

Charge State Equilibration of Nitrogen-Vacancy Center Ensembles in Diamond: The Role of Electron Tunneling

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The charge state stability of nitrogen-vacancy (NV) centers critically affects their application as quantum sensors and qubits. Understanding charge state conversion and equilibration is important not only for NV centers in diamond but also for defects and impurities in wide-bandgap materials in general. The mechanisms by which these centers change charge state upon optical or electronic excitation without the presence of mobile carriers remain unclear. Here, we elucidate this issue for the case of photoionization of NV center ensembles. Using pump-probe spectroscopy, we ionize negatively charged NV centers and monitor the recovery of NV^- on timescales of up to several seconds. We find that the recovery rate depends strongly on the concentration of surrounding nitrogen donors. Remarkably, the equilibration dynamics exhibit no discernible dependence on temperature, ruling out thermally activated processes. We develop a multiphonon-assisted electron-tunneling model, supported by density-functional calculations, that explains the measurements and identifies tunneling as the equilibration mechanism. Because tunneling rates depend exponentially on donor separation, the random distribution of nitrogen donors spreads recovery times from nanoseconds to hours or longer.

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The nitrogen-vacancy (NV) center in diamond [1] has become a versatile platform for testing and implementing quantum technologies in sensing, communication, and computing [2–6]. The negatively charged state (NV^-) is pivotal for these applications because it offers the required optical and spin properties. Stabilizing this charge state is therefore essential, yet control has remained elusive despite extensive efforts, because the microscopic mechanism behind charge-state fluctuations is not completely understood. The equilibrium charge state is known to be governed by interactions with nearby deep-level dopants [7]. To establish the negative charge state, NV typically captures an electron from a neighboring single-substitutional nitrogen (N) defect, forming an NV^- -N⁺ pair [8]. Such charge transfer between deep-level defects cannot be explained by the Shockley-Read-Hall model [9,10], which depends on thermal excitation and carrier capture. For deep

defects with high ionization energies, this mechanism is ineffective, suggesting that electron tunneling is responsible for the charge transfer [8]. Electron tunneling from the excited state of NV^- to nearby N⁺ defects has also been proposed as a mechanism for quenching NV^- photoluminescence (PL) [11,12]. Related studies of direct interdefect charge transfer in silicon [13], tunneling through deep levels in quantum-dot heterostructures [14], and first-principles estimates of the electronic coupling between NV defect pairs [15] highlight that tunneling between localized states can be highly efficient. Despite these indications, a quantitative phonon-assisted treatment of NV -N⁰ charge transfer has been lacking. Clarifying this mechanism is important for understanding the charge-state stability and dynamics of NV centers [16], as well as charge-transport phenomena observed in diamond [17,18]. More broadly, understanding tunneling mechanisms is essential for applications beyond the NV center, where optical or electronic excitation alters the charge state of deep defects or impurities in wide-bandgap semiconductors or insulators, such as phosphors, scintillators, or devices with (semi-) insulating layers.

In this Letter, we investigate the charge equilibration dynamics of an ensemble of NV centers following photoionization, which converts NV^- centers to the neutrally charged NV^0 state. Our transient spectroscopy results reveal that the recovery dynamics back to NV^- are governed by the concentration of N centers with no

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discernible dependence on temperature. Combining these measurements with density functional theory (DFT) calculations of the electron-phonon interaction, we demonstrate that the charge equilibration occurs via phonon-assisted electron tunneling between N^0 and NV^0 , facilitated by significant lattice relaxation of the N center. We also provide a microscopic empirical model that replicates the observed dynamics and explains the lack of temperature dependence. Because the tunneling rate depends exponentially on the NV-N separation, the random spatial distribution of donors produces a correspondingly broad spread of recovery times: the model predicts equilibration within a fraction of a second at 100 ppm nitrogen, but extends beyond an hour at 1 ppm. A short discussion of the microscopic assignment of this recovery channel, including possible alternative mechanisms, is provided in Sec. S1 of Supplemental Material (SM) [19]. Our approach should be applicable to other materials containing ensembles of deep-level defects, where electron tunneling serves as the mechanism for charge migration and equilibration.

Optical excitation can photoionize NV^- by promoting an electron to the conduction band (CB), thereby converting NV^- to NV^0 [16,20–22]. The threshold for direct ionization is estimated to lie between 2.6 and 2.74 eV, based on both experimental [16,23] and theoretical [22–24] studies. Time-resolved THz spectroscopy shows that electrons photoexcited from N to the CB recombine back to N within tens of picoseconds [25,26], indicating a strong recombination pathway. A similar recombination with N is likely to follow photoionization of NV. The ionization threshold of N from the neutral to the positively charged state is approximately 1.7 eV [7,27]. The resulting model of the tunneling transition that equilibrates the charge after photoionization is depicted in Fig. 1(a), illustrating the charge state transition (CST) levels: $(0/-)$ for the NV center and $(+/0)$ for the N defect. The tunneling of an electron from N^0 to NV^0 is an exothermic process that releases approximately 1 eV of energy.

To establish a theoretical foundation for the tunneling process, we consider the multiphonon emission mechanism, which involves an energy-conserving transition followed by rapid vibrational relaxation to thermal equilibrium; this relaxation typically occurs on picosecond timescales [28,29]. We employ a simplified microscopic model with three degrees of freedom: one for the electron and two for the vibrational motion associated with the NV center and the N donor, respectively. The phonon-assisted tunneling rate between two spatially separated states in the coupled NV-N system takes the same form as a multiphonon nonradiative transition rate [30–32]:

$$\Gamma(r, T) = \frac{2\pi}{\hbar} W_{fi}^2(r) A(\Delta E, 0, T), \quad (1)$$

where $W_{fi}(r)$ is the hopping matrix element representing the electronic charge transfer between the initial (i) and

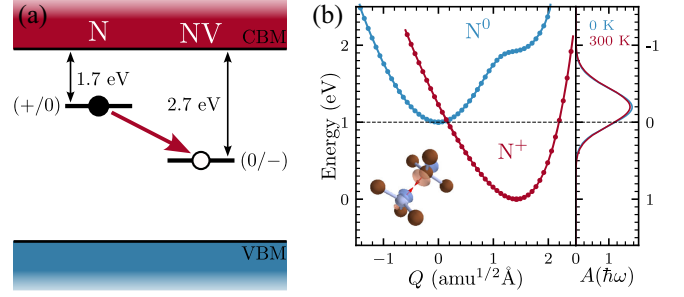


FIG. 1. Phonon-assisted electron tunneling from N^0 to NV^0 . (a) Exothermic charge transfer: the ionization threshold for N^0 is 1.7 eV, and the energy released when the electron is captured by NV^0 is about 2.7 eV. (b) Left: first-principles configuration coordinate (CC) potential energy surfaces of the N center. Inset: atomic structure of N^0 with antibonding orbital isosurfaces in neutral state; arrows show atomic motion along the positive CC Q direction. Right: optical spectral functions for the tunneling process at $T = 0$ K and 300 K, where the value at $E = 0$ corresponds to the vibrational factor $A(\Delta E; 0)$ in Eq. (1).

final (f) electronic states, and r denotes the spatial separation between the NV center and the substitutional nitrogen donor. The vibrational factor $A(\Delta E, 0, T)$ is the Franck-Condon weighted density of final vibrational states at energy ΔE , giving the probability that the electronic energy is entirely transferred to phonons. This factor corresponds to the value of the normalized spectral function $A(\Delta E, \hbar\omega, T)$ at $\hbar\omega = 0$, which describes the spectral density of phonon-assisted radiative transitions [33,34] and depends on the temperature T through thermal occupation of phonon modes. In our model, this spectral function takes the form

$$A(\Delta E, \hbar\omega, T) = \sum_{mlnk} w_m(T) w_l(T) |\langle \chi_{fn}^N | \chi_{im}^N \rangle \langle \chi_{fk}^{NV} | \chi_{il}^{NV} \rangle|^2 \times \delta(\Delta E + \varepsilon_{i,ml} - \varepsilon_{f,nk} - \hbar\omega), \quad (2)$$

where $\varepsilon_{i,ml}$ represents the vibrational energy of the system in the i electronic state, with N and NV having m and l excited phonons, respectively. The factors $w_l(T)$ are Boltzmann weights that account for the temperature-dependent occupation of vibrational states.

The vibrational overlap integrals, $\langle \chi_{fn}^N | \chi_{il}^{NV} \rangle$, quantify the coupling between vibrational states in the initial and final electronic manifolds. This electron-phonon interaction is commonly characterized by the Huang-Rhys (HR) factor S [30], which represents the average number of phonons excited during an electronic transition. For the NV center, the HR factor for the $(0/-)$ charge-state transition is $S \approx 1.3$ [22], indicating a low probability of exciting more than two phonons. In contrast, the N defect exhibits much stronger electron-phonon coupling, with $S \gg 1$ [35], making it the dominant contributor to the line shape function. This pronounced coupling arises from its structural configuration:

N^0 lacks a covalent bond with one adjacent carbon, forming an antibonding orbital in the region of the missing bond [see inset of Fig. 1(b)]. In its neutral state, this orbital is occupied, and the removal of the electron restores the covalent bond, leading to significant lattice relaxation. Given the distinct electron-phonon interactions, we assume $\langle \chi_{fn}^{NV} | \chi_{im}^{NV} \rangle = \delta_{nm}$, meaning the N defect solely determines the vibrational factor in Eq. (2). This simplifies the model's functional form to the well-known 1D problem of carrier capture at point defects [33,36].

We investigate the electron-phonon interaction of the N defect using DFT calculations within the one-dimensional configurational coordinate (CC) approximation [34]. The calculations were performed using the VASP code [37] with the r²SCAN density functional [38], which has proven effective in describing electron-phonon interactions in various deep-level defects [39–42]. Computational details are available in Sec. S1 of SM [19].

The left side of Fig. 1(b) shows the CC potential energy surfaces for electron tunneling from the neutral N defect to the neutral NV center, with a vertical offset of $\Delta E = 1$ eV. Both surfaces exhibit strong anharmonicity due to pronounced electron-phonon interaction. To accurately compute the spectral function (2), we numerically solved the one-dimensional nuclear Schrödinger equation. The right side of Fig. 1(b) shows spectral functions $A(\Delta E; \hbar\omega)$ calculated at $T = 0$ and 300 K. The approximate Huang-Rhys (HR) factor, estimated as the average number of emitted phonons, is $S \approx 14$. The vibrational factor $A(\Delta E; 0)$ corresponds to the no-photon-emission condition, and is represented by the horizontal dashed line. Notably, for $\Delta E = 1$ eV, the factor is near peak efficiency, indicating an effective channel for nonradiative tunneling. The calculated vibrational factor values are $A(1, 0) = 1.19$ eV⁻¹ at $T = 0$ and 1.16 eV⁻¹ at 300 K, indicating minimal temperature dependence.

For completeness, we also examined an alternative pathway where the NV⁻ center transitions to the metastable singlet ¹E state, located ~ 0.4 eV above the ground ³A₂ level [43]. However, the vibrational factors for this transition are about 50 times smaller [$A(0.6, 0) = 0.05$ eV⁻¹ at $T = 0$ and 0.07 eV⁻¹ at 300 K], making this pathway much less significant compared to the transition to the ground state.

For a qualitative estimate of the electronic transition matrix element W_{fi} and its dependence on distance, we employ the effective-mass approximation and the zero-range potential (ZRP) model [44–46] to approximate the short-range potential of deep-level defects. In this model, the wave function is expressed as

$$\psi_i(r) = \sqrt{\frac{\alpha_i}{2\pi}} \frac{e^{-\alpha_i r}}{r}, \quad (3)$$

where r is the radial distance from the defect center. Within the effective-mass approximation, the parameter $\alpha_i = \sqrt{2mE_i}/\hbar$ is determined by the ionization energy E_i .

In the ZRP model, the short-range potential is replaced by a boundary condition requiring that the logarithmic derivative of the radial part $r\psi_i$ equals $-\alpha_i$.

The electron transfer matrix element, analogous to the hopping term in a tight-binding model, can be expressed as $W_{fi} = E_{NV} \langle \psi_{NV} | \psi_N \rangle + \langle \psi_{NV} | V_{NV} | \psi_N \rangle$ [14]. Here, E_{NV} is the negative binding energy of the NV center electron, ψ_{NV} and ψ_N are the localized wave functions of the isolated NV and N defects, and V_{NV} is the potential of the NV center. Within the ZRP model, the matrix element is derived as follows (see Sec. S2 of SM [19] for details):

$$W_{fi} = \frac{\hbar^2}{mr} \frac{\sqrt{\alpha_1 \alpha_2}}{(\alpha_1^2 - \alpha_2^2)} (\alpha_2^2 e^{-\alpha_1 r} - \alpha_1^2 e^{-\alpha_2 r}), \quad (4)$$

where r is the separation between the centers.

To model the population dynamics of ionized NV centers, we assume that the electron tunnels from the nearest N^0 defect. This assumption is justified by the experimental protocol, which involves repeated intense optical pulses that ionize the NV⁻ centers and redistribute the local charge. As a result, the probability of finding a nearby positively charged nitrogen (N^+) immediately after excitation is significantly reduced. We therefore assume that nearly all substitutional nitrogen remains in the neutral charge state. The radial probability distribution of finding the nearest neighbor in the radial shell between r and $r + dr$ is given by [47]

$$w(r) = 4\pi r^2 n e^{-\frac{4}{3}\pi n r^3},$$

where n is the overall density of nitrogen defects. The function $w(r)$ peaks at a distance of $(2\pi n)^{-1/3}$, corresponding to 44.9, 20.9, and 17.1 Å for nitrogen concentrations of 10, 100, and 180 ppm, respectively.

Using the above distribution of nearest N donors, the temporal dependence of the relative concentration of neutral NV centers, $p(t) = [NV^0](t)/[NV^0](0)$, due to tunneling from N defects, becomes

$$p(T, t) = \int_0^\infty w(r) e^{-\Gamma(r; T)t} dr. \quad (5)$$

Having established a theoretical framework for modeling charge equilibration dynamics via electron tunneling, we now turn to experimental verification. We employ a pump-probe spectroscopy setup using two diamond substrates having low (10 ppm) and high (180 ppm) N concentrations. A pulsed pump laser ionizes the NV ensemble, while a continuous-wave (CW) laser monitors the time-resolved transmission through the sample [48]. The setup is illustrated in Fig. 2(a), with additional details provided in Sec. S4 of SM [19].

In brief, pump pulses with a duration of approximately 150 fs at a wavelength of 620 nm are emitted at a 10 kHz repetition rate. For the considered timescales, the pulsed excitation can be treated as a continuous excitation.

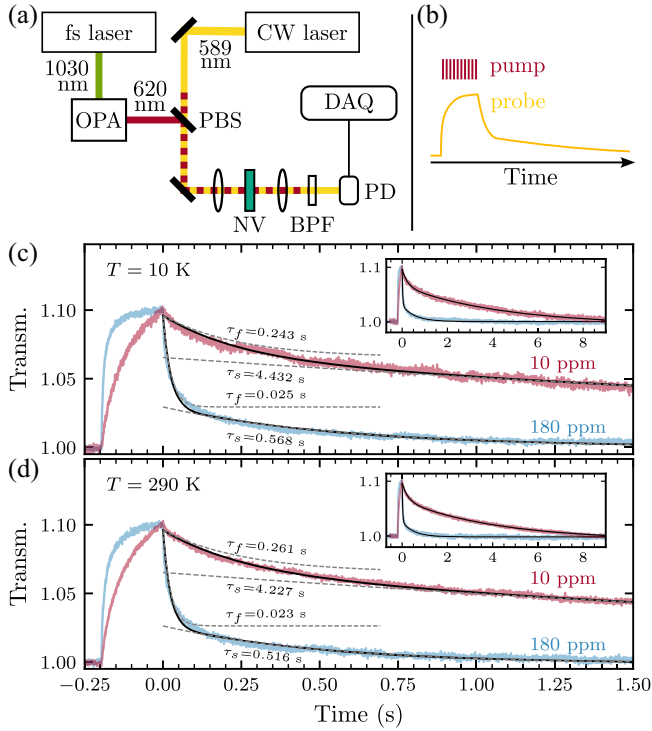


FIG. 2. (a) Schematic of the measurement setup. Abbreviations: OPA—optical parametric amplifier, PBS—polarizing beam splitter, BPF—bandpass filter, PD—photodiode, DAQ—Data acquisition card; (b) Excitation scheme illustrating pump and probe dynamics; Normalized probe transmission dynamics for both samples at temperatures of (c) 10 K and (d) 290 K, with biexponential fits to the data. The inset plots display graphs for a 10 s time window.

The average pump power is 30 mW over a beam spot size of 30 μm . The chosen wavelength selectively excites and, via two-photon absorption [22], ionizes NV^- without exciting NV^0 . The CW probe laser emits at a wavelength of 589 nm, again selectively addressing NV^- without probing NV^0 . While at higher temperature, a small portion of the NV^0 ZPL could be excited at 589 nm due to linewidth broadening, we estimate this to be negligible. The time-resolved measurement of the transmitted probe beam enables monitoring of the transient bleaching of the NV^- absorption. Figures 2(c) and 2(d) show the normalized probe transmission dynamics for both samples at 10 and 290 K, respectively, with the prepump signal set to unity and the maximum set to 1.1. The pump laser excites the sample for 200 ms, steadily building a nonequilibrium concentration of NV^0 centers, as evidenced by an increase in the probe transmission, i.e., bleaching of NV^- absorption. After switching off the pump, the system relaxes towards equilibrium for up to 10 s while the probe laser monitors the process. This cycle is repeated several times, and the recorded transient transmission data are averaged.

The relaxation dynamics can be approximately described by a biexponential model, as indicated by the fits shown in

Figs. 2(c) and 2(d), where the corresponding characteristic time constants are displayed. Notably, the dynamics remain nearly identical at both cryogenic and room temperatures. A more quantitative analysis is provided in Sec. S4 of SM [19], where the extracted time constants are plotted as a function of temperature for both samples, confirming the temperature independence predicted by our model.

To relate the theoretical model to the experimental conditions, we now consider the population buildup during the pumping stage. Applying ionizing excitation results in the accumulation of a population of NV^0 centers with longer equilibration times, while effectively filtering out contributions with tunneling rates higher than the average ionization rate. Accordingly, Eq. (5) is adjusted as

$$p_{\text{eff}}(T, t) = \int_0^\infty f(\tau[r; T]) w(r) e^{-\Gamma(r; T)t} dr, \quad (6)$$

where $f(\tau)$ is a filter function that describes how the population redistributes due to the pumping sequence, and $\tau = 1/\Gamma(r; T)$ is the tunneling lifetime, which depends on the distance between NV and N centers. The function $f(\tau)$ can be estimated by treating the pulsed excitation as continuous, replacing the pump sequence with a constant average rate G . In the weak-excitation limit ($G \ll \Gamma$), the steady-state population after a pump duration Δt takes the form (see Sec. S3 of SM [19] for details)

$$f(\tau) = G\tau(1 - e^{-\Delta t/\tau}). \quad (7)$$

The empirical model introduced above relies on two phenomenological parameters, α_1 and α_2 , which describe the spatial extent of the N and NV wave functions, respectively. Assuming an effective electron mass of $m = 0.57 m_e$, corresponding to the average conduction-band mass in diamond, and using a pump duration of $\Delta t = 0.2$ s, we simultaneously fit these parameters to the experimental decay curves at $T = 10$ K measured for both nitrogen concentrations. To enable direct comparison with the experiment, the simulated and experimental decay curves are normalized such that the prepump population is set to unity and the minimum value at $t = 9$ s is set to 0. Figure 3(a) shows the fitted curve overlaid on the measured data. The inset presents both simulated and experimental curves on an absolute population scale, with the experimental data rescaled so that the population change over the 9-sec interval matches the prediction of the theoretical fit. The model accurately captures the qualitative shape of the probe transmission and reproduces the overall trend observed in both nitrogen concentration samples, highlighting the difference between the two populations. The fitted parameters are $\alpha_1 = 0.40 \text{ \AA}^{-1}$ and $\alpha_2 = 0.89 \text{ \AA}^{-1}$. These values are comparable to those predicted by the phenomenological effective mass expression $\alpha_i = \sqrt{2mE_i}/\hbar$, which yields $0.51 \text{ \AA}^{-1}$ and $0.64 \text{ \AA}^{-1}$ for the respective ionization energies.

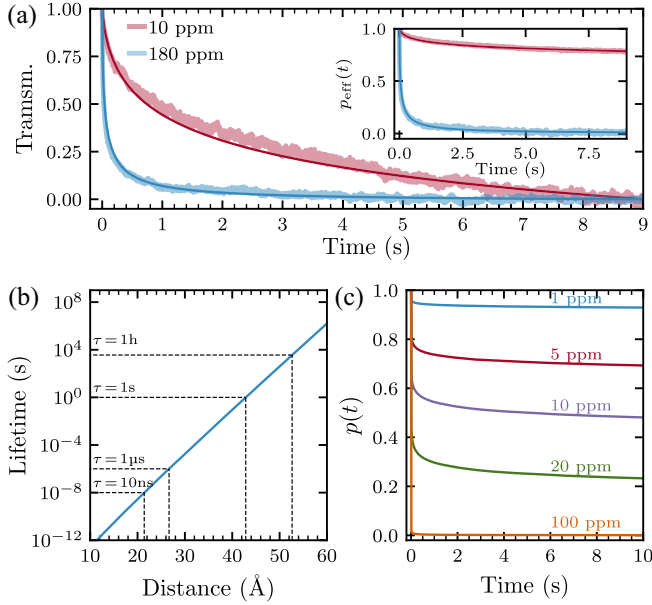


FIG. 3. (a) Simultaneous fit of the empirical tunneling model (thin solid lines) to the experimental decay curves at $T = 10$ K (thick blurry lines) for 10 and 180 ppm nitrogen concentrations. Both datasets are normalized such that the prepump population is one and the value at 9 s is zero. Inset: Same data plotted on an absolute scale, with experimental curves rescaled to match the predicted population difference. (b) Calculated tunneling lifetime $\tau = 1/\Gamma$ as a function of NV-N separation at $T = 0$ K. (c) Time evolution of the relative NV^0 population $p(t)$ at $T = 0$ K for different N concentrations (1–100 ppm), following a single-pulse ionization.

While the extracted parameters provide only a rough estimate, we assume that they capture the core aspects of the tunneling process and use them to determine the associated relaxation lifetimes. Figure 3(b) shows the calculated tunneling lifetime $\tau = 1/\Gamma$ as a function of NV-N separation at $T = 0$ K. The lifetime increases rapidly with distance, reflecting the strong exponential sensitivity of the tunneling process. According to our model, tunneling occurs on the nanosecond timescale when N donors lie within 20 Å of an NV center but reaches hours if the separation is above 50 Å. Such rapid decay at NV-N separations up to 20 Å qualitatively aligns with the estimate in Ref. [8], which suggests that NV^- centers appear dark if a positively charged N defect is within 12 Å, due to electron tunneling from the excited state of NV^- to a nearby N^+ center. Although the underlying process differs, the energy released by tunneling from NV^- to N^+ is also on the order of 1 eV, and the electron-phonon interaction strength is expected to be of similar magnitude due to the involvement of a charge state change of the N defect.

Figure 3(c) displays the theoretical prediction for how the relative fraction of NV^0 centers evolves over time at $T = 0$ K for N donor concentrations of 1, 5, 10, 20, and 100 ppm, assuming a single short-pulse ionization

[Eq. (5)]. On a linear scale, the decay dynamics exhibit two distinct regimes: an initial rapid decrease in $p(t)$, followed by a much slower decay, a characteristic behavior also observed in our experimental measurements with a finite pre-pump time. For the nitrogen concentrations considered here, the slow-decay regime can extend over several seconds. For example, at 10 ppm, the model predicts that $p(t)$ remains above 0.48 even after ten seconds. At higher nitrogen concentrations, charge equilibration happens much faster: at 20 ppm, the population drops to 0.23 after 10 s, while at 100 ppm, it falls below 1% [$p(t) = 0.001$] in less than 100 ms. At lower nitrogen concentrations, charge equilibration slows down significantly. For the 1 ppm case, our model predicts that only 11% of the population recovers after one hour [$p(t) = 0.89$].

Our combined experimental and theoretical analysis identifies electron tunneling between N donors and NV centers as the primary mechanism governing charge-state equilibration in ensembles. The results provide a quantitative basis for predicting and controlling NV charge stability and establish an experimental protocol for directly probing defect-defect charge transfer. Future research could explore how surface-induced band bending alters defect energetics and tunneling rates, particularly in sensing applications where NV centers are deliberately positioned near the surface. Achieving a comprehensive understanding of NV charge stability will also involve analyzing how other deep dopants in diamond influence these dynamics and how charge transfer among dopants (such as the movement of positive charge among nitrogen centers) alters the local charge environment. Our framework should also be applicable to other deep-level defects in wide-bandgap materials, especially in regimes where carrier interaction with the bands is suppressed and tunneling governs charge migration.

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Data availability—The data that support the findings of this article are available upon reasonable request.

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