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Optically pumped NMR in CdS single crystals

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Optically induced dynamic nuclear polarization in CdS (resistivity 1.8×10^{10} Ω cm, dark) is observed by radio-frequency detection of the ^{113}Cd nuclear magnetic resonance signal. At 2 K, the nuclear-spin transitions are emissive when compared to the thermal polarization, and no dependence on the helicity of the pumping light is observed. [S0163-1829(99)14103-1]

Optically induced dynamic nuclear polarization (DNP) in semiconductors can be observed by resonant interband irradiation with (a) unpolarized light, which saturates the electronic spin-resonance transitions, and (b) by irradiation with circularly polarized light, which generates spin-polarized electrons and holes.[1,2] In both cases, the enhanced nuclear polarization can be rationalized by an Overhauser-type cross-relaxation process[3,4] mediated through the contact hyperfine interactions with the perturbed electronic spin system.[5] This optical pumping process has been largely investigated in the context of optically detected NMR (ODNMR),[5–9] where the nuclear spins are irradiated by a resonant radio-frequency field, which induces depolarization of the electrons through the nuclear Hanle effect.[5] More recently, optically induced DNP experiments have been performed in high magnetic fields with direct NMR detection.[10] The experiments focused on cubic III-V bulk GaAs-based systems and heterostructures.[10–13]

Here we report an observation of optically induced DNP for II-VI semiconductors with hexagonal structure. Two undoped, *n*-type CdS single crystals with largely different resistivities were investigated. Optical enhancement of the ^{113}Cd spin polarization was only observed in the higher resistivity sample for $T\leqslant 2$ K. At this temperature, the optically induced spin polarization was negative when compared to the thermal polarization, irrespective of the helicity of the pumping light.

In cubic bulk semiconductors, spin-polarized photons induce transitions from both the upper (Γ_8) and the lower valence band (Γ_7), split off by the spin-orbit energy Δ_{SO}, to the conduction band Γ_{7c}. The relative probabilities of these transitions lead to a maximum degree of electronic orientation $|P_0|=0.5$,[5] where

$$P_0=\frac{n_+-n_-}{n_++n_-}. \tag{1}$$

Here $n_\pm$ denotes electronic carriers with their magnetic moments aligned parallel or antiparallel to the propagation vector of the light. In wurtzite-type semiconductors, the degeneracy of the upper valence band at the center of the Brillouin zone ($\boldsymbol{k}=0$) is lifted, and Γ_8 is split into two subbands Γ_9 and Γ_7 by the crystal-field energy Δ_{cr}. Transitions from Γ_9 to the conduction band occur only for irradiation with circularly polarized light along the *c* axis of the crystal with a maximum degree of orientation $|P_0|=1$.[14] For CdS at 1.8 K, the band gap $E_g=(\Gamma_{7c}-\Gamma_9)=2.583$ eV, $\Delta_{cr}=0.026$ eV, and $\Delta_{SO}=0.065$ eV.[15] Transitions from Γ_7 are allowed for both polarization vectors (parallel and perpendicular to the *c* axis).

The CdS single crystals of rectangular shape ($5\times7\times1$ mm^3) were purchased from Cleveland Crystals, Inc. One of the crystals had an as-grown resistivity (10 Ω cm, dark), the other a high resistivity (1.8×10^{10} Ω cm, dark, and 9.5×10^6 Ω cm, roomlight), referred to as ‘‘as grown’’ and ‘‘high resistivity,’’ respectively. With a Hall mobility of $\mu_{300\ \mathrm{K}}=360$ cm^2 V^{-1} s^{-1}, this corresponds to a carrier concentration of $N_D-N_A=1.8\times10^{15}$ cm^{-3} for the as-grown CdS. For the high-resistivity crystal, the Hall mobility is lower, resulting in a carrier concentration of $N_D-N_A=10^6-10^7$ cm^{-3} (dark), and 10^9-10^{10} cm^{-3} (roomlight).[16] The high-resistivity material was prepared by heating the as-grown CdS under sulfur pressure. This procedure reduces the number of S vacancies (donors), and increases the number of Cd vacancies which form deep acceptors. Overcompensation of the S vacancies leads to *p*-type CdS.

The samples were mounted with vacuum grease on a holder fixed to a home-built transmission-line probe assembly.[17] Temperature control was achieved with a dynamic continuous-flow helium cryostat CF1260N equipped with an optical window (Oxford Instruments, Inc.). Experiments were carried out in superfluid helium (2 K) or helium gas (5 K). An Ar$^+$ laser (Coherent, Inc.) served as the light source. The laser beam was split into six individual lines by a dispersing prism. The lines at 457.9 nm (2.71 eV), 476.5 nm (2.60 eV), and 488.0 nm (2.54 eV) were used in the experiments. The other lines were blocked with an aperture. Circularly polarized laser light (σ^+,σ^-) was obtained by inserting a $\lambda/4$ waveplate in the beam path as the last element before the optical window of the cryostat, with >90% polarization for $\lambda=476.5$ nm. The crystals were mounted with the 5×7 mm^2 face perpendicular to the propagation vector of the laser light, such that this vector was parallel to the optical axis of the crystals (*c* axis) and the magnetic field

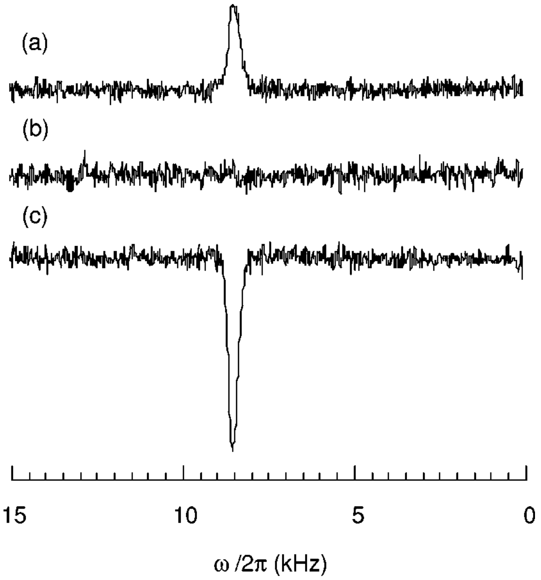

FIG. 1. ^{113}Cd NMR spectra of the high-resistivity CdS single crystal recorded at 2 K with a single scan. The Boltzmann signal is shown in (a), the optically enhanced signal after an irradiation time $\tau_L = 600$ s at 2.60 eV with circularly polarized light and $p = 520$ mW laser power in (c). (b) was obtained under identical conditions as (c), but with the shutter closed during τ_L.

$\mathbf{B}_0$. The laser spot size was estimated to be ~ 0.04 cm^2 at the sample. Experiments were performed on a home-built spectrometer operating at a ^{113}Cd frequency of $\omega_0/2\pi = 39.505$ MHz ($B_0 = 4.2$ T). The radio-frequency field strength was matched to $\omega_1/2\pi = 28$ kHz for all measurements. The equilibrium ^{113}Cd polarization was saturated with a series of $\pi/2$ pulses separated by a 50-ms delay, while a shutter blocked the laser light. After opening the shutter for a period τ_L, typically 100–600 s, the shutter was closed again. Following a delay of $\tau_1 = 500$ ms, the ^{113}Cd free-induction decay was stimulated by a $\pi/2$ pulse. In Fig. 1(a), the ^{113}Cd NMR signal of the high-resistivity single crystal is compared with an optically enhanced signal obtained after sample irradiation with circularly polarized light at 2.60 eV for $\tau_L = 600$ s (c). The control experiment obtained under identical conditions as in (c) but with the laser blocked is also included (b). At 2 K, an upfield shift of the ^{113}Cd resonance of 13 ppm with respect to 300 K is observed. This shift can be attributed to an intrinsic small change of the CdS lattice parameters upon cooling (the expansion coefficient of CdS is 4.6×10^{-6} K^{-1} perpendicular to the c axis[15]), and/or a possible strain induced in the crystal by the differential thermal contraction of the sample and of the sample mount. A calculation of the second moment[1] of the ^{113}Cd resonance based on the CdS crystal structure,[15] and considering the natural abundance of ^{113}Cd ($S = -\frac{1}{2}$, 12.26%) and ^{111}Cd ($S = -\frac{1}{2}$, 12.75%), results in a through-space dipolar linewidth of $\nu_{1/2} = 161$ Hz ($c \| \mathbf{B}_0$). The experimental line shape is Gaussian with $\nu_{1/2} = 380$ Hz. The larger experimental value is probably caused by residual magnetic-field inhomogeneities and scalar and anisotropic cadmium $\mathbf{J}$ interactions.[18]

From a saturation-recovery experiment at 2 K with a maximum recovery delay of 2.16×10^3 s we estimate a ^{113}Cd spin-lattice relaxation time $T_1 \sim 7 \times 10^3$ s in the initial-rate approximation. Kushida and Silver[19] reported $T_1 \sim 1.8 \times 10^5$ s (4.2 K, dark) for a CdS single crystal with a dc resistivity > 100 MΩ cm. When their sample was illuminated with white light, the value reduced to $T_1 \sim 1.8 \times 10^3$ s. The ^{113}Cd T_1 values in the order of 10^3 s found in this work and by Kushida and Silver[19] can be attributed to relaxation through paramagnetic centers resulting from the trapping of photoelectrons at defect sites;[19,20,21] remote ^{113}Cd spins are then relaxed through a spin-diffusion process.[22]

When the ^{113}Cd nuclei were detected during laser excitation (shutter open during τ_1 and the acquisition period), no change in signal intensity, shift, or linewidth was observed when compared to the spectrum shown in Fig. 1(c). Therefore, the optically pumped ^{113}Cd resonance was not affected by interactions with conduction electrons. This compares well with recent NMR results from bulk GaAs,[12] whereas an optical Knight shift was observed in p-type GaAs by time-sequenced ODNMR.[8] In GaAs/Al$_x$Ga$_{1-x}$As quantum wells, Knight shifts have been observed both with NMR detection[11] and ODNMR.[9]

No correlation of the intensity of the ^{113}Cd NMR signal with the helicity of the laser light was observed at 2.54, 2.60, or 2.71 eV. However, the signal intensity is linearly decaying with progressing measurement time at an irradiation energy of 2.60 eV ($\sim 60\%$ of the optically pumped ^{113}Cd signal was recovered after a total measurement time of 1 h at 2 K). A similar decay was found at 2.71 eV, but the effect is less pronounced at 2.54 eV, where the laser energy is below the band gap. Here the absorption coefficient is smaller and less energy is dissipated in the crystal.[23] Therefore, the decay can be attributed to heating of the crystal upon extended exposure to the laser light.[24] At a temperature of 5 K, longer irradiation times were necessary for detection of the optically enhanced ^{113}Cd signal: with irradiation at 2.54 eV ($\tau_L = 960$ s, $p = 520$ mW), 6% of the signal intensity observed at 2 K was detected; at 2.60 eV ($\tau_L = 960$ s, $p = 500$ mW), it was 3%; and at 2.71 eV ($\tau_L = 960$ s, $p = 210$ mW), it was 4%. The most pronounced effect at 2.60 eV is due to the fact that this energy corresponds closely to the band gap at 2 K. At higher temperatures the band gap experiences a redshift, and the largest percentage is recovered at the lowest irradiation energy. At 5 K, the NMR signals were absorptive for irradiation with both σ^+- and σ^--polarized light.

Assuming an Overhauser-type cross-relaxation mechanism for the dynamic polarization of the ^{113}Cd spins and implying that $|\gamma_N B_0 \hbar| \ll |g \beta B_0|$ and a single electronic spin temperature, the nuclear polarization P_N can be written as[1,25,26]

$$P_N = \frac{P - P_{eq}}{1 - P_{eq} P} \frac{T_1}{T_1 + T_{1e}}, \tag{2}$$

where P_{eq} denotes the thermal polarization of the electrons, and P is the electronic steady-state polarization. T_{1e} denotes the nuclear spin-relaxation time due to interactions with the polarized electrons. At 2 K and for irradiation times $\tau_L \ll T_1$, optical pumping can only be observed if $T_1 \gg T_{1e}$. The electronic g factor parallel to the c axis is $g_\| = 1.77$ in CdS,[15,27] so that $P_{eq} > 0$. In the following, we assume that the g factor of excitons differs negligibly from the value of

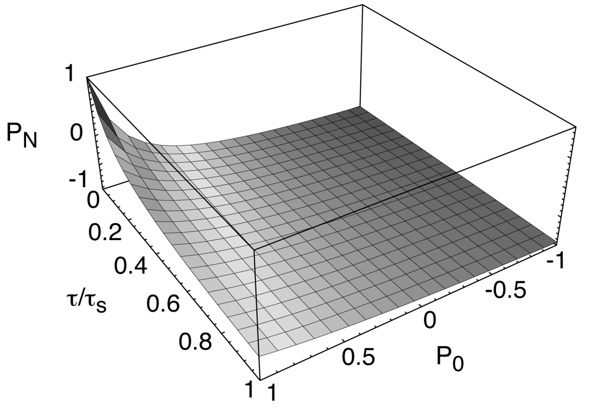

FIG. 2. Dependence of P_N on P_0 and τ/τ_s in the limit $T_{1e} \ll T_1$ at 2 K.

the conduction electrons. The sign of the nuclear polarization depends on the sign of P-P_{eq}. When $P > P_{eq}, P_N$ becomes positive, as $|P_{eq}P| < 1$. The electronic steady-state polarization P can be written as

$$P = P_0 \frac{1}{1-\tau/\tau_s}, \tag{3}$$

where τ is the electron lifetime, and τ_s denotes the electronic spin-relaxation time. If the condition $\tau/\tau_s \ll 1$ is not fulfilled, P is attenuated with respect to P_0, and the dependence of P_N on P becomes less pronounced. Figure 2 shows P_N of Eq. (2), in the limit $T_{1e} \ll T_1$, as a function of P_0 and $0 \leqslant \tau/\tau_s \leqslant 1$ for CdS at 2 K. For $\tau/\tau_s > 0.2, P_N$ is only weakly modulated by P_0 and negative. Implying a scalar $(\mathbf{I} \cdot \mathbf{S})$ electron-nucleus hyperfine coupling, and, since $\gamma(^{113}\mathrm{Cd})$ is negative, an emissive ^{113}Cd signal is expected, in agreement with the experiments. We therefore conclude that at 2 K, $\tau_s \simeq \tau$ and on the order of nanoseconds.[28]

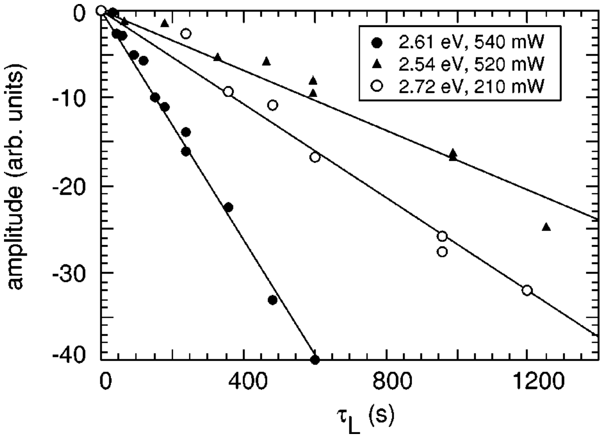

FIG. 3. Dependence of the ^{113}Cd NMR signal intensity on the irradiation time τ_L at different irradiation energies and constant laser power, 2 K. The regime of saturation of P_N is not reached, and the solid lines represent linear fits. For the ratio of the slopes we find $m_{2.60\ eV}/m_{2.71\ eV} = 2.3$ and $m_{2.60\ eV}/m_{2.54\ eV} = 4.1$.

Figure 3 shows the dependence of the signal intensity on τ_L for different laser energies. Irradiation at 2.60 eV, closest to the band gap, is most efficient. Irradiation with an energy larger than the band gap is more efficient than irradiation below the gap with twice the laser power. At 2.71 eV, transitions from the lowest valence bands can be induced, which reduce the maximum attainable degree of electronic polarization $|P_0|$.[5] For irradiation times longer than those shown in Fig. 3, it is expected that the nuclear polarization will reach a dynamic equilibrium state determined by the steady-state electronic polarization and nuclear T_1. The absorption coefficient of CdS at 4.2 K and 480 nm has been reported as $\alpha = 2 \times 10^5$ cm^{-1}.[29] Accordingly, a typical penetration depth of the laser light is ~ 0.05 μm into the sample. With a calculated average distance between closest ^{113}Cd neighbors of $\bar{a} = 4.75$ Å, a nuclear spin-diffusion coefficient[1] of $D_{sd} \sim 10^{-13}$ cm^2 s^{-1} can be estimated within an order of magnitude. Therefore, for irradiation times $\tau_L > 200$ s, the NMR active sample volume is limited by spin diffusion.

The as-grown crystal yielded no optically enhanced NMR signal under identical experimental conditions. At room temperature, it has a nuclear T_1 longer than the high-resistivity crystal despite its higher carrier concentration. It is conceivable that the presence of Cd vacancies in the high-resistivity sample leads to a more efficient ^{113}Cd spin relaxation, and to a shorter T_{1e}.

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[1] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).

[2] G. Lampel, Phys. Rev. Lett. **20**, 491 (1968).

[3] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).

[4] T. R. Carver and C. P. Slichter, Phys. Rev. **92**, 212 (1953).

[5] *Optical Orientation*, edited by F. Meier and B. P. Zakharchenya (Elsevier, Amsterdam. 1984).

[6] A. I. Ekimov and V. I. Safarov, Zh. Éksp. Teor. Fiz. **15**, 257 (1972) [Sov. Phys. JETP **15**, 179 (1972)].

[7] G. P. Flinn, R. T. Harley, M. J. Snellig, A. C. Trooper, and T. M. Kerr, Semicond. Sci. Technol. **5**, 533 (1990).

[8] S. K. Buratto, D. N. Shykind, and D. P. Weitekamp, Phys. Rev. B **44**, 9035 (1991); J. A. Marohn, P. J. Carson, J. Y. Hwang, M. A. Miller, D. N. Shykind, and D. P. Weitekamp, Phys. Rev. Lett. **75**, 1364 (1995).

[9] M. Krapf, G. Denninger, H. Pascher, G. Weimann, and W. Schlapp, Superlattices Microstruct. **8**, 91 (1990); M. Krapf, G. Denninger, H. Pascher, G. Weimann, and W. Schlapp, Solid State Commun. **78**, 459 (1991).

[10] S. E. Barrett, R. Tycko, L. N. Pfeiffer, and K. W. West, Phys. Rev. Lett. **72**, 1368 (1994); R. Tycko, Solid State Nucl. Magn. Reson. **11**, 1 (1998).

[11] S. E. Barrett, G. Dabbagh, L. N. Pfeiffer, K. W. West, and R. Tycko, Phys. Rev. Lett. **74**, 5112 (1995); R. Tycko, S. E. Barrett, G. Dabbagh, L. N. Pfeiffer, and K. W. West, Science **268**, 1460 (1995).

[12] T. Pietraß, A. Bifone, T. Rõõm, and E. L. Hahn, Phys. Rev. B **53**, 4428 (1996); T. Pietraß, A. Bifone, J. Krüger, and J. A. Reimer, *ibid.* **55**, 4050 (1997).

[13] P. L. Kuhns, A. Kleinhammes, T. Schmiedel, W. G. Moulton, S. Sloan, P. Chabrier, E. Hughes, and C. R. Bowers, Phys. Rev. B **55**, 7824 (1997); C. R. Bowers, Solid State Nucl. Magn. Reson. **11**, 11 (1998).

[14] E. F. Gross, Á. I. Ekimov, B. S. Razbirin, and V. I. Safarov, Pis'ma Zh. Éksp. Teor. Fiz. **14**, 108 (1971) [JETP Lett. **14**, 70 (1971)].

[15] *Semiconductors Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors*, edited by K. H. Hellwege, Landolt-Bornstein, New Series, Group III, Vol. 17, Pt. b (Springer, Berlin, 1982).

[16] L. Shiozawa (private communication).

[17] The 5×7-mm faces of the crystals were polished with a slurry of powdered Al_2O_3 (particle size 3 μm) in water on commercial polishing paper (Polytex, Rodel Inc.).

[18] A. Nolle, Z. Phys. B **34**, 175 (1979).

[19] T. Kushida and A. H. Silver, Phys. Rev. **137**, A1591 (1965).

[20] J. Lambe, J. Baker, and C. Kikuchi, Phys. Rev. Lett. **3**, 270 (1959).

[21] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

[22] N. Bloembergen, Physica (Amsterdam) **15**, 386 (1949).

[23] K. Maeda and A. Kasami, in *II-VI Semiconducting Compounds* (Benjamin, Providence, RI, 1967), p. 1323.

[24] M. V. Klein and S. P. S. Porto, Phys. Rev. Lett. **22**, 782 (1969).

[25] C. Hermann and G. Lampel, Ann. Phys. (Paris) **10**, 1117 (1985).

[26] The sign in Eq. (3) of Ref. 12 is reversed.

[27] K. A. Müller and J. Schneider, Phys. Lett. **4**, 288 (1963).

[28] P. Wiesner and U. Heim, Phys. Rev. B **11**, 3071 (1975).

[29] J. O. Dimmock in *II-VI Semiconducting Compounds* (Ref. 23), p. 277.