

Optical Absorption of N-Doped Diamond

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This paper presents calculations of the color of diamond as a function of the type of nitrogen impurities. For this purpose we use a combination of ground-state density functional theory and Bethe-Salpeter equation calculations. Experiment shows that nitrogen is the main component for impurities in diamond and may be the cause of yellow or green color, depending on the nitrogen concentration. Here we discuss the color evolved by the following structures: one nitrogen dopant, A-center, B-center, and N3-center nitrogens. Our simulation suggest that the N2-V0 (or N2-defect) structure contributes to the yellow color of a diamond.

I. INTRODUCTION

Diamonds are highly coveted in the jewelry and industries, in particular, recent interest has arise in color diamonds. Although pure diamond is transparent, natural and synthetic diamond can range from violet to red. Both pure and colored diamonds are created in high temperature and high pressure environments.^{2,3} The origin of these colors resides in the selective absorption of certain light frequencies. In pure diamonds, all incident light is transmitted through whereas, in colored ones, light is absorbed at given frequencies. Defects and impurities in the crystal lattice cause these absorptions. The most common impurities are boron and nitrogen while the most common defects are vacancies. The substitution of a carbon atom with nitrogen provides the system extra electrons that are coupled to the impurities but decoupled from the system. Thus, for these structures, there could be absorption at low energy states which lies within the visible range, resulting in colored diamonds.

Experimental results show that boron and nitrogen impurities produce blue- and yellow-colored diamonds, respectively.^{1,2,4} Theoretical results reproduce the experiment by predicting that boron doping results in a dark blue colored diamond.⁵ However, the atomistic origin of color in yellow diamonds is still unknown.⁶ Collins suggested that yellow diamonds may have N2 centers (i.e. two nitrogen with a bond in the diamond) and N3 centers (i.e. three nitrogen surrounding a vacancy in the diamond) impurity systems.⁷ Therefore, we have decided to explore various diamond structures with nitrogen and/or vacancy defects. This paper presents an approach using Density Functional Theory (DFT) and Bethe Salpeter Equation calculations (BSE) in search of a structure that produces a yellow-colored diamond.

II. THEORY AND CALCULATION

A. Theory

In this project, light absorption was simulated with a combination of Density Functional Theory (DFT) and the Bethe-Salpeter Equation (BSE). The BSE, with electron-hole interaction and screened Coulomb interaction many body effects produces $\epsilon_2(\omega)$, the imaginary part of dielectric constant $\epsilon(\omega)$:⁸

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (1)$$

In the BSE approximation, $\epsilon_2(\omega)$ is

$$\epsilon_2(\omega) = -4\pi\text{Im} \left[\left\langle P \left| \left(\frac{1}{\omega - H_{eff} + i\eta} \right) \right| P \right\rangle \right] \quad (2)$$

where P is the polarization operator, H_{eff} is the effective Hamiltonian, and η is the energy broadening parameter.⁹ ϵ_1 can be obtained similarly:

$$\epsilon_1(\omega) = -4\pi\text{Re} \left[\left\langle P \left| \left(\frac{1}{\omega - H_{eff} + i\eta} \right) \right| P \right\rangle \right] + 1 \quad (3)$$

BSE calculations require wavefunctions and density data from DFT calculations. These are obtained from the Kohn-Sham equations and Hamiltonian for DFT:¹⁰

$$\left\{ -\frac{1}{2}\nabla^2 + [\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))] \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (4)$$

where $-\frac{1}{2}\nabla^2$ is the kinetic energy, $\varphi(\mathbf{r})$ is the Coulomb potential, $\mu_{xc}(n(\mathbf{r}))$ is the exchange correlation energy.

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \quad (5)$$

The density, $n(\mathbf{r})$ could be obtained by calculating the wavefunction $\psi_i(\mathbf{r})$.

$$\varphi(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d(\mathbf{r}') \quad (6)$$

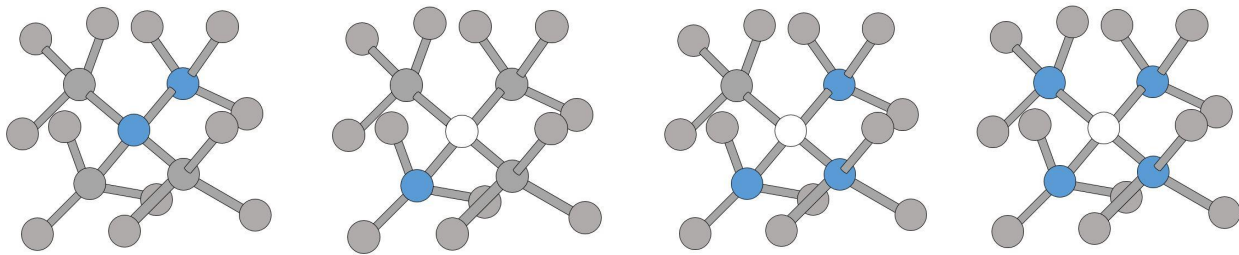


FIG. 1: Schematic diagram of defected structures. The gray sphere stands for a carbon atom, blue stands for nitrogen atom, and the white stands for a vacancy. From left to right: N2-V0, N1-V1, N3-V1, N4-V1

$\varphi(\mathbf{r})$ is the sum of $v(\mathbf{r})$, the potential, and the interaction potential between electrons. The Hamiltonian for calculating DFT is the following:

$$E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + G[n] \quad (7)$$

$$G[n] \equiv T_s[n] + E_{xc}[n] \quad (8)$$

where $v(\mathbf{r})$ is the potential, $T_s[n]$ is the kinetic energy, and $E_{xc}[n]$ is the exchange correlation energy. With $E_{xc}[n]$ approximated by the local density approximation (LDA):

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}[n(\mathbf{r})]d\mathbf{r} \quad (9)$$

Using ϵ_2 and ϵ_1 , we calculated the intensity, i_T

$$i_T = (1 - r(\omega))e^{-\mu D} \quad (10a)$$

$$\mu(\omega) = 2\frac{\omega}{c}\kappa(\omega) \quad (10b)$$

$$n(\omega) + i\kappa(\omega) = \epsilon(\omega)^{\frac{1}{2}} \quad (10c)$$

where $r(\omega)$ is the reflectivity, D is the thickness of the diamond, and $n(\omega)$ is the index of refraction.⁸ Finally, using this intensity, we rendered RGB color values from the spectra.

B. Computational Details

1. Optimization of Structure of Models

All optimizations were performed with VASP¹¹ using a $2 \times 2 \times 2$ k-point grid and the PBE functional. The simulations used PAW potentials as well as a plane wave cutoff of 755 eV. Initial structures were obtained by doubling the conventional 8-atom cell of diamond in every direction, resulting in a cubic simulation cell of 64 atoms and 7.1336 Å sides. The initial conformations for the different defect models were generated by simply substituting a C atoms for an N atom to create an impurity, or by removing a C atoms to generate a vacancy.

We optimized and investigated the following structures: one nitrogen with near-neighbor vacancy (N1-V1), N3 structure (N3-V1), B-center nitrogen (N4-V1), and two nitrogens without vacancy (N2-V0). The initial supercell of a pure diamond had 64 atoms with bond length of 1.544 angstrom between carbon atoms. The structure are shown in Figure 1. We replaced a carbon atom in the center of the supercell and removed one of the nearby carbon atom for a N1-V1 system. For N3-V1, we removed a carbon atom in the center of the supercell and replaced three of the nearby carbon atoms with nitrogen atoms. Similarly, we created a N4-V1 system by removing a carbon atom in the center of the supercell but replaced all four near-neighbor carbon atoms with nitrogen atoms. Lastly, we created a N2-V0 system by replacing two neighbor carbon atoms near the center of the supercell with nitrogen atoms. Then we allowed all the impurity structures to relax. The supercell was fixed but the bond length and position of atoms were allowed to change.

2. Optical Spectrum

Our main program for calculation is AI2NBSE which is a combination of ABINIT and NBSE.¹² ABINIT calculates the ground state wavefunction and density whereas NBSE solves the Bethe-Salpeter equation.¹³⁻¹⁵ In each calculation for an optimized structure, the size of the supercell is 64 atoms with k-point grid of $4 \times 4 \times 4$ or 63 atoms (if there is a vacancy), potential cutoff at 12 Hartree, and LDA (Troullier-Martins) pseudopotential for carbon and nitrogen atoms.

3. Color Simulation

Diamond color simulations were done with Diam-Calc by using the optical absorption spectrum from AI2NBSE¹⁶. These simulations used a Tiffany diamond (128.54 carats or 25.108g). If the color simulated was too dark, the ordinates can be multiplied to get a less absorbing diamond.

Structure	Bond	Bond Length (Å)	Deviation (Å)
Pure Dia.	C-C	1.544	0
N1-V1	C-N	1.481	-0.063
	C-C(N)	1.554	+0.010
	C-C(N)	1.536	-0.008
	C-C(V)	1.486	-0.058
	C-C(V)	1.502	-0.042
N3-V1	C-N	1.478	-0.066
	C-N	1.485	-0.059
	C-C(N)	1.547	+0.003
	C-C(N)	1.552	+0.008
	C-C(V)	1.486	-0.058
N4-V1	C-N	1.476	-0.068
	C-C(N)	1.554	+0.010
N2-V0	N...N	2.188	+0.644
	C-N	1.448	-0.096
	C-C(N)	1.560	+0.016
	C-C(N)	1.519	-0.025

TABLE I: Table of optimization effects in the structures for our AI2NBSE calculations. (‘-’ stands for bond between two atoms, ‘()’ stands for second degree bond of the atom, ‘...’ stands for a broken bond between the two atom)

III. RESULTS / DISCUSSION

A. Defect Structures

Every modification to the initial state (pure diamond) has a varying effect on the bond length between the atoms. Table I shows the bond lengths between atoms of different structures after optimization. In all cases, everything beyond the second shell essentially did not change. In the N1-V1 and N3-V1 structure, the bond length between carbon and nitrogen bond decreased and the bond length between carbon atoms that are next to the vacancy decreased. In the N2-V0 structure, the bond between the two nitrogen atoms broke apart and the distance between the two atoms increased, resulting in a more flat tetrahedron structure between the nitrogen and its neighboring carbon atoms. Although, we only dealt with optimization of a 64-atom supercell in some cases, we optimized a 63-atom supercell and a 215-atom supercell for the N4-V1 structure. The number of atoms is significantly different but the local structure around the defect is very similar. In both cases, the bond length between carbon and nitrogen atom decreases and the next nearest bond (carbon-carbon) slightly increases by the same amount. These resulting optimized structures were used in AI2NBSE.

B. Density of States

Figure 2 shows the density of states of our N-doped diamond structures of non-interacting case. Compared to pure diamond, there are transitions at lower frequencies. In N2-V0, transition can occur from the middle peak at

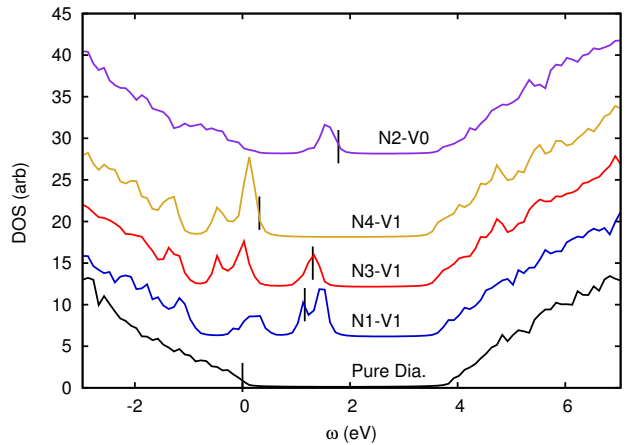


FIG. 2: Density of states of various structures; vertical line represents the highest occupied state in a system; data sets have been shifted along the y axis for clarity

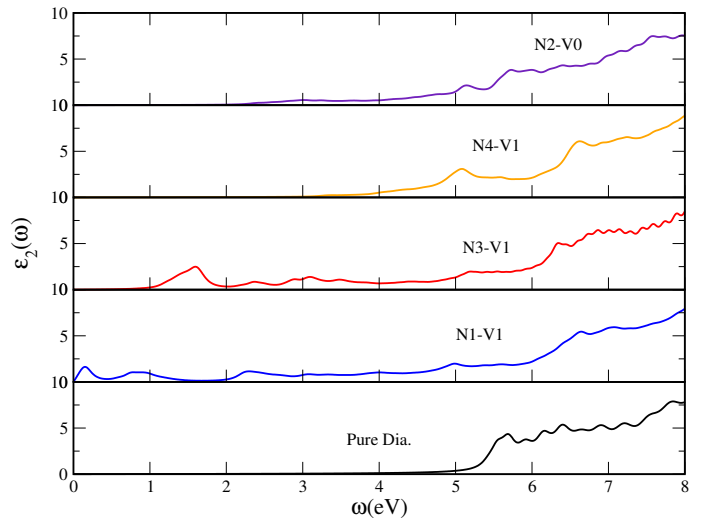


FIG. 3: Calculated $\epsilon_2(\omega)$ with various combination of nitrogen and vacancy. Included a pure diamond calculation for comparison from 0 to 8 eV.

about 1.8 eV to the unoccupied states starting around 4 eV. Therefore, it is expected that there would be some absorption around 2.2 eV. For N4-V1, the smallest possible transition is from around 0.3 eV to 4 eV. N3-V1 is half occupied in its peak at around 1.3 eV. There will be transition from 1.3 eV the half occupied state to an unoccupied state at 4 eV or higher and from other occupied states to the half occupied state at 1.3 eV. In that case, the lowest possible transition would be from 0 eV to 1.3 eV. Lastly, N1-V1 have a very small transition from 1.2 eV to 1.6 eV and a larger transition from 1.2 eV to other unoccupied state starting around 4 eV.

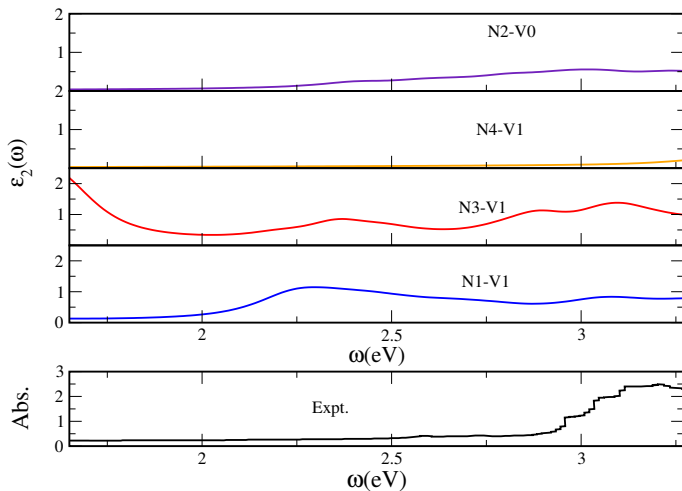


FIG. 4: Calculated $\epsilon_2(\omega)$ with various combination of nitrogen and vacancy with experimental data¹⁷. Note that the experimental data is absorption rather than $\epsilon_2(\omega)$

C. Optical Absorption

Figure 3 shows the optical absorption spectra we obtained in AI2NBSE for interacting cases. Therefore, there is difference between the density of states and the optical absorption spectra. For example, we start to see absorption around 5 eV for pure diamond whereas in the density of state shows transition from 0 eV to 4 eV. Although that is the case, we still know around where transitions are located and if the system has a low energy transition or absorption using the non-interacting density of states. Figure 4 shows only the visible range of the optical absorption spectra. Pure diamond between 1.65 eV and 3.27 eV has zero absorption so we did not include it in Figure 4. The transitions mentioned in density of state section are evident in these figures. There is absorption starting around 2.2 eV in the N2-V0 case, 3.25 eV in N4-V1, and 2.3 eV in N1-V1. In N3-V1, there is absorption in < 1 eV along with multiple absorption in different energies in the visible range due to the half occupied state.

D. Color Simulation

Figure 5 shows the diamond simulation from data obtained from AI2NBSE.¹⁶ N2-V0 is the closest match to a yellow colored diamond. N1-V1 produced a dark red/pink color, N3-V1 produced a brown diamond, and N4-V1 is transparent. Referring back to Figure 4, violet and blue light is absorbed when green, orange, yellow, and red light is transmitted. Green and red light will mix to form an orange-yellow colored diamond. Therefore, we will see the diamond as orange-yellow.

We suspect that there are two limitations in a 64-atom supercell which may result in an inaccurate approxima-

tion of a physical yellow diamond. The nitrogen impurity to number of atoms ratio is too large. In the smallest ratio case, it is one nitrogen in a 63-atom supercell whereas nitrogen impurity of a real diamond is ppm (parts per million).¹⁸ Secondly, there might be multiple impurities in a real-colored diamond. Due to the limitations of a 64-atom supercell, we could not place two different impurity structures in the supercell without having interaction between them.

Furthermore, the range for yellow color is small (i.e. 565 - 590 nm or 2.19 to 2.10 eV). Therefore, many factors can affect the color simulation significantly. The thickness D , can affect the result dramatically (see equation 7): too small of a distance would allow all light to be transmitted, too large would allow no light to be transmitted. The number of points in the data we have in the visible spectrum can also have an effect in its color. A small set of data points has a much larger error due to its estimation between the data points.

IV. CONCLUSIONS

In this project, we investigated various nitrogen defect diamond structures including: N2-V0, N1-V1, N3-V1, and N4-V1. Vacancies in diamond, according to our calculations, are not contributing to yellow colored diamond. The closest candidate for producing a yellow colored diamond within the four structures we have presented in this paper is N2-V0, the di-nitrogen center diamond without vacancy. Furthermore, color is very sensitive to impurities. And this project further proves that it is feasible to do these optical spectra calculation in solid.

In this paper, we have not looked into one of the most common nitrogen defect in yellow-colored diamond: single nitrogen doped diamond (N1-V0). But, we plan to address this in future work. Furthermore, we will also look into one vacancy defected diamond (N0-V1) to see how does vacancy affect the color of a diamond.

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FIG. 5: Diamond color simulations using a Tiffany diamond model of 110 cts with absorbance divided by 10. From left to right: N2-V0, N1-V1, N3-V1, N4-V1¹⁶

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