The effect of electron-phonon interactions on the spectral properties of single defects in hBN

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(Dated: September 3, 2018)

We investigate the temperature dependent spectral properties of a single defect in hexagonal boron nitride (hBN). We observe a sharp zero-phonon line (ZPL) emission accompanied by Stokes and anti-Stokes optical phonon sidebands assisted by the Raman active low-energy (∼ 6.5 meV) interlayer shear mode of hBN. The spectral lineshape around the ZPL is measured down to 78 K, where the linewidth of the ZPL is measured as 172 μeV. By employing a quadratic electron-phonon interaction, the temperature dependent broadening and the lineshift of the ZPL are found to follow $T + T^2$ and $T + T^3$ dependence, respectively. Furthermore, the temperature dependent lineshape around the ZPL is modeled with a linear electron-phonon coupling theory, which allowed us to calculate the Debye-Waller factor as 0.59.

Understanding the basic optical properties of the isolated quantum light sources and controlling their emission properties allow these sources to be used effectively in many areas within quantum information technologies. In the literature, semiconductor quantum dots, single molecules, and nitrogen vacancy centers in diamond are widely studied systems among a large number of known single photon sources [1]. In particular, isolated color centers in three-dimensional materials (i.e., diamond, silicon carbide, zinc oxide) with wide bandgap are of great interest as single-photon sources. Recently, efficient single-photon generation from transition metal dichalcogenides (TMDC) and defects in hBN are demonstrated [2–5]. Each of these materials has their own advantages in terms of operating conditions (such as working temperature or radiation energy), which can be important for different applications.

In particular, defects in hBN have attracted a great interest due to their unique advantages. The quantum nature of the emission obtained from defects in this material is not limited to only cryogenic temperatures, which indeed can be preserved for up to 800 K [6]. In addition, because of its large bandgap (∼ 6 eV), it can host several defect types which can emit over a large spectral range [2]. Finally, due to the two-dimensional nature, the optically-active defects in the hBN can be very close to the sample surface and they can interact very efficiently with other two-dimensional structures and photonic devices [7]. Despite the novel properties, the ZPL emission from a defect in hBN seems to be strongly affected by the vibrational properties of the crystal [2, 9, 11], which might influence the performance of these sources greatly for the applications.

In this letter, we present a quantitative study on spectral properties of an optically active single defect in hBN. A sharp ZPL and Raman-active interlayer shear mode assisted optical phonon sidebands are observed in the low-temperature emission spectrum. We perform temperature dependent photoluminescence measurements and compare the spectra with the theoretical model which is based on the electron-phonon interaction by taking into account the linear and quadratic displacement terms. With acoustic phonons couple to electronic states of the defect through the deformation potential and piezoelectric coupling, we show that the spectral properties of ZPL emission are strongly governed by the vibrational properties of the hBN. An excellent agreement between the experimental and theoretical calculations reveal that the relevant theoretical model can be used to accurately calculate the Debye-Waller and Huang-Rhys factors, both of which are commonly used to determine the potential of the emitter for applications.

In this work, multilayer hBN flakes (obtained in a solution from Graphene Supermarket) drop-casted on silicon dioxide substrate were used as the material system. Optical properties of the sample were investigated using a confocal micro-PL system as shown in Fig. 1(a). The sample is placed in a liquid nitrogen cryostat and mounted on a high precision XYZ translation stage. A microscope objective (NA = 0.5) is used to focus the excitation source (Argon laser at 488 nm) on the sample and to collect the emission, which is later dispersed on a monochromator equipped with an 1800 grooves/mm grating and an EM-CCD camera (spectral resolution ≈ 120 μeV at the studied wavelength). Figure 1(b) shows a spatially resolved normalized PL map of a multilayer hBN structure. Five isolated defects (∼ 1.2 μm in size, limited by the spot size) with different ZPL energies are clearly visible. All results reported here were obtained from the selected defect that has an asymmetric ZPL emission around 2.2 eV (563 nm) at 103 K as shown in Fig. 1(c). The linewidth of the peak is about 200 μeV, which is close to the resolution of the system. The spectrum also shows a small peak on the lower energy side of the ZPL with a detuning of −6.6 meV.

To understand the origin of the spectral features, such as the position of the peaks with respect to each other and the asymmetric lineshape of the ZPL, the interac-
The phonon sideband emission from the defect. It is assisted by the emission of low energy Raman active phonon mode of the hBN crystal at the $\Gamma$ point. As the thermal energy $k_B T = 8.8$ meV at 103 K is larger than the energy of the phonon mode, a weak sideband on the higher energy side of the ZPL (anti-Stokes emission) due to the absorption of this phonon is expected. As shown in the inset of Fig. 1(c), a small peak with a detuning of $\approx 6.3$ meV is observed on the higher energy side of the ZPL. The slight asymmetry between the energies of the Stokes and the anti-Stokes peaks might arise from different coupling strength of ground and excited states of the defect to the phonon mode [19]. To the best of our knowledge, this is the first observation of low energy Raman-active phonon modes in a PL spectrum of a defect in hBN.

To quantify the influence of electron-phonon interaction on the spectral properties of the observed emission, we performed systematic temperature dependent micro-PL measurements on the selected defect under same excitation power and polarization conditions. Figure 2(a) shows the normalized PL spectra of the defect taken at different temperatures from 333 K to 78 K. While the room temperature spectrum is mainly dominated by a broad asymmetrical peak at 2.195 eV, two distinct emission lines appear (Stokes and anti-Stokes phonon sidebands as discussed before) at the lower temperatures with a strongly narrowed and energetically shifted ZPL emission. As seen in Fig. 2(b), the detuning between the sidebands and the ZPL emission reduces almost linearly as the temperature is increased (See supplementary information). This can be explained by the positive thermal expansion coefficient of the hBN crystal along c-axis [20], which increases the interlayer spacing and, therefore, reduces the energy of the low-energy $E_{2g}$ phonon mode. A very similar temperature dependent behaviour of this mode is reported in Raman scattering experiments [15, 17, 18] but has not been observed in an emission spectrum of a single defect in hBN before.

In addition to the properties of the optical phonon sidebands, we also investigated the effect of temperature on the spectral properties of the ZPL emission. Figure 2(b) shows the temperature dependent linewidth with a strong narrowing at the lower temperatures. Due to the spectral resolution of the micro-PL setup, the FWHM values below 100 K were deconvoluted with the instrument response function. The linewidth at 78 K is extracted as 172 $\mu$eV, which is even narrower than the reported values at 5 K for defects in hBN [7] and defects in diamond (i.e., silicon or chromium vacancies) [21, 22]. However, it is still broader than the temperature-independent natural linewidth for a typical ZPL emission of a defect in hBN reported as $< 0.35$ $\mu$eV for a lifetime of 2 ns) [7].

At finite temperatures, the spectral diffusion and the acoustic phonon sidebands broaden the lineshape of the ZPL emission from quantum emitters in solid crystals.
The temperature dependent linewidth of the ZPL emission from semiconductor quantum dots and defect centers in diamond were studied with the phonon assisted theoretical frames. Recently, the linewidth of ZPL from defects in hBN were investigated by an effective single frequency phonon-mediated mechanism or employing excitonic states for emission near band gap of hBN.

Here, the temperature dependent behavior of ZPL linewidth is studied with a phonon assisted broadening mechanism with continuum of phonon modes interacting with the deep and isolated electronic states of a single defect. The broadening of the ZPL is considered through the phonon processes involving linear and quadratic electron-phonon coupling terms which is valid for systems exhibiting weak interaction with acoustic phonons. Considering the density of states in 2D ($D(\omega) \propto \omega$) and the quadratic electron-phonon coupling, acoustic phonon modes introduce a broadening to the ZPL emission via piezoelectric coupling ($V(\omega) \propto 1/\sqrt{\hbar \omega}$) proportional with $T$ and deformation potential ($V(\omega) \propto \hbar \omega / \sqrt{\hbar \omega}$) with $T^5$ (See ref. and supplementary information for details). The PL spectra from the sample were taken well below the Debye temperature, which justifies a constant contribution from the linear electron-phonon coupling to broadening. Therefore, the temperature dependent linewidth of ZPL emission from a defect in hBN is obtained as:

$$\Gamma(T) = \Gamma_0 + aT + bT^5$$

where the first term has the contribution from the both natural linewidth of the ZPL and the linear electron-phonon coupling while the second and third terms represent the contributions from the quadratic electron phonon coupling by piezoelectric coupling and deformation potential. The solid line in Fig. 2(c) is a fit to the measured linewidth data using the Equation 1 which shows a good agreement. The natural linewidth $\Gamma_0$ of the emission is, thus, estimated as 0.83 $\mu$eV.

The energy of the ZPL has also a strong temperature dependence as observed on the emission spectra. This behavior was also observed for several types of single quantum emitters in solids, such as semiconductor quantum dots and defects in diamond. Recently, a red shift of the ZPL from the defects in hBN were reported due to the lattice contraction or fluctuating fields with the other nearby defects. In the latter, the temperature dependent lineshift was analyzed with the model used for defects in a sp$^3$ carbon 3D lattice (diamond). In order to understand the red shift
that is observed in Fig. 2(a), we consider the coupling to the LA phonons through deformation potential and piezoelectric coupling with the density of states in 2D. The lowest non-vanishing contribution from the electron-phonon interaction to the lineshift is the quadratic coupling term, which is calculated as proportional to $T$ and $T^3$ for piezoelectric coupling and deformation potential, respectively. The solid line in the Fig. 2(d) represents the fit to the experimental data with the function given as $\Lambda(T) = cT + dT^3$. As seen, the phonon-mediated mechanism describes the lineshift behaviour very well (see Supplementary Information for the details).

Finally, the lineshape of the ZPL emission at a finite temperature is modeled with the linear electron-phonon coupling theory, which is shown to be valid as long as the electron-phonon interaction is small [25, 32] at low temperatures. Phonon assisted modeling of the lineshape was widely used to study the emission spectrum from quantum dots [25, 29, 33], defect centers in diamond [28, 34] and more recently point defects in hBN [11]. Here, the lineshape is calculated up to two-phonon process (O($S^2$)) with ZPL, one-phonon line (OPL), and two-phonon line (TPL). The lineshape function is given as the overlap of the initial and final vibrational states [29]:

$$G(\omega) = AV \sum n \prod_{\alpha} |\sigma(n_\alpha, n_\alpha')|^2 \delta(\omega - \omega_{ij,nn'}) \tag{2}$$

where $n_\alpha'$ is the occupation number of the phonon mode $\alpha$. The frequency of the emitted photon is given by $\hbar\omega_{ij,nn'} = E_{in} - E_{jn'}$, which is the energy difference between the excited defect state $i$ in phonon state $\{n_\alpha\}$ and the ground $j$ in phonon state $\{n_\alpha'\}$. In linear coupling model this energy difference is equal to $\hbar\omega_{2PL} = (n-n')\hbar\omega$, where $\hbar\omega_{2PL}$ is zero phonon line energy. Here also a thermal averaging is performed over the initial phonon states. The lattice oscillator overlaps for different modes can be expressed in terms of Huang-Rhys factors $S_\alpha$ as [32]:

$$|\sigma(n_\alpha, m_\alpha)|^2 = S_{n_\alpha-m_\alpha} e^{-S_{m_\alpha} m_\alpha} \left\{ \mathcal{L}_{n_\alpha-m_\alpha}(S_\alpha) \right\}^2 ,$$

where $S_\alpha = (V(\omega_\alpha)/\hbar\omega_\alpha)^2$.

Finally, the lineshape function defined in Eqn. 2 is obtained as:

$$G(\omega) = AV \sum m_\alpha \prod_{\alpha} S_{n_\alpha-m_\alpha} e^{-S_{m_\alpha} m_\alpha} \left\{ \mathcal{L}_{m_\alpha-m_\alpha}(S_\alpha) \right\}^2 \delta(\omega - \omega_{ij,nn'}).$$

From the above expression, the ZPL is calculated to the second order in Huang-Rhys factor as follows:

$$G_0(\omega) \approx \left[ 1 - \sum_{\alpha} \left(\langle n_\alpha \rangle + 1\right) S_{\alpha} + \sum_{\alpha} \langle n_\alpha \rangle^2 S_{\alpha}^2 \right]$$

$$+ \sum_{\alpha,\beta} \langle n_\alpha \rangle S_{\alpha} \langle n_\beta \rangle S_{\beta} + \sum_{\alpha,\beta} S_{\alpha}(2 \langle n_\beta \rangle S_{\beta})$$

$$\times \delta(\omega - \omega_{ij})$$

where $S(\omega)$ is the energy dependent Huang-Rhys factor and $n(\omega)$ is the Bose-Einstein distribution function. Similarly, emission part of the OPL is given as:

$$G_1(\omega) = \sum_{n_\alpha, m_\beta} \left\{ 1 - \sum_{\alpha} S_{\alpha} \sum_{\beta} \langle n_\alpha \rangle S_{\alpha} \right\}$$

$$+ \sum_{\alpha,\beta} \langle n_\beta \rangle S_{\beta} - \sum_{\alpha} \langle n_\alpha \rangle S_{\alpha}^2$$

$$\times \delta(\omega - \omega_{ij} - \omega_{\alpha}).$$

The absorption part of the OPL is calculated by replacing the $n(\omega)$ terms with $(n(\omega)-1)$ in the $G_1$ function (see Fig.1 in supplementary information for details). Finally, the TPL function ($G_2$) is obtained from the convolution of the OPL with only O($S$) terms.

To produce a lineshape that fits to the measured spectrum, the discrete phonon peaks are replaced with the convolution of the ZPL ($G_0$) lineshape. Additionally, the lineshape is calculated up to a maximum phonon energy of $k_BT$, where $k_B$ is Boltzman constant and $T$ is the temperature at which the data was taken. The Huang-Rhys terms for the phonons with the frequency of $\omega_\alpha$ is given as $S_\alpha \propto 1/\omega_\alpha^4$ for the deformation potential while it is $S_\alpha \propto 1/\omega_\alpha^3$ for the piezoelectric coupling. The effect of the piezoelectric coupling is observed to be weak compared to the deformation potential and therefore it is ignored. Figure 3(a) shows the experimental spectrum (symbols) obtained at 93 K and the result of the fit with the theoretical lineshape including up to two phonon processes with O($S^2$) and considering the phonon sidebands from LA phonons. As seen from the figure, the dominant contribution to the lineshape is due to the ZPL while the OPL and the TPL contribute mainly to the lineshape on the tails of the emission spectrum. The fraction of the ZPL (known as the Debye-Waller factor) within the total emission lineshape is calculated approximately by using $G_0/(G_0 + G_1 + G_2)$, where the terms in the denominator have contributions from the phonon-sidebands due to LA phonons. We note that, at low temperatures (<124 K) the occupation of the optical phonons [15] is negligible and the weak contribution from the sidebands are ignored for the calculation of the ZPL fraction. Therefore, a ZPL fraction of 0.39 is calculated at 93 K. To determine the temperature dependence of the Debye-Waller factor, the
In conclusion, temperature dependent spectral properties of a single defect in hBN are investigated both experimentally and theoretically. It is shown the linear and quadratic electron-phonon coupling with acoustic phonons via the deformation potential and the piezo-electric coupling play significant role on the linewidth, lineshift, and lineshape of the ZPL emission. We found that the linewidth of ZPL varies with $T + T^5$ while its energy shifts with $T + T^3$. In particular, the temperature dependent lineshape analysis of the ZPL has enabled to calculate the Debye-Waller factor as low as 0.59 at 0 K. Finally, in addition to the ZPL, optical phonon sidebands assisted by the emission (Stokes) and absorption (anti-Stokes) of the low-energy Raman active $E_{2g}$ phonon mode is observed for the first time from a low temperature PL spectrum of a single defect in hBN.

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**References**

1. I. Aharonovich, D. Englund, and M. Toth, Nature Photonics 10, 631 (2016).
2. Y.-M. He, G. Clark, J. R. Schaibley, Y. He, M.-C. Chen, Y.-J. Wei, X. Ding, Q. Zhang, W. Yao, X. Xu, C.-Y. Lu, and J.-W. Pan, Nature Nanotechnology 10, 497 (2015).
3. A. Srivastava, M. Sidler, A. V. Allain, D. S. Lembke, A. Kis, and A. Imamolu, Nature Nanotechnology 10, 491 (2015).
4. C. Chakraborty, L. Kinnischtzke, K. M. Goodfellow, R. Beams, and A. N. Vamivakas, Nature Nanotechnology 10, 507 (2015).
5. T. T. Tran, K. Bray, M. J. Ford, M. Toth, and I. Aharonovich, Nature Nanotechnology 11, 37 (2015).
6. M. Kianinia, B. Regan, S. A. Tawfik, T. T. Tran, M. J. Ford, I. Aharonovich, and M. Toth, ACS Photonics 4, 768 (2017).
7. N. R. Jungwirth, B. Calderon, Y. Ji, M. G. Spencer, M. E. Flatté, and G. D. Fuchs, Nano Letters 16, 6052 (2016).
8. S. Kim, J. E. Fröch, J. Christian, M. Straw, J. Bishop, D. Totonjian, K. Watanabe, T. Taniguchi, M. Toth, and I. Aharonovich, Nature Communications 9, 2623 (2018).
9. T. Q. P. Vuong, G. Cassabois, P. Valvin, A. Ouerghi, Y. Chassagneux, C. Voisin, and B. Gil, Physical Review Letters 117, 097402 (2016).
10. N. R. Jungwirth and G. D. Fuchs, Physical Review Letters 119, 057401 (2017).
11. A. L. Exarhos, D. A. Hopper, R. R. Grote, A. Alkauskas, and L. C. Bassett, ACS Nano 11, 3328 (2017).
12. R. Geick, C. H. Perry, and G. Rupprecht, Physical Review 146, 543 (1966).
13. T. Kuzuba, K. Era, T. Ishii, and T. Sato, Solid State Communications 25, 863 (1978).
14. R. J. Nemanich, S. A. Solin, and R. M. Martin, Physical Review B 23, 6348 (1981).
15. R. Cuscó, B. Gil, G. Cassabois, and L. Artús, Physical Review B 94, 155435 (2016).
16. L. J. Martínez, T. Pelini, V. Waselowski, J. R. Maze, B. Gil, G. Cassabois, and V. Jacques, Physical Review B 94, 121405 (2016).
17. T. Q. P. Vuong, G. Cassabois, P. Valvin, V. Jacques, R. Cuscó, L. Artús, and B. Gil, Physical Review B 95, 045207 (2017).
18. I. Stenger, L. Schue, M. Boukhicha, B. Berini, B. Pla?ais, A. Loiseau, and J. Barjon.
[19] A. Norambuena, S. A. Reyes, J. Mejía-López, A. Gali, and J. R. Maze, Physical Review B 94, 134305 (2016).

[20] W. Paszkowicz, J. Pelka, M. Knapp, T. Szyszko, and S. Podsiadlo, Applied Physics A: Materials Science & Processing 75, 431 (2002).

[21] T. Müller, I. Aharonovich, Z. Wang, X. Yuan, S. Castelletto, S. Prawer, and M. Atatüre, Physical Review B 86, 195210 (2012).

[22] E. Neu, C. Hepp, M. Hauschild, S. Gsell, M. Fischer, H. Sternschulte, D. Steinmüller-Nethl, M. Schreck, and C. Becher, New Journal of Physics 15, 043005 (2013).

[23] J. Wolters, N. Sadzak, A. W. Schell, T. Schröder, and O. Benson, Physical Review Letters 110, 027401 (2013).

[24] K.-M. C. Fu, C. Santori, P. E. Barclay, L. J. Rogers, N. B. Manson, and R. G. Beausoleil, Physical Review Letters 103, 256404 (2009).

[25] I. Favero, G. Cassabois, R. Ferreira, D. Darson, C. Voisin, J. Tignon, C. Delalande, G. Bastard, P. Roussignol, and J. M. Gérard, Physical Review B 68, 233301 (2003).

[26] L. Besombes, K. Kheng, L. Marsal, and H. Mariette, Physical Review B 63, 155307 (2001).

[27] V. Hizhnyakov, H. Kaasik, and I. Sildos, Physica Status Solidi (B) Basic Research 234, 644 (2002).

[28] G. Davies, Journal of Physics C: Solid State Physics 7, 3797 (1974).

[29] A. M. Stoneham, Theory of Defects in Solids (2001).

[30] T. Tohei, A. Kuwabara, F. Oba, and I. Tanaka, Physical Review B 73, 064304 (2006).

[31] B. Sontheimer, M. Braun, N. Nikolay, N. Sadzak, I. Aharonovich, and O. Benson, Physical Review B 96, 121202 (2017).

[32] T. H. Keil, Physical Review 140, A601 (1965).

[33] B. Krummlheuer, V. M. Axt, and T. Kuhn, Physical Review B 65, 195313 (2002).

[34] A. Alkauskas, B. B. Buckley, D. D. Awschalom, and C. G. Van de Walle, New Journal of Physics 16, 073026 (2014).
Supplemental Information for
The effect of electron-phonon interactions on the spectral properties of single defects in hBN

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EMISSION PROCESS FROM DEFECTS IN HBN

A typical emission process from a defect in hBN is shown in Fig. S1. The transitions for the zero-phonon line and the phonon sidebands are labelled as $G_0$ and $G_{-2,-1,1,2}$, respectively.

FIG. S1. The electron-phonon system for defect center in hBN in the configuration coordinate space. Parabolas represents the harmonic potentials of the lattice in the electronic states.

TEMPERATURE DEPENDENT OPTICAL PHONON SIDEBANDS

FIG. S2. Temperature dependent spectra of the defect taken between 78 K and 138 K. The ZPL energy is centered in each spectrum to observe the temperature dependent detuning between the sidebands and the ZPL energies.

TEMPERATURE DEPENDENT BROADENING AND LINESHIFT OF ZPL

The temperature dependent broadening and shift of the ZPL energy can be determined by considering the coupling of low energy LA phonons to the electronic states of the defect. The linear electron-phonon coupling terms introduce a linear temperature dependence to the linewidth as [1]:

$$\Gamma(T) = \left\{ 8 \ln(2) \sum_{\alpha} (\hbar \omega_\alpha)^2 S_{\alpha 0} \coth(\hbar \omega_\alpha / 2k_B T) \right\}^{1/2}$$  (1)
where $S_{\omega}$ is the Huang-Rhys factor for the phonon with the frequency of $\omega_\alpha$, $k_B$ is the Boltzmann constant. The integral form of the above-equation can be written as:

$$
\Gamma(T) = \left\{ 8\ln(2) \int_0^{\omega_M} d\omega (\hbar \omega)^2 D(\omega) S(\omega)(2n(\omega) + 1) \right\}^{1/2}
$$

(2)

where $S(\omega)$ is Huang-Rhys factor $D(\omega)$ is density of states, $n(\omega)$ is the Bose-Einstein distribution function, and $\omega_M$ is the maximum phonon frequency. Considering the coupling to LA phonons through deformation potential ($V(\omega) \propto \hbar \omega / \sqrt{\hbar \omega}$) and piezoelectric coupling ($V(\omega) \propto 1 / \sqrt{\hbar \omega}$) with Huang-Rhys parameter $S(\omega) = (V(\omega) / \hbar \omega)^2$ and the density of states in 2D ($D(\omega) \propto \omega$), the contribution to the broadening from linear electron-coupling terms becomes $T^{3/2}$ and $T^{1/2}$, respectively.

The quadratic electron-phonon coupling results in a temperature dependent broadening of the ZPL as [1]:

$$
\Gamma(T) \propto \int_0^{\omega_M} d\omega \left\{ \sum_q |V_q|^2 \delta(\omega - \omega_q) \right\}^2 n(\omega) \{n(\omega) + 1\}
$$

(3)

where $V_q$ is the electron-phonon coupling parameter. Alternatively the integral form of the Equation 3 is:

$$
\Gamma(T) \propto \int_0^{\omega_M} d\omega \left\{ V^2(\omega) D(\omega) \right\}^2 n(\omega) \{n(\omega) + 1\}
$$

(4)

Considering the coupling to LA phonons through deformation potential with the density of states in 2D, the contribution to the broadening of the ZPL from the quadratic electron-phonon coupling is derived as:

$$
\Gamma(T) \propto T^5
$$

(5)

Additionally, the coupling of LA phonons through piezoelectric coupling with the density of states in 2D, the contribution to the broadening of the ZPL from the quadratic electron-phonon coupling is derived as:

$$
\Gamma(T) \propto T
$$

(6)

The general temperature dependence of the width from the emission centered at ZPL becomes:

$$
\Gamma(T) = \Gamma_0 + aT^{1/2} + bT^{3/2} + cT + dT^5
$$

(7)

However, second and third terms approaches to a constant value at low temperatures. In Figure S3 fits to the experimental FWHM data with the only quadratic electron-phonon coupling terms and linear plus quadratic coupling terms are shown. Both models represent the experimental data quite efficiently. Therefore, temperature dependence of the FWHM is modelled by considering only the quadratic electron-phonon coupling terms.
FIG. S3. Temperature dependence of the FWHM of the defect center exhibiting a ZPL at 2.2 eV. The experimental data is shown with black dots, while the solid line represents the fit of quadratic coupling terms ($\Gamma(T) = \Gamma_0 + aT + bT^3$) and the dashed line shows the fit of linear and quadratic coupling terms ($\Gamma(T) = \Gamma_0 + aT^{1/2} + bT^{3/2} + cT + dT^5$) together.

The lowest non-vanishing contribution from the electron-phonon interaction to the lineshift is the quadratic coupling which is given as [1]:

$$\Lambda(T) \propto \int_0^{\omega_M} d\omega \left\{ \sum_q |V_q|^2 \delta(\omega - \omega_q) \right\} \{ n(\omega) + 1 \}$$

(8)

$$\Lambda(T) \propto \int_0^{\omega_M} d\omega \left\{ V^2(\omega)D(\omega) \right\} \{ n(\omega) + 1 \}$$

(9)

Similarly, considering the coupling to LA phonons through deformation potential and piezoelectric coupling with the density of states in 2D, the temperature dependence of the lineshift becomes $\Lambda(T) = cT + dT^3$. 

FIG. S4. PL emission spectrum from the ZPL (2.2 eV) at various temperatures (a) 78 K, (b) 103 K, (c) 113 K, (d) 123 K are given with symbols. The blue solid lines represent the lineshape calculated from the linear electron coupling theory with the contributions from ZPL (orange line), OPL (green line), and TPL (red line). Calculated Huang-Rhys and Debye-Waller parameters at relevant temperature are given in the insets.

Figure S4(a) shows the experimental (symbols) spectral lineshape obtained at 78 K, 103 K, 113 K, 123 K and the result of the fitting with the theoretical lineshape given in the main text including up to two phonon process involving the phonon sidebands from LA phonons coupled to electronic states through deformation potential.

[1] A. M. Stoneham, in *Theory of Defects in Solids* (2001).