Supplemental Material for:
"Optical hyperpolarization of nitrogen donor spins in bulk diamond"

M. Loretz[1], H. Takahashi[1], T. F. Segawa[1,2], J. M. Boss[1], C. L. Degen[1]

[1]*Department of Physics, ETH Zurich, Otto Stern Weg 1, 8093 Zurich, Switzerland*

[2]*Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir Prelog Weg 2, 8093 Zurich, Switzerland.*

Orientation of the diamond chip in the EPR setup

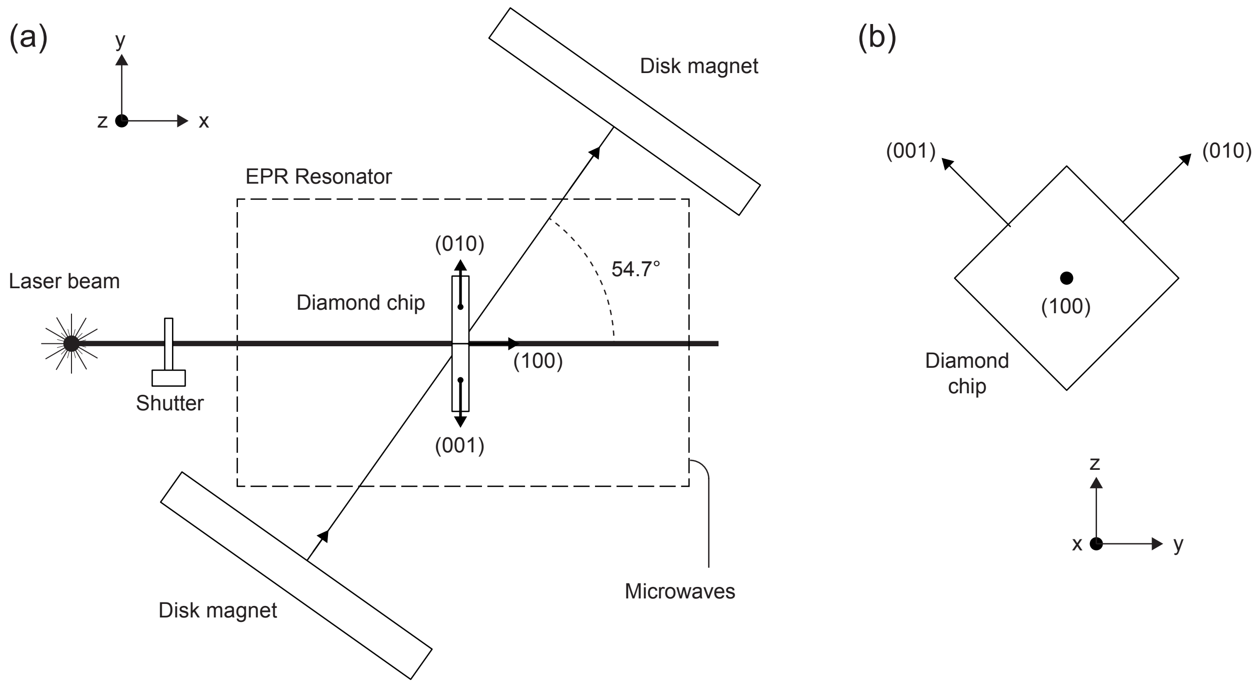

FIG. S1. (a) Schematic of the EPR setup. The diamond chip was mounted in the EPR resonator with its flat (100) surface oriented along the x axis, and then rotated around the x axis such that the (010) and (001) side walls were at 45° with y and z (see b). The magnetic field of 51 mT was provided by two permanent disk magnets at an angle of 54.7° between the x and y axes. With this arrangement, the magnetic field is oriented along the {111} crystal axis, which corresponds to one of the four diagonals of the diamond unit cell. We called NV centers whose N-V symmetry axes were along the {111} diagonal "aligned" and NV centers whose symmetry axes were along one of the other three diagonals "not aligned". The EPR setup also incorporated a field modulation coil and a central sample tube connected to a flow of cold nitrogen purge gas (not shown). (b) View of the diamond chip along the x axis.

Experimental EPR spectra at X-band (9.855 GHz)

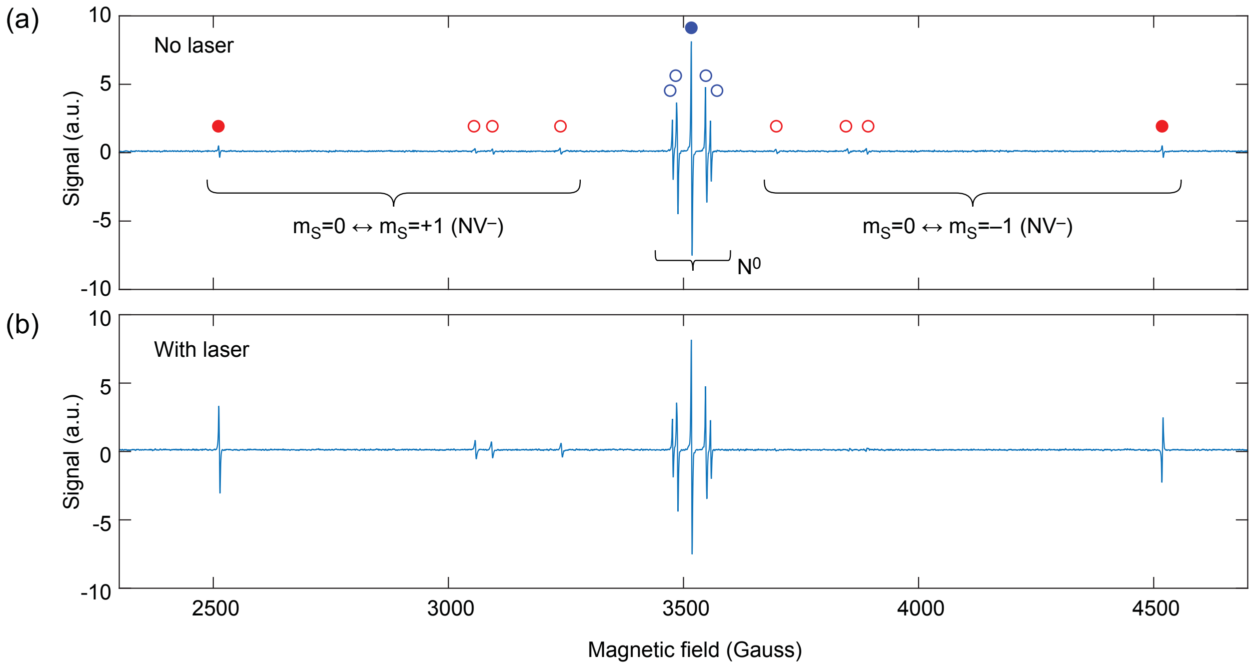

FIG. S2. EPR spectrum of diamond chip A taken at X-band. The chip was oriented such that the {111} crystal axis was approximately parallel to the magnetic field. (a) Spectrum with no laser illumination. Blue dots identify N^0 (S=1/2). The filled dot marks the central transition and empty dots mark the hyperfine satellite transitions. Red dots identify NV^- (S=1). Filled dots mark the transitions of aligned NV centers and empty dots mark the transitions of not aligned NV centers (cf. caption of Fig. S1). (b) Spectrum with laser illumination by a few mW. The signal of NV peaks is clearly enhanced. No enhancement is seen for nitrogen donor spins because cross-relaxation is negligible.

Calculated EPR spectrum of NV$^-$ at 51 mT

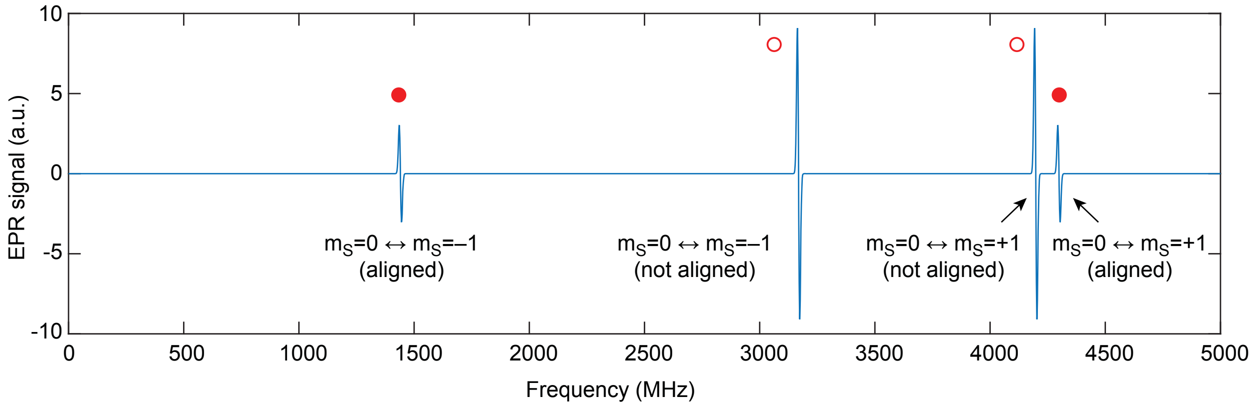

FIG. S3. Calculated EPR spectrum with a magnetic field of 51 mT applied along the {111} crystal orientation. Filled red dots mark the transitions of NV$^-$ spins aligned with the field and empty dots mark the transitions of NV$^-$ spins not aligned with the field. Note that compared to Fig. S2, only two (rather than six) "not aligned" transitions are resolved because their are three-fold degenerate. In Fig. S2, the degeneracy is lifted by a small misalignment of the magnetic field. The relevant transition exploited in our experiment is the $m_S = 0 \leftrightarrow m_S = -1$ transition at approximately 1450 MHz. A line broadening of 5 MHz was applied for better visibility.

Simulated NV and N_0 populations

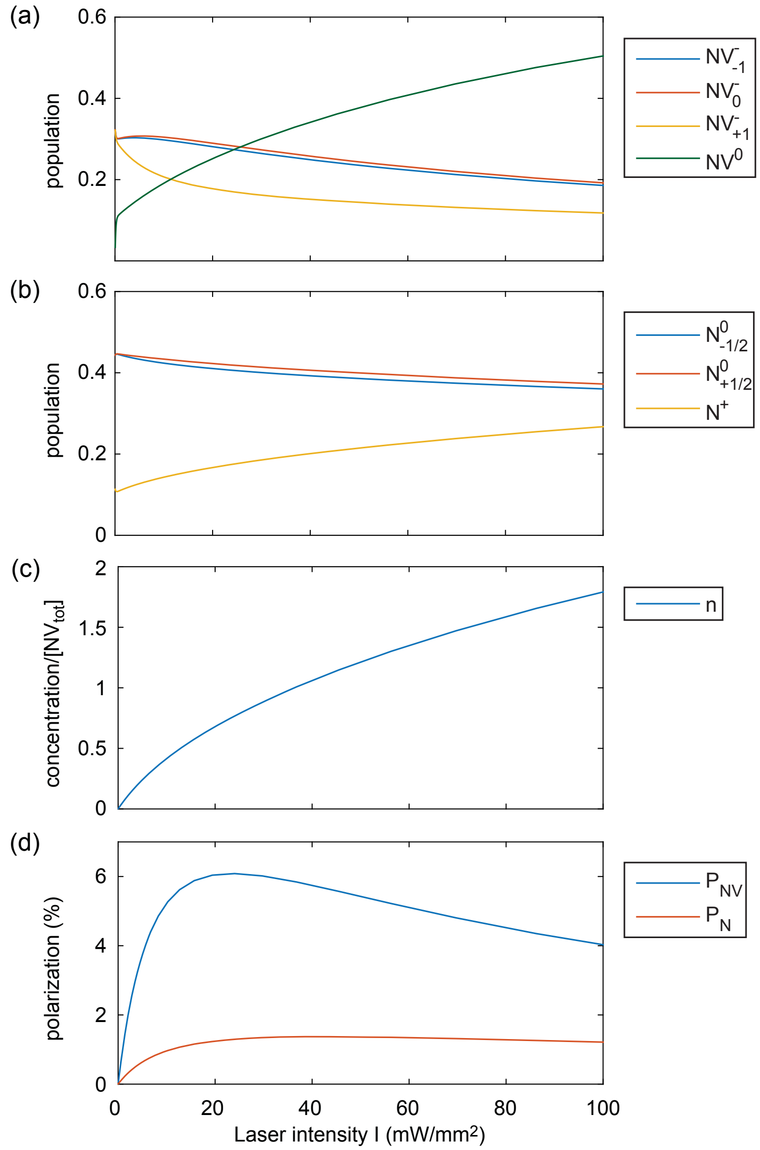

FIG. S4. Simulated populations corresponding to Curve (4) in Fig. 3 and Table II of the main manuscript. (a,b) Populations for NV and P1 spin and charge states, respectively, on a scale between 0 and 1. (c) Density of conduction electrons $n = R' p_{\mathrm{N}^+} - p_{\mathrm{NV}^-}$, which in our simple model corresponds to the number of charges that have been removed from NV^- and N_0. The charge density is in units of $[\mathrm{NV_{tot}}]$. (d) Polarization of NV^- and N^0 corresponding to Curve (4) in Fig. 3.