

Temperature dependent energy level shifts of nitrogen-vacancy centers in diamond

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(Received 30 July 2011; accepted 28 September 2011; published online 18 October 2011)

Magnetic resonance and fluorescence spectra of nitrogen-vacancy (NV) color centers ensemble in high purity diamond sample were measured, with temperature ranging from 5.6 K to 295 K. Both microwave and optical transition energies have similar nonlinear temperature dependent changes, which might mainly originate from the local thermal expansion. As the frequency shifts will reduce the fidelity of resonant quantum control, the present results demonstrate the necessity of taking temperature fluctuation into consideration. For temperature below 100 K, the transition energies show tendencies to be constant, which indicate higher stability and performance in applications with NV centers. © 2011 American Institute of Physics. [doi:10.1063/1.3652910]

The negatively charged nitrogen-vacancy (NV^-) centers in diamond are excellent candidates for qubits of solid quantum computation¹⁻³ and nanoscale detectors of magnetic^{4,5} and electric⁶ fields. The center consists of a substitutional nitrogen atom and an adjacent vacancy with C_{3v} symmetry. The spin coherent manipulation can be realized at room temperature due to its long spin coherence time.^{7,8} However, for high fidelity quantum control and ultra sensitive detection, the system's interaction with environment should be considered. Therefore, it is crucial to detect the temperature dependent properties of the defect.⁹⁻¹¹ In detail, Acosta *et al.*,^{11,12} summarized the NV^- ensemble magnetic resonance spectroscopy in broad range of temperature. It shows the nonlinear relationships between zero field splitting (ZFS) parameters and temperature.

In this paper, we study both the magnetic resonance and fluorescence emission spectra with temperature down to 5.6 K. These resonant transition frequencies represent different energy gaps of NV center, but have similar nonlinear temperature dependent shifts, which are mainly induced by the local thermal expansion. The results would help to optimize the design of high quality application based on diamond and understand the intrinsic properties of NV center.

The NV centers usually appear in either of two forms, the neutral (NV^0) and negative (NV^-) charge state, which have zero phonon lines (ZPL) at 575 nm and 637 nm, respectively. The ground state of NV^- is spin triplet with $S=1$. The sublevels $m_s=0$ and $m_s=\pm 1$ are split by $D \approx 2.87$ GHz without external field. The electron spin of NV^- can be optically initialized and detected through the inter-system crossing (ISC),¹³ which is widely used in spin dynamics research.

Our experiments were carried out in a Janis 4 K Closed Cycle Refrigerator with a two-stage cold head. Using a closed loop temperature controller, the temperature fluctuation can be kept within 0.01 K. The samples used in the experiments were single crystal chemical vapor deposition diamond plates from Element-Six Company. The diamond plates were placed on the copper cold head and excited by

532 nm laser. Microwave was applied via a 15 μm diameter copper wire close to the laser focus spot.

In the applications of NV^- electron spin, one of the most concerned is the transition between sublevels of the ground state, which can be well studied by the optically detected magnetic resonance (ODMR) method.¹⁴ A continuous laser (532 nm) is used to polarize NV^- center into $|m_s=0\rangle$ state. When the applied microwave is resonant with the split between ground state sublevels, the color center will be pumped into $|m_s=\pm 1\rangle$. Consequently, it leads to the decrease of fluorescence intensity. The measured room temperature ODMR spectrum of NV^- ensemble in diamond with nitrogen concentration $[N] < 1$ ppm is shown in Fig. 1(a). The spectrum was obtained by averaging several frequency scans at the same temperature. Three resonant frequencies, labeled as f_1 , f_2 , and f_3 , are 2.8687, 2.8710, and 2.8731 GHz, respectively. The emergence of multi-peak with zero external field is due to local strain.¹⁴ For simplicity, the average of f_1 and f_3 is used to present D , and the split between peaks is denoted by $Q=f_3-f_1$.

A series of ODMR spectra for the same sample at temperatures ranging from 5.6 K to 295 K are shown in Fig. 1(b). The ZFS parameter D nonlinearly depends on temperature and is getting larger with temperature decreasing. The change is $\Delta D \approx 7$ MHz between 5.6 K and 295 K. To offer reference data for frequency compensation, $D(T)$ of this diamond sample is fitted with the fifth-order polynomial

$$D(T) = \sum_{n=0}^5 d_n T^n, \quad (1)$$

with coefficients $d_0 = 2.87771$ GHz, $d_1 = -4.625 \times 10^{-6}$ GHz/K, $d_2 = 1.067 \times 10^{-7}$ GHz/K², $d_3 = -9.325 \times 10^{-10}$ GHz/K³, $d_4 = 1.739 \times 10^{-12}$ GHz/K⁴, and $d_5 = -1.838 \times 10^{-15}$ GHz/K⁵. The other parameter Q does not show any obvious change, which might be limited by the accuracy of our measurements.

Optical resonant excitation is also an important method to manipulate the spin states of NV centers.^{15,16} To detect this optical transition energy between excited state and

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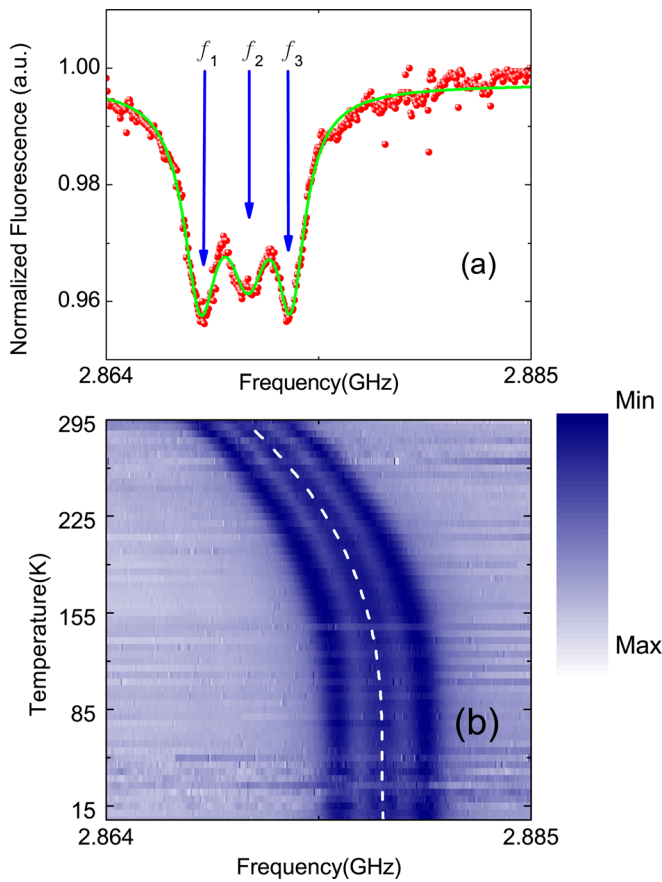


FIG. 1. (Color online) (a) ODMR spectrum of NV^- ensemble at 295 K. The three peaks are indicated by arrows, and the green solid line represents the fit of Lorentz function. (b) Contour plot of a series of ODMR spectra with different temperatures. The white dashed line is a fifth-order polynomial fit of D with Eq. (1).

ground state, the fluorescence emission spectra at different temperatures were measured. ZPL with phonon sidebands of both charge states are shown in Fig. 2. All the peaks of NV center become sharper at lower temperature.¹⁰ Besides the

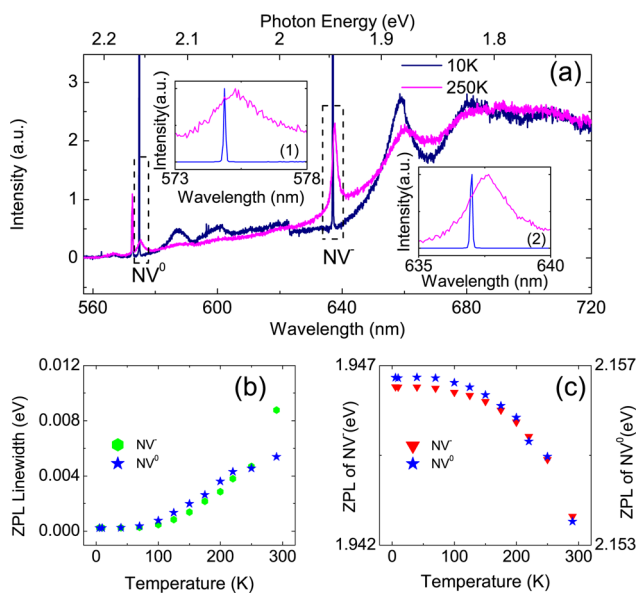


FIG. 2. (Color online) (a) Fluorescence spectra at 250 K (red line) and 10 K (blue line). The insets (1) and (2) show the normalized ZPL details of NV^0 and NV^- , respectively. The changes of linewidth (b) and photon energy (c) are obtained in the spectra.

smaller width, blue shifts are also observed with decreasing temperature, which are highlighted in the insets of Fig. 2(a). The details are plotted in Figs. 2(b) and 2(c). It shows that the two charge states have similar temperature dependences.

Like D , ZPL energies depend nonlinearly on temperature and tend to be stable at low temperature. To compare the different energy shifts of the same charge state, we put D and the ZPL energy of NV^- together in Fig. 3(a). The shapes of two lines match very well, and the rates of shift are also at the same order. The results indicate that the temperature dependent shifts are universal for different charge states and different energy gaps. All the shifts should have the same origin, which is the intrinsic property of this defect.

In solid materials, one of the most important and common temperature dependent phenomena is thermal expansion. To examine the relations between energy shifts and thermal expansion, we plot D and ZPL photon energies as functions of bulk diamond lattice parameter a (given in Ref. 17) in Fig. 3(b). All the resonant energies near linearly depend on lattice parameter; this is easy to understand if we take thermal expansion as the main factor of energy shifts.

However, the bulk thermal expansion is not a perfect explanation. In the experiments, we also measured another diamond sample with $[N] \approx 200$ ppm (results are not shown). This N -rich diamond has a lattice parameter different from the pure sample used before,¹⁸ the difference is about 28 ppm at low temperature (several Kelvin). But in experiments, we did not find any significant difference between these two samples.

Also, the bulk thermal expansion predicts smaller shifts of energy than those in experiments, it is also mentioned in Ref. 12. For example, D is believed to be mainly determined by spin-spin interaction between two unpaired electrons.^{19,20} We can simply write it as $D \propto \langle 1/r^3 \rangle$, where r is the dipole interaction distance. For two well localized spins, shift of D

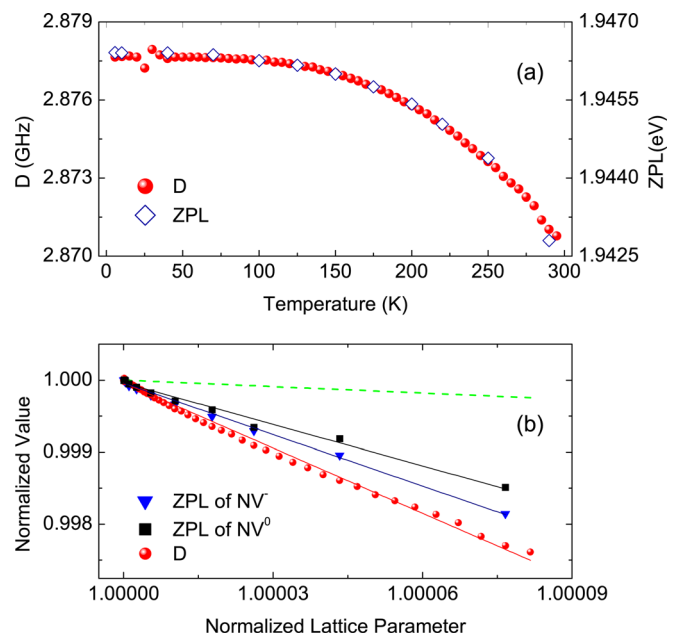


FIG. 3. (Color online) (a) D and ZPL of NV^- versus temperature. (b) The resonant transition energies are plotted as functions of lattice parameter with linear fits. All the parameters are normalized by their own values at 5.6 K.

should be about three times of thermal expansion (the green dashed line in Fig. 3(b)). But the linear fit gives $\Delta D/D = -30.2(3)\Delta a/a$. The shifts of ZPL are also much larger than bulk thermal expansion, $(\Delta ZPL/ZPL)|_{NV^-} = -23.8(5)\Delta a/a$, $(\Delta ZPL/ZPL)|_{NV^0} = -19.2(7)\Delta a/a$.

Therefore, it should be the local expansion, rather than bulk's, that causes the energy shifts. For quantitative study, the defect's various atom bonds should be considered. Since the bonds' lengths are quite different,²¹ the interaction distance r is not directly proportional to a . Somehow, r changes faster than a . As measured, a mainly denotes C-C bond length, bulk thermal expansion cannot explain all the change of local structure. The different slope coefficients in Fig. 3(b) reflect the different relations between energies and r . The precise solution is beyond our ability, and more experimental and theoretical studies are needed.

The energy shifts with temperature are so remarkable that they provide an approach to adjust the resonant frequencies. But on the other hand, the shifts will reduce the stability of system based on NV centers, and could affect the fidelity of quantum manipulation and ultra-sensitive nanoscale detector. For NV^- centers in a mm-scale diamond plate, the D fluctuation around room temperature (290 K) is about $dD/dT = -84(4)$ kHz/K, which would cover 8000 V/cm electric field Stark shift of ground state ODMR.⁶ Therefore, it is important to keep the environment stable. Also, to reduce the fluctuation induced by temperature, the experiments could be operated at low temperature.

In summary, we have measured the temperature dependent spectra of magnetic resonance and fluorescence of NV color centers in diamond. Both the optical and microwave resonant frequencies show similar temperature dependent shifts. They are nonlinear with temperature and tend to be stable with decreasing temperature. The shifts are several times larger than those are predicted by bulk thermal expansion. Local atomic structure should be taken into consideration for the shifts. As the fluctuations of resonant frequencies will have a negative impact on the stability, these experimental results point out the advantage of low temperature study and could help to improve the performance of NV centers in applications of quantum computation and ultra-sensitive detector.

This work was supported by the National Fundamental Research Program of China under Grant No. 2011CB921200, the Knowledge Innovation Project of Chinese Academy of Sciences (60921091), National Natural Science Foundation of China under Grant No. 11004184, and Fundamental Research Funds for the Central Universities.

- ¹F. Jelezko, T. Gaebel, I. Popa, A. Gruber, and J. Wrachtrup, *Phys. Rev. Lett.* **92**, 076401 (2004).
- ²E. Togan, Y. Chu, A. Trifonov, L. Jiang, J. Maze, L. Childress, M. Dutt, A. Sørensen, P. Hemmer, A. Zibrov, and M. D. Lukin, *Nature* **466**, 730 (2010).
- ³B. Buckley, G. Fuchs, L. Bassett, and D. D. Awschalom, *Science* **330**, 1212 (2010).
- ⁴G. Balasubramanian, I. Y. Chan, R. Kolesov, M. Al-Hmoud, J. Tisler, C. Shin, C. Kim, A. Wojcik, P. R. Hemmer, A. Krueger, T. Hanke, A. Leitenstorfer, R. Bratschitsch, F. Jelezko, and J. Wrachtrup, *Nature* **455**, 648 (2008).
- ⁵J. M. Taylor, P. Cappellaro, L. Childress, L. Jiang, D. Budker, P. R. Hemmer, A. Yacoby, R. Walsworth, and M. D. Lukin, *Nature Phys.* **4**, 810 (2008).
- ⁶F. Dolde, H. Fedder, M. W. Doherty, T. Nöbauer, F. Rempp, G. Balasubramanian, T. Wolf, F. Reinhard, L. C. L. Hollenberg, F. Jelezko, and J. Wrachtrup, *Nature Phys.* **7**, 459 (2011).
- ⁷P. Neumann, J. Beck, M. Steiner, F. Rempp, H. Fedder, P. R. Hemmer, J. Wrachtrup, and F. Jelezko, *Science* **329**, 542 (2010).
- ⁸G. D. Fuchs, V. V. Dobrovitski, D. M. Toyli, F. J. Heremans, and D. D. Awschalom, *Science* **326**, 1520 (2009).
- ⁹L.-S. Bouchard, V. M. Acosta, E. Bauch, and D. Budker, *New J. Phys.* **13**, 025017 (2011).
- ¹⁰K.-M. C. Fu, C. Santori, P. E. Barclay, L. J. Rogers, N. B. Manson, and R. G. Beausoleil, *Phys. Rev. Lett.* **103**, 256404 (2009).
- ¹¹V. M. Acosta, E. Bauch, M. P. Ledbetter, A. Waxman, L. S. Bouchard, and D. Budker, *Phys. Rev. Lett.* **104**, 070801 (2010).
- ¹²V. M. Acosta, A. Jarmola, L. J. Zipp, M. P. Ledbetter, and E. Bauch, *Proc. SPIE* **7948**, 79480W (2011).
- ¹³N. B. Manson, J. P. Harrison, and M. J. Sellars, *Phys. Rev. B* **74**, 104303 (2006).
- ¹⁴A. Gruber, A. Dräbenstedt, C. Tietz, L. Fleury, J. Wrachtrup, and B. C. von, *Science* **276**, 2012 (1997).
- ¹⁵L. Robledo, H. Bernien, I. van Weperen, and R. Hanson, *Phys. Rev. Lett.* **105**, 177403 (2010).
- ¹⁶C. Santori, P. Tamarat, P. Neumann, J. Wrachtrup, D. Fattal, R. G. Beausoleil, J. Rabeau, P. Olivero, A. D. Greentree, S. Praver, F. Jelezko, and P. Hemmer, *Phys. Rev. Lett.* **97**, 247401 (2006).
- ¹⁷S. Stoupin and Y. V. Shvyd'ko, *Phys. Rev. Lett.* **104**, 085901 (2010).
- ¹⁸T. Sato, K. Ohashi, T. Sudoh, K. Haruna, and H. Maeta, *Phys. Rev. B* **65**, 092102 (2002).
- ¹⁹X.-F. He, N. B. Manson, and P. T. H. Fisk, *Phys. Rev. B* **47**, 8816 (1993).
- ²⁰A. Lenef and S. C. Rand, *Phys. Rev. B* **53**, 13441 (1996).
- ²¹A. Gali, M. Fyta, and E. Kaxiras, *Phys. Rev. B* **77**, 155206 (2008).