and the field ramp rate can be as slow as 0.15 T/ms, even at the steepest part of the field sweep. Also in contrast with capacitor-driven magnets, the Long-Pulse magnet is powered by a 1.4 GVA motor-generator which allows for the field profile of the magnet pulse to be user-defined. A typical symmetric “flat-top” field profile is shown in Figure 1, where maximum field is maintained for a full 100 ms (a short-pulse field profile is also shown
for comparison). Coupled with modern fast-scanning charged-coupled array (CCD) detectors, complete PL spectra can be continuously acquired in this magnet at rates up to 1 kHz. The expanded portion of Figure 1 shows the fields at which PL spectra were taken. The variation in magnetic field during the 1.2 ms exposure in this particular experiment is 0.36 Tesla; this value can be reduced over 50% by stretching the final magnet ramp (from 30T to 60T) to 180ms instead of the 80ms shown.

Fiberglass helium cryostats permit operation at temperatures down to 1.5K, and a He3 refrigerator extends this range to ~350mK. Laser excitation and collected PL are coupled to and from the sample through a single 200μm or 600μm diameter optical fiber. Low numerical aperture fibers and a fast (f/4) imaging spectrometer are used for optimum detection efficiency. The CCD is a liquid nitrogen cooled, 1340x100 pixel backthinned device (Princeton Instruments) with a high quantum efficiency (45% at 350nm, 90% at 600nm), fast vertical shift time, and a 1MHz 14-bit low noise A/D converter. The full array can be binned and digitized in 2.1ms (476Hz), and hardware re-definitions allow operation to 1kHz. Data are continuously streamed to computer, and ~2000 full spectra are typically acquired during a single magnet shot. The sensitivity of the CCD, efficient optical coupling, and the comparatively long millisecond exposures allow excellent signal/noise (>100) even with low excitation intensity (100μW at 400nm in the present experiments).

To fabricate magnetic 2DEGs, the magnetic species (Mn²⁺, S=5/2) is “digitally” incorporated into a 105Å ZnSe/ZnCdSe modulation doped quantum well in the form of equally-spaced fractional-monolayer planes of MnSe (Fig.2a). Details of the MBE growth of the samples, as well as magneto-transport measurements and low-field
magneto-optical spectroscopy are published elsewhere [2-4]; the samples studied here contained five equally spaced MnSe layers of 1/2, 1/4, 1/8, and 0 monolayer thickness, the latter serving as a nonmagnetic control 2DEG. Electron (and hole) wavefunctions overlap and interact with the Mn$^{2+}$ moments via the strong $s$-$p$-$d$ exchange interaction, giving rise to amplified spin (Zeeman) splittings of the electron spin subbands. As a result, the "ordinary" Landau fan diagram for nonmagnetic 2DEGs (with Landau levels equally spaced by $\hbar\omega_c$) is replaced by that shown in Fig. 2b, where the Brillouin-like Zeeman splitting of the spin sublevels has been added. [4] Thus, even at low applied fields the electron gas is highly spin polarized.

PL from the magnetic 2DEG containing 1/8ml MnSe planes is shown in Figure 3a and is characteristic of the optical response from all the measured magnetic 2DEGs. At zero field, the PL shows a single peak arising from recombination of holes with electrons at the conduction band minimum near $k=0$. This view is consistent with the assumption that (at least at $B=0$) the holes are not strongly localized in the plane of the well, and so are not expected to recombine with higher momentum electrons within the electron gas. With small applied magnetic field, this peak rapidly Zeeman shifts to lower energies in concert with the Brillouin-like sample magnetization and becomes entirely $\sigma^+$ circularly polarized, corresponding to recombination of electrons in the lower energy ($s_z=-1/2$) spin subband with low energy holes ($j_z=-3/2$). The higher energy ($\sigma^-$) transition ($s_z=+1/2$ electrons with $j_z=+3/2$ holes) blueshifts as expected but is visible only below 1 T, after which its intensity falls below the detection limit. At intermediate fields (2 T $<$ B $<$ 20 T), the PL spectra develop an additional peak (also of the same polarization) roughly 10 meV above the band-edge PL peak. However, beyond $\sim$20 T ($\nu<1$), the PL spectra collapse
back to a single peak which grows dramatically in intensity before saturating at ~35 Tesla and falling slowly thereafter to 60T. A full discussion of the nature of the additional peak -- as well as of striking anomalies in the magnetic field dependence of the intensity and position of both PL peaks -- is beyond the scope of the present paper and will be given elsewhere.

The integrated intensity of the PL spectra are shown in Figure 3b, revealing clear modulations which can be ascribed to the Fermi level moving through integer quantum Hall states. Undoped magnetic quantum wells exhibit no such PL structure, as expected (not shown). Intensity minima are common in PL studies of II-V electron gases [6], and are usually ascribed to the reduced screening of the photoexcited hole by the electrons which are localized at integer filling factors; as such, the electron-hole wavefunction overlap is reduced and the radiative recombination decreases. More detailed many-body considerations involve fluctuations in the Landau-level half width and therefore oscillations in the density of states, leading to similar intensity fluctuations. [7] From the positions of the intensity minima we compute the carrier density. The results are 5.1, 3.9, and 4.8 x10¹¹/cm² for the nonmagnetic, 1/8 and 1/4 monolayer magnetic 2DEGs respectively, as compared with 5.3, 4.2, and 6.5 x10¹¹/cm² determined from transport experiments. [3] The discrepancy may arise from the fact that the samples were illuminated during cooldown in the transport experiments (but not in the PL experiments), which has been observed to generate a ~10% increase in carrier density. In contrast to all the magnetic 2DEGs, the nonmagnetic 2DEG does not exhibit a many-fold increase in PL intensity. This result, though not understood, is however consistent with
PL studies in insulating magnetic and nonmagnetic II-VI quantum wells, which show a similar contrast.

At very high magnetic fields, although the magnetic 2DEGs are near the fractional quantum Hall filling factor $v=1/3$, no clear evidence of FQH effects can be seen in the PL, possibly because the present electron mobilities ($\sim 10^3$ cm/Vs) are not sufficiently high. However, the energy of the PL peaks do reveal spin realignments within the sublattice of Mn$^{2+}$ moments. Figure 4 shows clear jumps in the wavelength of the detected PL in the $1/8$ml magnetic 2DEG at roughly 19 T, 36 T, and 54 T. These steps indicate an incremental increase in the sample magnetization, and are identified with the partial unlocking of antiferromagnetically-bound Mn$^{3+}$-Mn$^{2+}$ pairs. Steps are expected to occur at integer multiples of the nearest-neighbor exchange field between Mn spins, $H=n*2J_{dd}/\mu_B$. The steps observed in the magnetic 2DEGs indicate $J_{dd} \sim 12$K, in agreement with published values for $J_{dd}$ in zincblende ZnMnSe. [8] As expected, these steps can also be observed in PL from insulating magnetic quantum wells. The steps lose clarity in samples with thicker fractional–monolayer MnSe planes, in which larger and larger spin clusters develop, reducing the probability of forming isolated Mn$^{2+}$-Mn$^{3+}$ pairs.

To summarize, high-resolution low-noise PL spectra of magnetic 2DEGs have been measured at fields up to 60 Tesla. Over 2000 spectra are acquired in a single magnet pulse, permitting easy recognition of fluctuations that occur in the PL lineshape and wavelength. In particular, minima in the integrated PL intensity at integer filling factors can be used to determine the 2DEG carrier concentration, and steps in the PL
energy indicate the strength of the $J_{dd}$ exchange interaction between nearest-neighbor Mn$^{2+}$ spins.

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References


Figure Captions

Figure 1: A “flat-top” field profile of the 60 Tesla Long-Pulse magnet (a capacitor-driven 60T magnet profile is shown for comparison). The field profile is user-definable. Expanded portion shows the actual points at which full spectra were acquired, every 1.2ms (0.36T) in this case.

Figure 2: a) Schematic of a n-type (chlorine) modulation-doped magnetic 2DEG structure. b) The Landau fan diagram for the highly spin-polarized 1/8 monolayer magnetic 2DEG, where the large Zeeman splitting dominates. Solid (dashed) lines correspond to spin-down (spin-up) Landau levels, and the dark line indicates the position of the Fermi level. Parameters used in this calculation are: $E_F = 7$ meV at $B = 0$, $m_e^* = 0.14 m_0$ and $T = 360$ mK. The modified Brillouin function parameters are obtained by fitting magneto-optical data: $T_0 = 2.1$ K and a saturation conduction band spin splitting of 12.9 meV. The effective mass is determined from cyclotron resonance measurements [5].

Figure 3: a) Collected PL from the 1/8 monolayer magnetic 2DEG during a 1.5K magnet shot. Spectra shown are spaced at 1 Tesla intervals and are offset for clarity. b) The integrated PL at 1.5K from the 2DEGs indicated.
Figure 4: The Zeeman shift (absolute value) of the fundamental P1 peak, showing steps corresponding to incremental jumps in the sample magnetization, originating in the unlocking of Mn$^{2+}$-Mn$^{2+}$ antiferromagnetically bound pairs.
Full spectra at each point
a) 25 nm
n-ZnSe
↓
Fractional monolayers of MnSe
↓
12.5 nm
i-ZnSe
↓
10.5 nm
[Zn,Cd]Se
↓
12.5 nm
i-ZnSe
n-ZnSe

b) $E_f$ (meV) vs. $B$ (T)
$J_{d-d} = 12K$

$S=1$

$S=2$

$S=3$

$1/8m \text{ MnSe}$

$350mK$

**Figure 4**