Optically detected magnetic resonance in negatively charged nitrogen-vacancy centers in diamond under resonant optical excitation at cryogenic temperatures

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We study optically detected magnetic resonance (ODMR) in diamond NV^- centers at cryogenic temperatures. We find that when we use resonant optical excitation at zero phonon line wavelength, turning on microwave radiation leads to an increase in fluorescence. This is different from the conventional case of nonresonant optical pumping where microwave radiation instead leads to a decrease in fluorescence. In addition, we observe a significant increase in contrast compared to the nonresonant ODMR. To explain this effect, we propose a theoretical model based on the interaction of the resonant optical radiation with different groups from the inhomogeneously broadened ensemble of NV^- centers. We find that the effect is temperature dependant and can only be observed at temperatures below 35 K.

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I. INTRODUCTION

Nitrogen-vacancy (NV) center in diamond is a defect in the crystal lattice characterized by its distinct fluorescence profile. It can exist in two different charge states: neutral NV^0 centers and negatively charged NV^- centers. NV^- centers have several key features that make them attractive for various applications [1]. They demonstrate bright and stable fluorescence and have good coherence times even at room temperature. As a result, NV centers are promising candidates for quantum information processing [2–5], quantum metrology, and magnetic sensing [6,7]. NV-based magnetic sensing is particularly interesting because it has several advantages compared to other methods like transmission electron microscopy (TEM) or magnetic-resonance force microscopy (MRFM) [8]. Though TEM has good spatial and temporal resolution, it is limited to small external fields and the measurement itself is destructive to the sample, which prohibits long study times. MRFM disturbs the magnetism of the sample and requires cryogenic cooling to achieve good signal-to-noise ratios. In comparison, NV-based magnetometry has potential for nonperturbative and nondestructive sensing with good resolution in a wide range of external magnetic fields.

These applications are made possible by the unique level structure of the NV center. The ground state triplet $^3A_2$ is split via hyperfine interaction into $m_s = 0$ and $m_s = \pm 1$ levels, separated by around 2.87 GHz at zero external magnetic field. Similarly, the excited state is also split, but the structure is more complicated and heavily depends on temperature of the sample and the existence of induced or natural strain in the crystal [1]. The direct transitions between these levels correspond to the 637-nm zero phonon line of the NV^- center, while the transitions to the vibrational levels of the ground state form a broad fluorescence band extending into lower energies. In addition, it was found that the brightness of the observed fluorescence depends on the spin projection of the NV^- center state with the $m_s = 0$ projection being noticeably brighter. This behavior can be explained by different decay pathways for the two projections. While the excited $m_s = 0$ level mostly decays directly into the $m_s = 0$ level of the ground state, the $m_s = \pm 1$ levels have an additional relaxation path involving $^1A_1$ and E_1 intermediate states that is accompanied by fluorescence in the infrared 1042-nm region. The existence of the competing decay path makes the fluorescence of the $m_s = \pm 1$ excited level dimmer. The difference in fluorescence can be used to read out the state of the NV center optically. Furthermore, unlike the optical decay, this second decay pathway leads the population of the excited $m_s = \pm 1$ level into the $m_s = 0$ level of the ground state instead of the $m_s = \pm 1$ level. As a result, constant optical radiation polarizes the NV^- center, leaving its population in the $m_s = 0$ state. The extent of polarization is mostly limited by existence of weak diagonal optical transitions.

Different behavior of the two spin projections leads to another important feature of the NV center fluorescence: It becomes sensitive to microwave radiation in the 2.87-GHz range. When the microwave radiation is resonant with the ground state $m_s = 0$ to $m_s = \pm 1$ transition, it affects the population distribution, increasing the population of the dimmer $m_s = \pm 1$ levels, which, in turn, leads to a decrease in fluorescence. This technique is known as optically detected magnetic resonance (ODMR). ODMR allows one to find the exact values of the ground-state splitting (it is worth noting that similar approach is well known and commonly used for studying rare-earth-ion-doped crystals [9,10]). As the levels with nonzero spin projections are shifted by external magnetic field, the ODMR approach is essential for NV-based magnetic sensing.

The process described above implies simultaneous involvement of all optical transitions for every NV center, which is usually achieved by using off-resonant excitation with wavelengths lower than the zero phonon line wavelength. However, we find that the behavior changes drastically when

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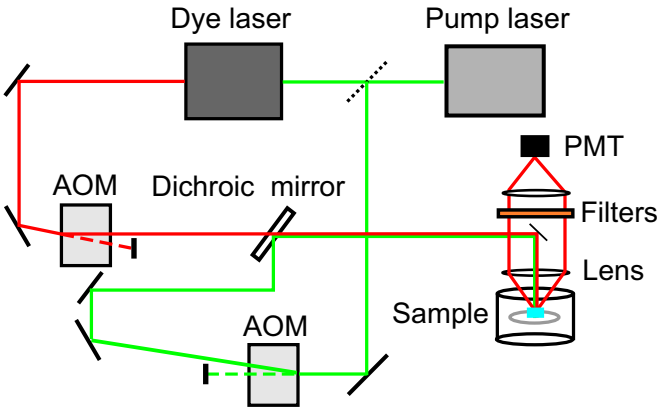

FIG. 1. Experimental setup.

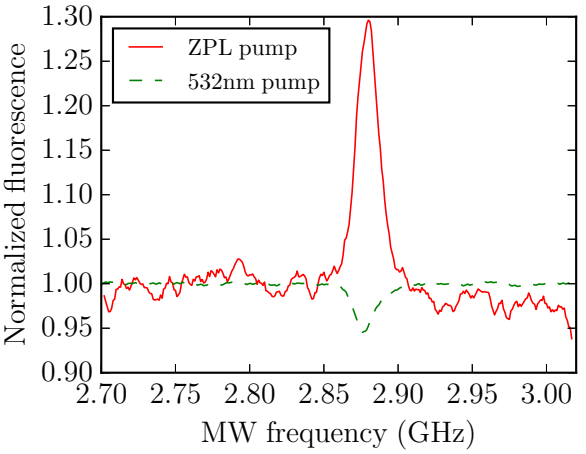

FIG. 2. ODMR spectra obtained at 2 K using resonant (solid red line) and off-resonant (dashed green line) optical excitations respectively.

this condition is not satisfied. In this paper we present ODMR spectra obtained at cryogenic temperatures with resonant optical excitation tuned to the zero phonon line wavelength. Under these conditions, resonant microwave radiation leads to a sharp increase in fluorescence instead of the dip commonly observed with off-resonant optical excitation. We investigate the temperature dependence of this effect and propose a simple model describing it. The effect is interesting because of the noticeable increase in contrast compared to the conventional ODMR which can be used to improve the sensitivity of NV-based magnetometry.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Our experimental setup is shown in Fig. 1. An off-resonant 532-nm green laser is used to observe the NV center fluorescence spectrum while the tunable dye laser set to 637 nm is used to address the NV^- center optical transitions directly. We use a set of acousto-optical modulators to create the desired sequences of optical pulses. Our monocrystalline diamond (a 200-μm-thick CVD diamond layer grown on an HPHT substrate) together with a microwave antenna is put into a liquid helium cryostat where it can be cooled to temperatures as low as 2 K. Excitation and collection of fluorescence photons is done confocally using a lens mounted in front of the cryostat window. The collected photons are then detected using a photomultiplier tube. We use long-pass filters with threshold around 650 nm to get rid of leftover laser radiation.

First, we use the green laser to confirm that there are NV^- centers present in the sample by measuring the fluorescence spectrum. When the microwave radiation is turned on and scanned around 2.87 GHz, we observe a dip in the intensity of NV^- center fluorescence that corresponds to magnetic resonance; this is typical ODMR. After that, we switch to the dye laser that is tuned to the zero phonon line wavelength and repeat our ODMR measurements. We find that when the sample is cooled to liquid helium temperature, the ODMR spectrum changes drastically. The results are shown in Fig. 2. Instead of a decrease in fluorescence, there is a sharp increase. More importantly, the contrast of the resonant ODMR is significantly higher than what was previously observed with the green laser.

In order to explain the effect, we propose a simple model. Unlike the room-temperature case where the excited-state structure is similar to that of the ground state, at low temperatures the excited state triplet is split by spin-orbit and spin-spin interaction into a complicated structure of levels [1,11]. In addition, this structure heavily depends on the value of local strain. As the linewidths of the NV^- center optical transitions are small at cryogenic temperatures compared to differences in the transition frequencies, the red optical excitation becomes transition selective. As a result, the red laser will only interact with several groups of NV^- centers from the inhomogeneously broadened ensemble. For each such group, the transition resonant with the optical excitation will be different. While the ratio between spin-conserving and spin-changing transitions depends on the strain value and the excited state level involved in the transition [12], both types of transitions are allowed (see, e.g., Ref. [13]). In this case, every group will become polarized by the resonant optical excitation and the population will be driven to the nonfluorescing levels of the ground state (see Fig. 3). As a result, the level of fluorescence induced by the red laser should decay to a small value determined by the extent of the ground-state polarization, which is mostly limited by the

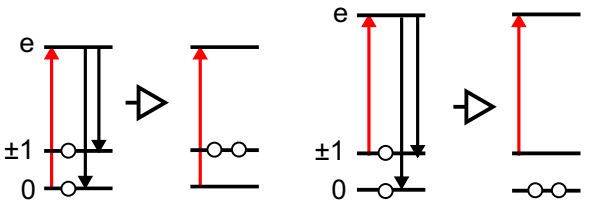

FIG. 3. The model describing polarization of different NV^- center groups selected from the inhomogeneously broadened ensemble by the single frequency red laser. The excited level e is not specified as it will be different for different groups. As long as both spin-conserving and spin-changing transitions are allowed, the population will be transferred into the nonfluorescing states for each such group.

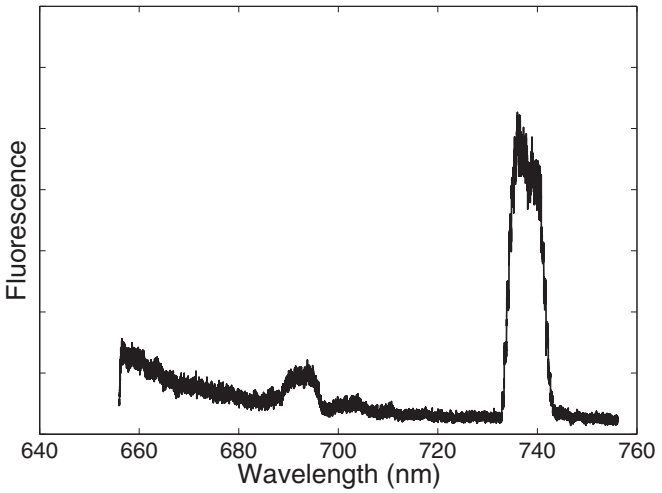

FIG. 4. The fluorescence spectrum observed by illuminating the sample with the red laser.

relaxation time of the ground state. When the microwave radiation is turned on, part of the population will be transferred back into the original levels, giving rise to fluorescence. Since the longitudinal relaxation times can reach seconds in diamond samples [14], it is reasonable to expect almost total polarization of each group and, consequently, very high values of contrast. However, while we do observe an increase in fluorescence at the microwave resonance instead of a dip, the highest contrast we see in the original sample is only around 23%.

One of the possible explanations for the imperfect contrast in our measurements involves background fluorescence in the 650+ nm range. To test this, we measure the spectrum of the fluorescence induced by the red laser and find two notable features in the 650+ nm region: a small peak around 690 nm and another bright feature around 738 nm (see Fig. 4). The first peak most likely corresponds to raman scattering and is shifted by around 1332 cm^{-1} from the red laser, which is typical for the diamond lattice. The second peak is given by another defect present in our sample, the silicon-vacancy center. While the contribution of the first peak seems to be negligible, the second one is rather significant and may add to background fluorescence, reducing the contrast of the ODMR spectra. This suggests that using additional shortpass filters may improve the contrast.

In order for the model to work, it is required that the spin-changing optical transitions are allowed. To find out whether it is true, we perform additional pulse measurements with the resonant red laser. We initialize the system using a pulse of nonresonant green laser and then send in the red pulse, obtaining the fluorescence decay profile (see Fig. 5, top). We find that this decay is characterized by two separate time scales: the shorter one around 5 μs and the longer one around 100 μs. We believe that the first timescale corresponds to the decay caused by weak spin-changing optical transitions that transfer population to nonfluorescing states and the longer time scale corresponds to a different process where NV^- centers are converted into NV^0 centers or other dark states by the red pulse [15]. To confirm this, we perform another measurement where the sample is illuminated continuously by the red laser and

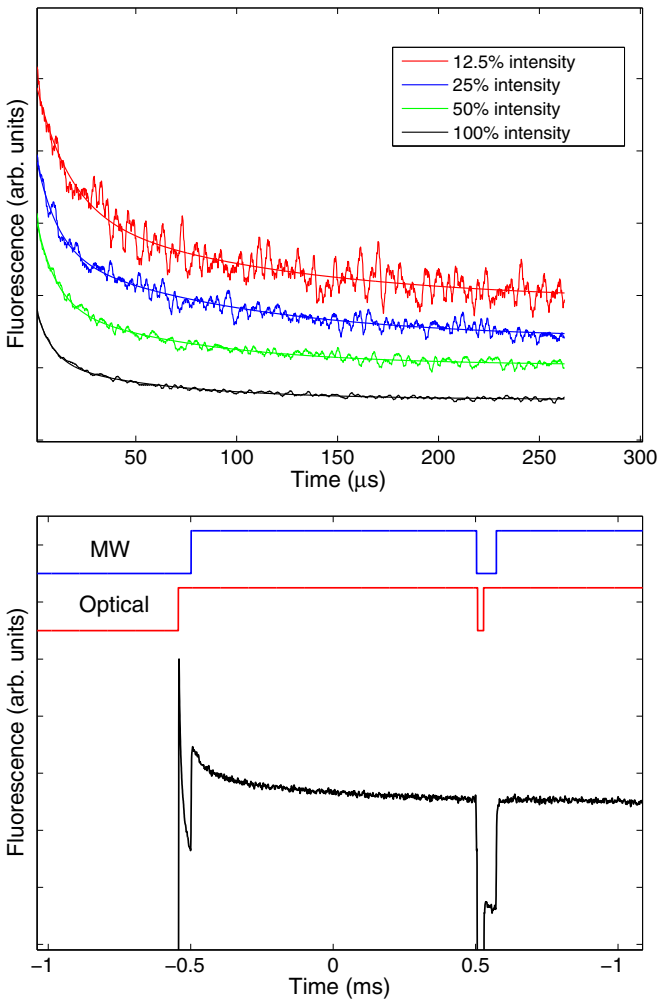

FIG. 5. Temporal profiles of the fluorescence decay induced by the resonant optical excitation for different intensities (top to bottom: 12.5%, 25%, 50%, and 100% intensity respectively) (top). Fluorescence profile observed under pulses of resonant red and microwave radiation; the pulse sequence is shown above (bottom).

a short pulse of microwave radiation is sent into the sample, causing a change in fluorescence. When the microwave pulse ends, we again observe a decay in fluorescence. However, this decay is characterized by a single shorter timescale while the longer time scale is gone, which confirms our assumption about the nature of the two time scales. It is worth noting that while in some works it was found that the NV^- centers were completely transferred into NV^0 centers or nonfluorescing dark states [16]; in our case this process is either sufficiently slow not to hinder our measurements or limited by some properties of the sample (see, e.g., Ref. [17]). Even after long pulses of strong resonant radiation a large portion of our NV^- center ensemble remains in the NV^- state. This is confirmed by measurements presented in Fig. 5 (bottom), where the microwave field is turned on and off during a long red laser pulse. The increase in fluorescence induced by the second microwave pulse is comparable to the decrease observed after the long fluorescence decay, which shows that the fraction of NV^- centers transferred to nonfluorescing states is unlikely to be larger than 50%.

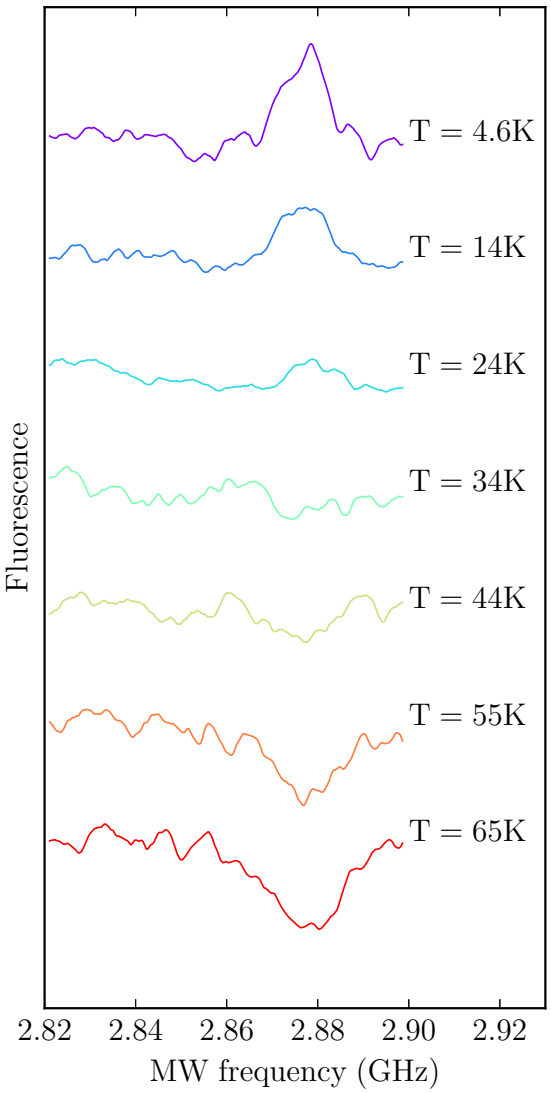

FIG. 6. ODMR spectra measurements performed at different temperatures of the sample.

As the model relies on optical transitions being narrow enough not to overlap, the observed effect is temperature dependent. We perform a series of ODMR measurements at different sample temperatures and find that the increase in fluorescence disappears around 35 K (see Fig. 6). At higher temperatures we observe a dip in fluorescence similar to what is obtained using nonresonant optical excitation. This is consistent with the available data on the widths of the NV^- center optical transitions [18]: 35 K corresponds to GHz linewidths which is comparable to typical splittings between energy levels. When the temperature is raised further and the transitions begin to overlap, the model is no longer valid and the red laser acts in the same way as was described for the nonresonant optical excitation in the introduction.

To confirm that this behavior is not unique to our particular sample, the measurements are successfully repeated using other samples. These samples were created in the Lebedev Physical Institute using Element Six synthetic diamonds as base. Those diamonds were irradiated with an electron

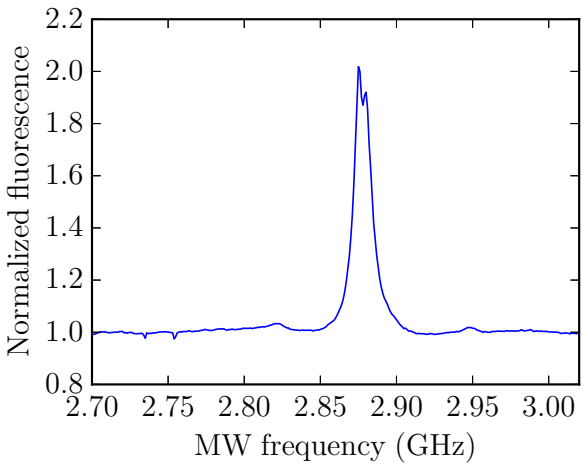

FIG. 7. ODMR spectrum measured in a different sample using resonant optical excitation at 2 K.

beam and subsequently annealed at 800 °C, which resulted in high NV-center concentrations. More importantly for our measurements, these samples are free of silicon vacancies. As a result, the contrast of ODMR spectra is higher than the contrast observed in the original sample, reaching 50% for the best samples (see Fig. 7). For these samples the contrast may be limited by shorter longitudinal relaxation times due to higher defect concentrations.

III. CONCLUSION

To sum up, in this paper we present an effect in diamond NV^- centers. We find that the well-known ODMR spectra become inverted when we use resonant optical pumping at liquid helium temperature. In addition, the contrast of ODMR is significantly increased under these conditions, making resonant approach interesting for potential magnetometric applications. The highest values of contrast observed in our experiments are around 50%, which is comparable to the best results obtained in silicon carbide defects [19]. We investigate the temperature dependence of the effect and find that in practical applications the sample would have to be kept at temperatures lower than 35 K for the effect to be used. However, this is not too demanding a task for modern closed-circuit cryogenic systems. Moreover, there is evidence to suggest that working with NV^- centers at cryogenic temperatures can be beneficial for practical applications because of increased stability [20].

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[1] M. W. Doherty, N. B. Manson, P. Delaneyc, F. Jelezko, J. Wrachtrup, and L. C. L. Hollenberg, Phys. Rep. **528**, 1 (2013).
[2] K. Heshami, C. Santori, B. Khanaliloo, C. Healey, V. M. Acosta, P. E. Barclay, and C. Simon, Phys. Rev. A **89**, 040301 (2014).
[3] E. Poem, C. Weinzetl, J. Klatzow, K. T. Kaczmarek, J. H. D. Munns, T. F. M. Champion, D. J. Saunders, J. Nunn, and I. A. Walmsley, Phys. Rev. B **91**, 205108 (2015).
[4] E. Togan, Y. Chu, A. S. Trifonov, L. Jiang, J. Maze, L. Childress, M. V. G. Dutt, A. S. Sorensen, P. R. Hemmer, A. S. Zibrov, and M. D. Lukin, Nature (London) **466**, 730 (2010).
[5] E. Togan, Y. Chu, A. Imamoglu, and M. D. Lukin, Nature (London) **478**, 497 (2011).
[6] H. Clevenson, M. E. Trusheim, C. Teale, T. Schroder, D. Braje, and D. Englund, Nat. Phys. **11**, 393 (2015).
[7] K. Jensen, N. Leefer, A. Jarmola, Y. Dumeige, V. M. Acosta, P. Kehayias, B. Patton, and D. Budker, Phys. Rev. Lett. **112**, 160802 (2014).
[8] A. Waxman, Y. Schlussel, D. Groswasser, V. M. Acosta, L.-S. Bouchard, D. Budker, and R. Folman, Phys. Rev. B **89**, 054509 (2014).
[9] L. E. Erickson, Phys. Rev. B **16**, 4731 (1977).
[10] P. Goldner, A. Ferrier, and O. Guillot-Noel, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by J.-C. G. Bunzli and V. K. Pecharsky (Elsevier, Amsterdam, 2015), pp. 1–78.
[11] J. R. Maze, A. Gali, E. Togan, Y. Chu, A. Trifonov, E. Kaxiras, and M. D. Lukin, New J. Phys. **13**, 025025 (2011).
[12] Ph. Tamarat, N. B. Manson, J. P. Harrison, R. L. McMurtrie, A. Nizovtsev, C. Santori, R. G. Beausoleil, P. Neumann, T. Gaebel, F. Jelezko, P. Hemmer, and J. Wrachtrup, New J. Phys. **10**, 045004 (2008).
[13] Y. Chu, M. Markham, D. J. Twitchen, and M. D. Lukin, Phys. Rev. A **91**, 021801 (2015).
[14] A. Jarmola, V. M. Acosta, K. Jensen, S. Chemerisov, and D. Budker, Phys. Rev. Lett. **108**, 197601 (2012).
[15] T. Gaebel, M. Domnan, C. Wittmann, I. Popa, F. Jelezko, J. Rabeau, A. Greentree, S. Prawer, E. Trajkov, P. R. Hemmer, and J. Wrachtrup, Appl. Phys. B **82**, 243 (2006).
[16] G. Waldherr, J. Beck, M. Steiner, P. Neumann, A. Gali, T. Frauenheim, F. Jelezko, and J. Wrachtrup, Phys. Rev. Lett. **106**, 157601 (2011).
[17] N. B. Manson, and J. P. Harrison, Diamond Relat. Mater. **14**, 1705 (2005).
[18] K.-M. C. Fu, C. Santori, P. E. Barclay, L. J. Rogers, N. B. Manson, and R. G. Beausoleil, Phys. Rev. Lett. **103**, 256404 (2009).
[19] P. G. Baranov, V. A. Soltamov, A. A. Soltamova, G. V. Astakhov, and V. G. Dyakonov, Mat. Sci. Forum **740–742**, 425 (2013).
[20] X.-D. Chen, C.-H. Dong, and F.-W. Sun, Appl. Phys. Lett. **99**, 161903 (2011).