Raman heterodyne detected electron-nuclear-double-resonance measurements of the nitrogen-vacancy center in diamond

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We report two new applications of the Raman heterodyne detection technique. Raman heterodyne detected electron-nuclear double resonance and a double rf resonance technique are used to obtain the hyperfine structure of the nitrogen-vacancy center in diamond.

In a recent paper we reported what are to our knowledge the first Raman heterodyne detected electron paramagnetic resonance (EPR) signals. The Raman heterodyne technique applies to any three-level system for which all the transitions are allowed and was originally demonstrated in the detection of nuclear magnetic resonance (NMR) signals. In the Raman heterodyne detection scheme a laser field drives the transition \( 1 \rightarrow 3 \), whereas a rf field drives the \( 1 \rightarrow 2 \) transition between adjacent levels. This produces a coherence between levels \( 2 \rightarrow 3 \) and results in a Raman signal that can be detected on the transmitted laser beam by using heterodyne detection. The experimental equipment is simple, based on a spectrum analyzer and a tracking generator. The rf from the tracking generator is amplified and passed through the coil around the sample to a matched load. A fast P-I-N photodiode detects the transmitted light, and the component of the photocurrent oscillating at the rf frequency is amplified before being displayed on a spectrum analyzer.

In this Letter we show that a second rf source inducing transitions between the nuclear hyperfine levels affects the size of the Raman heterodyne detected EPR signal. This in effect results in Raman heterodyne detected EPR signals from ground-state electron-nuclear double resonance. The terms on the right-hand side of Eq. (1) give the Zeeman, the second-order crystal field, the magnetic hyperfine, the nuclear Zeeman, and the electric quadrupole interactions, respectively. EPR measurements give a value of \( g = 2.0028 \) and a magnitude of the crystal field splitting of the triplet \( |D| = 2.88 \, \text{GHz} \). The hyperfine structure is associated with nitrogen, the only atom in the center with a nonzero nuclear spin, resulting in an EPR spectrum consisting of three lines separated by \( A = -2.3 \, \text{MHz} \). The nuclear Zeeman splitting of nitrogen is known to be \( \mu_B g = 3 \, \text{MHz} / T \). However, EPR is not sensitive to terms that depend only on nuclear spin, and consequently the value of the quadrupole interaction parameter \( P \) in the last term in Eq. (1) has not been determined previously.

For the experiment a 1 mm \( \times \) 1 mm \( \times \) 1 mm sample with faces perpendicular to the \( \langle 110 \rangle \), \( \langle 110 \rangle \), and \( \langle 001 \rangle \) crystallographic directions was mounted in exchange He gas at 5 K within the bore of a superconducting magnet. The light propagated perpendicular to the \( \langle 110 \rangle \) faces, and the axis of a four-turn rf coil was aligned with the light direction. The \( E \) vector of the light, the \( H \) vector of the rf, and the field directions were then mutually perpendicular.

When the static magnetic field is along a \( \langle 111 \rangle \) direction it is aligned along the axis of one of the four orientations of the trigonal centers in the diamond. This center then gives a linear splitting of the ground \( S_z = \pm 1 \) doublet such that one of the Zeeman components approaches the spin singlet \( S_z = 0 \) level (Fig. 1). Between fields of 700 and 1400 G the two levels approach each other to within 1 GHz, and it is for this range that the Raman heterodyne detected EPR signals have been reported. With only axial Zeeman terms there would be degeneracy at a field of 1030 G (Fig. 1), but in the neighborhood of this field the off-diagonal Zeeman and hyperfine terms in Eq. (1) as well as the crystal strain become important and pre-
vent the levels from crossing. This effect is called level anticrossing.

The Raman heterodyne detected EPR signal for magnetic field strengths close to those resulting in level anticrossing was reported in Ref. 1. In the present study it is found that with a second rf applied to the same coil there are frequencies at which the second rf changes the magnitude of the initial Raman heterodyne signal. No new coherent effects due to the second source need be considered since any process that affects the coherent admixture of states induced by the first (EPR) rf field will affect the Raman heterodyne signal. Only the frequencies of the second rf source are of interest, and no phase information is required.

The Raman heterodyne signals associated with the N-V center are all obtained with the laser in resonance with the inhomogeneously broadened \( ^3A \rightarrow ^3E \) transition at 638 nm (Fig. 1). The rf from the tracking generator is swept through the \( S_z = 0 \rightarrow |S_z| = 1 \) electron-spin transition, and this gives a response on the spectrum analyzer as shown in Fig. 2(a), where the structure is due to the hyperfine interaction associated with the single neighboring nitrogen atom. For the double-resonance measurements the rf frequency of the tracking generator and the spectrum analyzer is fixed at a frequency within the three-line pattern, and a second rf signal is applied to the coil around the sample. The signal from the spectrum analyzer is then monitored as this second rf is swept from 0 to 10 MHz; an average of 30 such scans is shown in Fig. 2(b).

This gives the Raman heterodyne detected ENDOR spectrum.

A second double-resonance measurement was possible within a narrow range of magnetic field strengths, where some of the hyperfine resonances could be detected directly by using the Raman heterodyne technique. With good crystal alignment two hyperfine resonances could be detected on the low-field side of the anticrossing situation between fields of 1000 and 1020 G and on the high-field side between 1035 and 1070 G. The resonances often gave dispersion line shapes owing to interference with a much broader background signal. However, of the two resonances, only one could be detected easily [Fig. 3(a)], but by
monitoring the amplitude of this signal as a second rf
was swept from 0 to 10 MHz all six hyperfine reson-
cances could be detected, including those not ob-
served directly [Fig. 3(b)]. This gives a Raman het-
erodyne detected double NMR spectrum.

There is a one-to-one correspondence between the
Raman heterodyne detected ENDOR and the Raman
heterodyne detected double NMR spectrum in Figs
2(b) and 3(b), respectively. The resonances arise
from hyperfine transitions both within the electron
spin $S_z = 0$ level and within the electron spin $S_z = 1$ (or
$S_z = 1$) level, three in each that account for the six
signals in total.

For magnetic fields other than those close to the
anticrossing, the hyperfine levels associated with the
$S_z = 0$ spin state are only affected by the last two terms
in Eq. (1), that is, by the quadrupole interaction plus a
small splitting of 0.67 MHz of the $I_z = 1$ levels by the
nuclear Zeeman interaction. The frequencies of the
hyperfine transitions within the $S_z = 0$ and $S_z = -1$
multiplets are

$$\nu(\Delta I_z = \pm 1) = P \pm mH_g(\pm A),$$
(2)

$$\nu(\Delta I_z = 2) = 2mH_g(+2A),$$
(3)

where the terms on the right-hand side in parentheses
represent the diagonal magnetic hyperfine term applicable
only to the $S_z = -1$ multiplet.

For magnetic fields near the level anticrossing situa-
tion, such as those in Figs. 2 and 3, the off-diagonal
Zeeman and magnetic hyperfine interactions cause
significant shifts in the levels from those given by Eqs.
(2) and (3), and determination of the quadrupole pa-
rameters requires fitting to the complete Hamiltonian
in Eq. (1). A simpler approach is to measure the
Raman heterodyne detected ENDOR signal at mag-
netic field strengths away from the level anticrossing
situation, where Eqs. (2) and (3) can be used. The
4.68- and 5.35-MHz signals associated with the $S_z = 0$
state can be followed to higher magnetic field values,
and at these field values their average gives the value
of $P$. This approach gives $P = 5.1 \pm 0.1$ MHz, which is
consistent with the full diagonalization.

Note that the group of three resonances at 0.67, 4.68,
and 5.35 MHz [Figs. 2(b) and 3(b)] associated with the
$S_z = 0$ level are stronger than the other three at 3.2, 3.6,
and 6.8 MHz associated with the $S_z = -1$ level. The
greater strength of the resonances associated with the
$S_z = 0$ state undoubtedly arises from optical pump-
ing's giving a greater population in the $S_z = 0$ level
than in the $S_z = -1$ level. Such an optical pumping effect
has already been established from optical hole-
burning measurements, in which the spectrum is
asymmetric, and from EPR measurements, in which
there are emissive as well as absorptive signals. The
direction of the optical pumping, however, was not
known, whereas the present data indicate that the
optical pumping is into the $S_z = 0$ level rather than
into the $S_z = -1$ level. By taking this information
with the observed absorptive and emissive 9.4-GHz
ENDOR signals at low and high fields, respectively, it
can be concluded that the $S_z = \pm 1$ levels lie above the $S_z = 0$
levels at zero field. That is, the crystal field splitting
$D$ is positive.

In summary, novel double-resonance techniques
have been used to study the hyperfine resonance in a
color center in diamond. One of the techniques is
alogous to ENDOR, which is commonly used as an
extension of conventional EPR studies. Signals have
been obtained with this technique over the entire
range of magnetic field strengths for which the EPR
signal can be detected with the Raman heterodyne
scheme (currently limited by the system response to
<1 GHz). A second double-resonance measurement
with two low-frequency rf sources has given the same
spectral features as the Raman heterodyne detected
ENDOR technique but only over a restricted range of
magnetic field strengths. Its value, however, lies in
the fact that the lines are exceedingly narrow and
permit a more accurate determination of their fre-
quencies than can be obtained from the Raman het-
erodyne detected ENDOR measurements. This has
permitted a precise determination of the strength of
the electric quadrupole and magnetic hyperfine inter-
actions at the N-V site in diamond. Also, optical
pumping effects have led to the conclusion that the
trigonal crystal field splitting is positive.

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