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Temperature dependent energy gap shifts of single color center in diamond based on modified Varshni equation

Cong-Cong Li, Ming Gong, Xiang-Dong Chen*, Shen Li, Bo-Wen Zhao, Yang Dong, Guang-Can Guo, Fang-Wen Sun

Key Lab of Quantum Information, Chinese Academy of Sciences, School of Physics, University of Science and Technology of China, Hefei 230026, PR China
Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026, PR China

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A B S T R A C T

Although the diamond has the similar structure (diamond cubic) and symmetry (O_h) as many other conventional semiconductor materials, the extraordinary large Debye temperature and small lattice expansion coefficient make the temperature dependence of energy gaps in diamond to be totally different from those in other semiconductors. Here we propose a modified Varshni formula to describe the temperature dependent zero field splitting and zero phonon line of the nitrogen vacancy center in diamond. The shift of energy gaps shows a T^4 scaling at low temperature and a T^2 scaling at high temperature. The crossover between these two regimes is determined by two positive parameters in the modified formula. This empirical formula can give an excellent prediction of the temperature dependent energy gaps up to 700 K. We experimentally verify this temperature dependent behavior with single negatively charged nitrogen vacancy centers in diamond. These observations demonstrate the leading role of electron-acoustic phonon interaction in the temperature dependent shift of energy gaps in diamond. This empirical equation can benefit the diamond-based applications such as quantum sensing and computing.

1. Introduction

The negatively charged nitrogen vacancy (NV^-) center in diamond with stable photon emission and long spin coherence time has been widely studied in quantum information science [1–4]. The robustness of this defect as well as the susceptibility to external environment, such as electromagnetic field, temperature and pressure [5–10], make it to be an ideal candidate for quantum sensor. According to the recently achieved progress in super-resolution microscopies [11–15], this quantum sensor is capable of detecting physical fields with both high sensitivity and high spatial resolution, which is essential for material and biological studies[16,17]. Among these applications, the nanoscale temperature sensing is one of its most outstanding advantages. To this end, various temperature sensors using NV color centers [18–24] have been proposed and experimentally demonstrated based on the temperature dependent electronic energy level shift [8,9,25-27].

The ground state of NV^- center is a spin triplet with $S = 1$, where the $m_s = 0$ state and the $m_s = \pm 1$ degenerate states are split by a zero-field splitting (ZFS), $D \approx 2.87$ GHz, in the absence of external magnetic field [4,8,26]. This splitting is arose from the electronic spin-spin interactions in the carbon atoms adjacent to the vacancy [28]. The value of D can be measured using the optically detected magnetic resonance (ODMR) method [29–32]. In experiments, D shows significant nonlinear temperature dependence [8,9,33], which is the foundation of NV-based thermometry. In the conventional semiconductor materials, it is generally accepted that the temperature dependent energy gap shift is due to the electron-(acoustic and optical) phonon interaction effect and thermal expansion effect. This is a very complicated process, although in experiments the energy gap shift usually exhibits some simple monotonic behavior as a function of temperature T. For the study of NV color centers in previous literatures, a fifth-order polynomial function has been proposed [9,27] to fit the experimental data of $D(T)$ for temperature lower than 300 K. While at high temperature ranging from 300 to 700 K, the data can be well described by a third-order polynomial function [26]. However, heretofore, an empirical formula which could cover the whole temperature range is still lacked and the underlying origin of this shift of energy gaps is still controversial.

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* Corresponding author at: Key Lab of Quantum Information, Chinese Academy of Sciences, School of Physics, University of Science and Technology of China, Hefei 230026, PR China.
E-mail address: xdch@ustc.edu.cn (X.-D. Chen).

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2. Modified Varshni equation

In experiments the much referenced Varshni empirical equation [34],

$$E(T) = E_0 - \frac{\alpha T^2}{T+\beta}, \tag{1}$$

has been used to describe the temperature dependent energy gaps in various conventional semiconductors. The parameters α and β are positive to ensure the monotonicity of energy gap as a function of temperature. The value of β is generally believed to be related and comparable to the Debye temperature Θ_D. This empirical equation has turned out to be an extreme success in the history of fitting the temperature dependent energy gaps in many semiconductor materials, including not only the bulk materials but also their nanostructures [35–41]. In the low temperature limit, the quadratic scaling $E(T) - E_0 \propto T^2$ from Eq. (1) is inconsistent with the Debye model. However, this disagreement is not so important, since the agreement between the model predictions and the experimental observations is excellent in the room temperature and high temperature regime, which is direct relevant to most of their applications. Therefore, this empirical equation provides a practical guideline for experiments and applications. Based on this equation, only the results at three different temperatures are needed to roughly estimate the optical properties of the material in the whole temperature regime. Although a lot of other physical models have been proposed to describe the energy gap shifts in semiconductors [42,43], this empirical equation is still one of the most widely quoted models due to its irreplaceable simplicity and monotonicity.

Unfortunately, the Varshni empirical equation fails to describe the energy gap shifts in diamond [9,26,27]. Although the diamond has the similar atomistic structure (diamond cubic) and symmetry (O_h) as many other semiconductor materials, it still possesses some unique features, which are not shared by other semiconductors. For instance, the Debye temperature ($\Theta_D = 2220$ K) and optical phonon frequency ($\omega_0 \sim 165.2$ meV) [44,45] are generally 3–4 times larger than those in other conventional semiconductor materials such as Si (diamond cubic structure) and GaAs (Zinc-blende structure) [46,47]. Moreover the lattice expansion coefficient in diamond is much smaller than those in other semiconductors [40,48]. This means that the electron-acoustic phonon interaction should be the major mechanism for the energy gap shifts in diamond. Therefore, at low temperature, this energy gap shift should be more accurately described by the Debye model [49], in which the electron phonon matrix is linearly proportional to the momentum $k = |\mathbf{k}|$. This gives the well-known scaling law, $E(T) - E(0) \propto T^4$, which has been found in semiconductor Si [49] at extremely low temperature. However, this assumption is insufficient when considering the real condition that the electron-phonon coupling strength should decay to zero very fast for large momentum k. In the simplest case when the coupling strength can be written as $k/(1+\mathcal{B}k^2)$, where $\mathcal{B}$ is a positive constant, the energy gap should decay as T^2 in the high temperature regime (yet still much smaller than the Debye temperature Θ_D). Therefore, for NV$^-$ center in diamond, the above two interesting limits can be interpolated by the following modified Varshni formula,

$$E(T) = E_0 - \frac{AT^4}{(T+B)^2}, \tag{2}$$

which shares the same simplicity and monotonicity as the original Varshni equation in Eq. (1). The two parameters A and B are restricted to positive values.

While the applications in quantum sensing and quantum information technique are mainly based on the manipulation of single NV$^-$ centers, most of the previous experiments on the temperature-dependent energy gaps were carried out on the color center ensembles in the bulk diamond with different nitrogen impurity concentrations [9,25,27]. Here, we studied the energy gap shifts in the single NV$^-$ center level with temperature ranging from 5 to 285 K. We find that the modified empirical Varshni formula, Eq. (2), can be used to describe the temperature dependent energy level shifts extremely well with error typically of the order of 0.1 MHz in the 5–285 K temperature regime. And the error is still less than 8.6 MHz when the prediction is extrapolated to 700 K. Moreover this empirical equation can be used to fit not only the ZFS and the optical spectral zero phonon line (ZPL) of the NV$^-$ center, but also the temperature dependent energy gaps for the other defects in diamond. Unlike the widely used Varshni formula in semiconductor materials, this empirical equation seems to be unique in diamond due to its distinctive electronic parameters. These results demonstrate the leading role of electron acoustic phonon interaction in the shift of energy gaps in diamond.

3. Results for ZFS

In our experiment, the diamond samples were high-quality chemical-vapor-deposition diamond plates (from Element Six) with intrinsic nitrogen concentrations less than 5 ppb (single NV center) or 1 ppm (NV center ensemble). NV center ensemble was observed in the diamond plate with higher intrinsic nitrogen concentration. The single NV$^-$ centers were produced by further nitrogen ions implanting into the diamond plate (intrinsic nitrogen concentration <5 ppb) with an energy of 20 keV and a dosage of 5×10^{10} cm^{-2}. The depth of implanted nitrogen atoms distributed among 8–20 nm. Then the samples were annealed at high vacuum (8×10^{-6} Pa) and high temperature (800°C) for 2 h to mobilize vacancies and generate single NV$^-$ centers. To remove non-diamond carbon on the surface, the samples were cleaned in a 1:1:1 boiling mixture of sulfuric, nitric, and perchloric acid for 1 h. The ODMR signal was measured with a home-build confocal microscopy system, in which a 532 nm CW laser (200 μW) was used to excite the NV$^-$ color center from ground state to excited state via an objective (N.A. = 0.7). The fluorescence was collected after passing through a 647 nm long-pass filter and the ODMR spectra of NV color center were measured by scanning the frequency of microwave. The samples were settled in a helium-free cryostat (Montana Instruments) with the temperature tuned from liquid helium to room temperature, while the temperature instability was less than 30 mK over the measurement time.

Three different single NV$^-$ centers were measured in our experiments (see Table 1). In Fig. 1 (a) and (b), we showed the results for the second single center (NV2) and NV center ensemble, respectively. The value of D decreased monotonically with the increasing of temperature, as expected from previous literatures. Note that, there was a slightly difference in D of the single NV and NV ensemble. It might be attributed to the different impurity concentrations [27,50], and needs to be further studied in future works. To quantitatively study the evolution of D as a function of temperature, we applied three different functions to fit the experimental data. The first fitting procedure was based on a fifth-order polynomial function, which has been used to describe the NV$^-$ center ensemble in type Ib bulk diamond [27]. In Ref. [27], some of the coefficients were predetermined (see the annotation in Table 1) by considering both the electron-phonon interaction and lattice expansion effect. We have adopted the same assumption here and found that $b_4 = 3.01 \times 10^{-12}$ GHz/K^4, $b_5 = -0.80 \times 10^{-14}$ GHz/K^5 in the single NV center (NV2) and $b_4 = 1.56 \times 10^{-12}$ GHz/K^4, $b_5 = -0.31 \times 10^{-14}$ GHz/K^5 in the color center ensemble. The fitting is acceptable at room temperature. However, one critical drawback of this method is the non-monotonicity of the energy gap as a function of temperature. It becomes much more