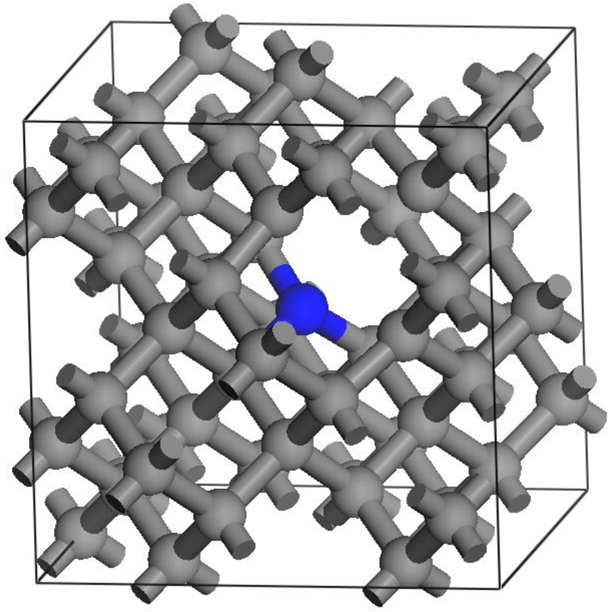
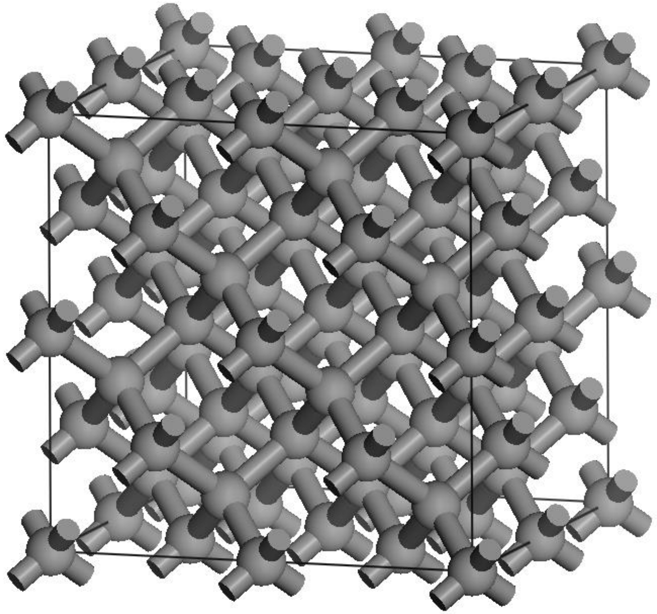
Optical Absorption of N-Doped Diamond

Presentation by: Winnie H. Liang

INT REU: University of Washington





Outline

- Motivation
- Introduction
  - Absorption + Colors
  - Goal
  - AI2NBSE
- Nitrogen Doped Diamond Structures
- Results
- Conclusion

Motivation

Diamonds…

- are fascinating
- (natural) are formed in lithospheric mantle (high temperature and pressure)
- One of the hardest material on Earth

Colored Diamonds

- can be rare and expensive

R. W. Carlson, The Mantle and Core, Elsevier, (2005).
Erlich, E.I.; Dan

W. Hausel, *Diamond Deposits*. Society for Mining, Metallurgy, and Exploration. , (2002).

Blue Diamond
(Hope Diamond)

F. Farges, J. Vinson, J. J. Rehr, J. E. Post, Europhysics
News 43(1), 20 (2012).

What about yellow colored diamond?

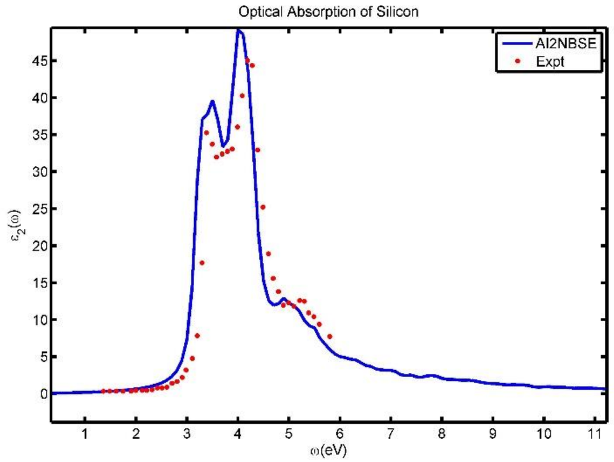
Absorption in Light

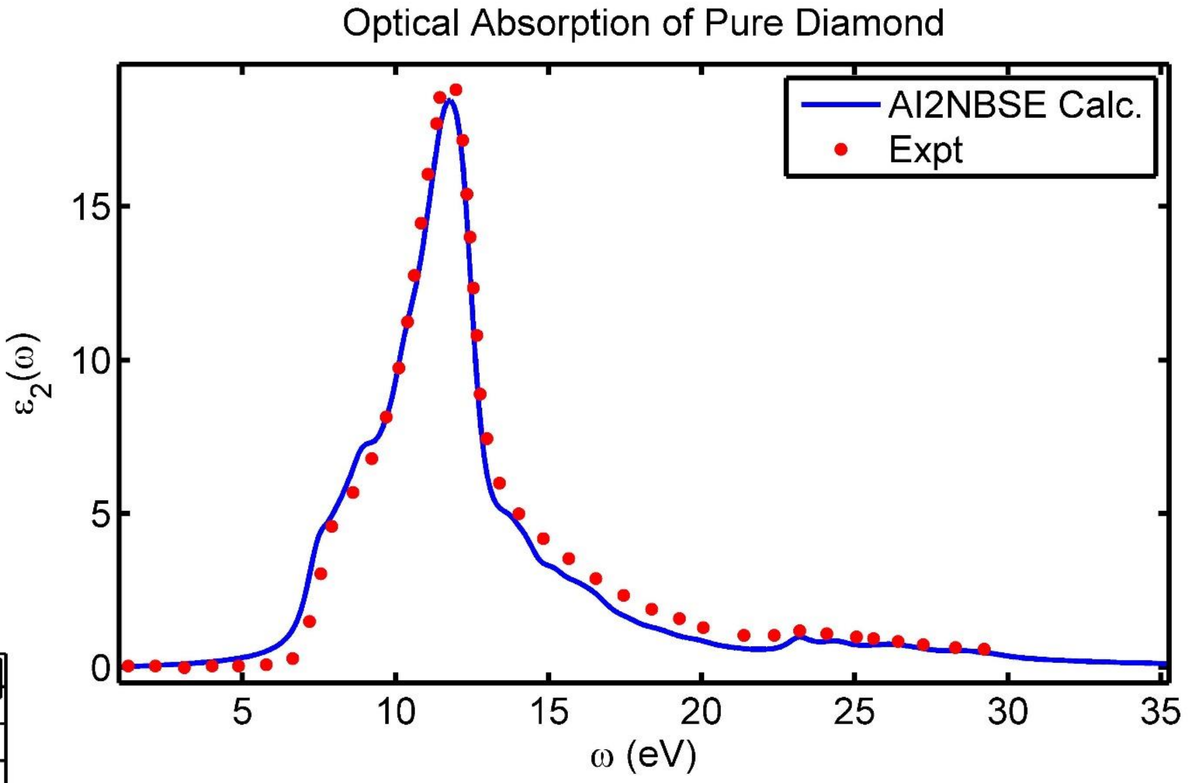
Dielectric constant

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

Relates to index of refraction

Relates to absorption





High level of correspondence is only possible with most recent code.

H. M. Lawler, J. J. Rehr, F. Vila, S. D. Dalosto, E. L. Shirley and Z. H. Levine, Phys. Rev. B 78, 205108 (2008).

Absorption

Dielectric constant

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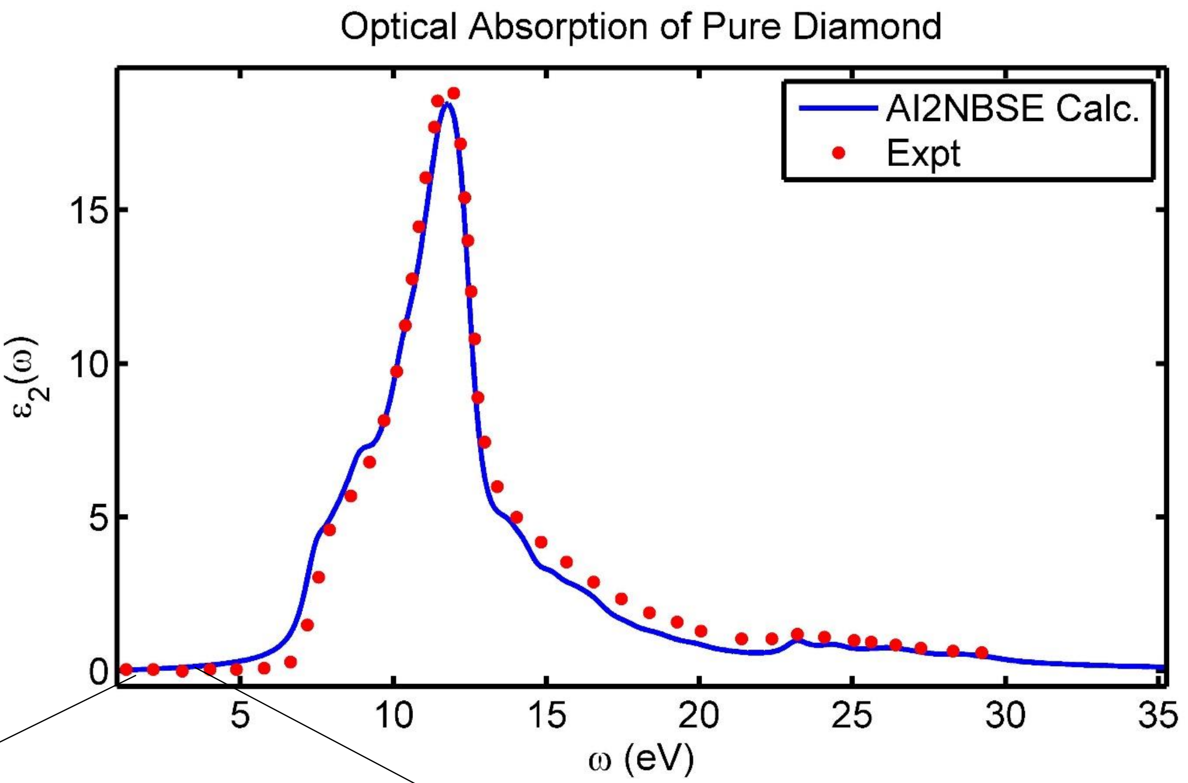
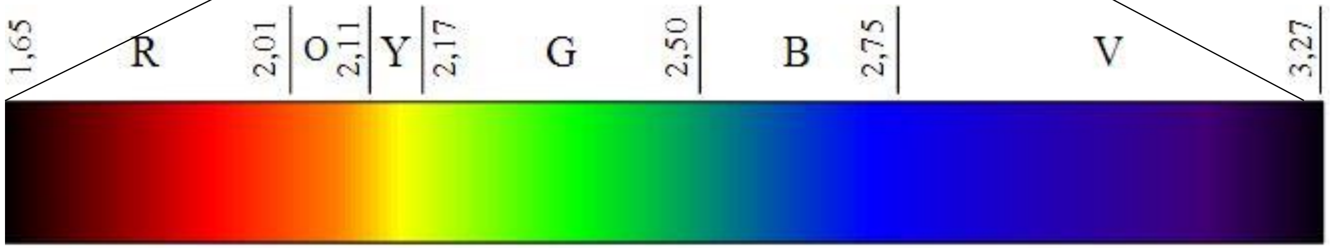




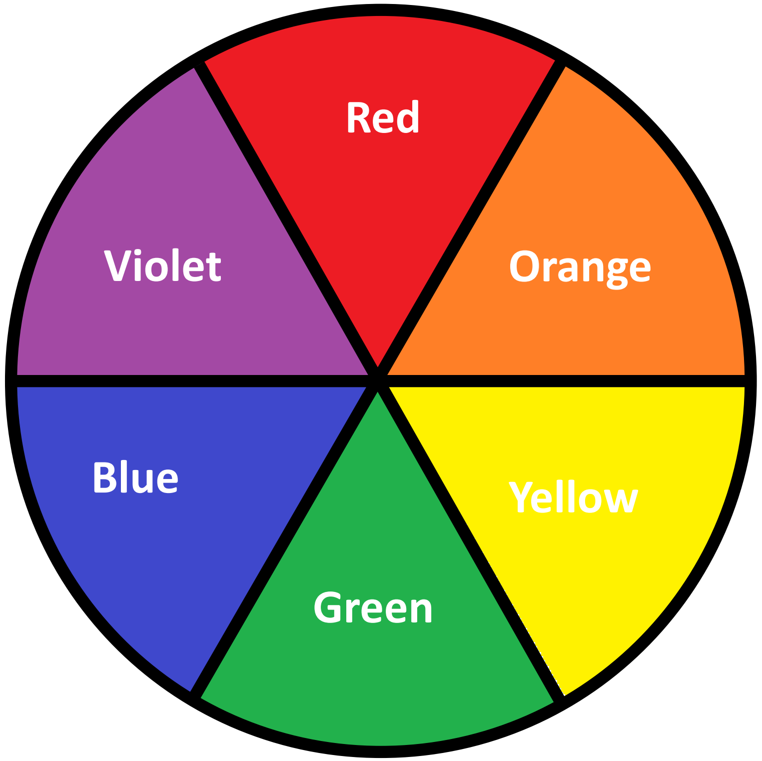
Spectrum from : http://upload.wikimedia.org/wikipedia/commons/7/7f/Colors_in_eV.svg

H. M. Lawler, J. J. Rehr, F. Vila, S. D. Dalosto, E. L. Shirley and Z. H. Levine, Phys. Rev. B 78, 205108 (2008).

Goal of the project

- Determine the structure that produces yellow diamond and calculate the color

Yellow Diamond Figure from:
http://www.scarselli.com/?page=search&cat=diamonds



The AI2NBSE Program

- First step: ABINIT
  - Ground state density functional theory (DFT) calculations
- Second step: NBSE (by NIST)
  - Bethe Salpeter equation (BSE) calculation
  - Accurate many body theory for excited state

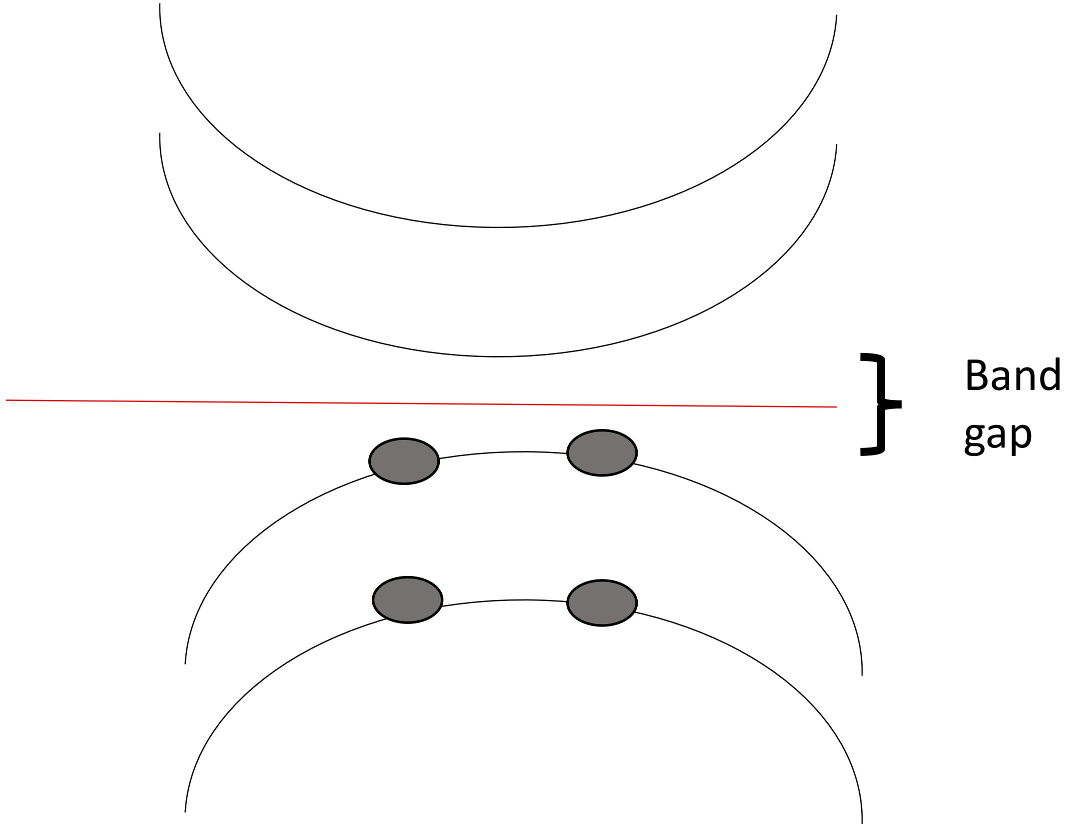
H. M. Lawler, J. J. Rehr, F. Vila, S. D. Dalosto, E. L. Shirley and Z. H. Levine, Phys. Rev. B 78, 205108 (2008).
X. Gonze *et al.*, Comput. Mater. Sci. **25**, 478 2002.
L. X. Benedict and E. L. Shirley, Phys. Rev. B **59**, 5441 1999

NBSE – Optical Response

Conduction Band

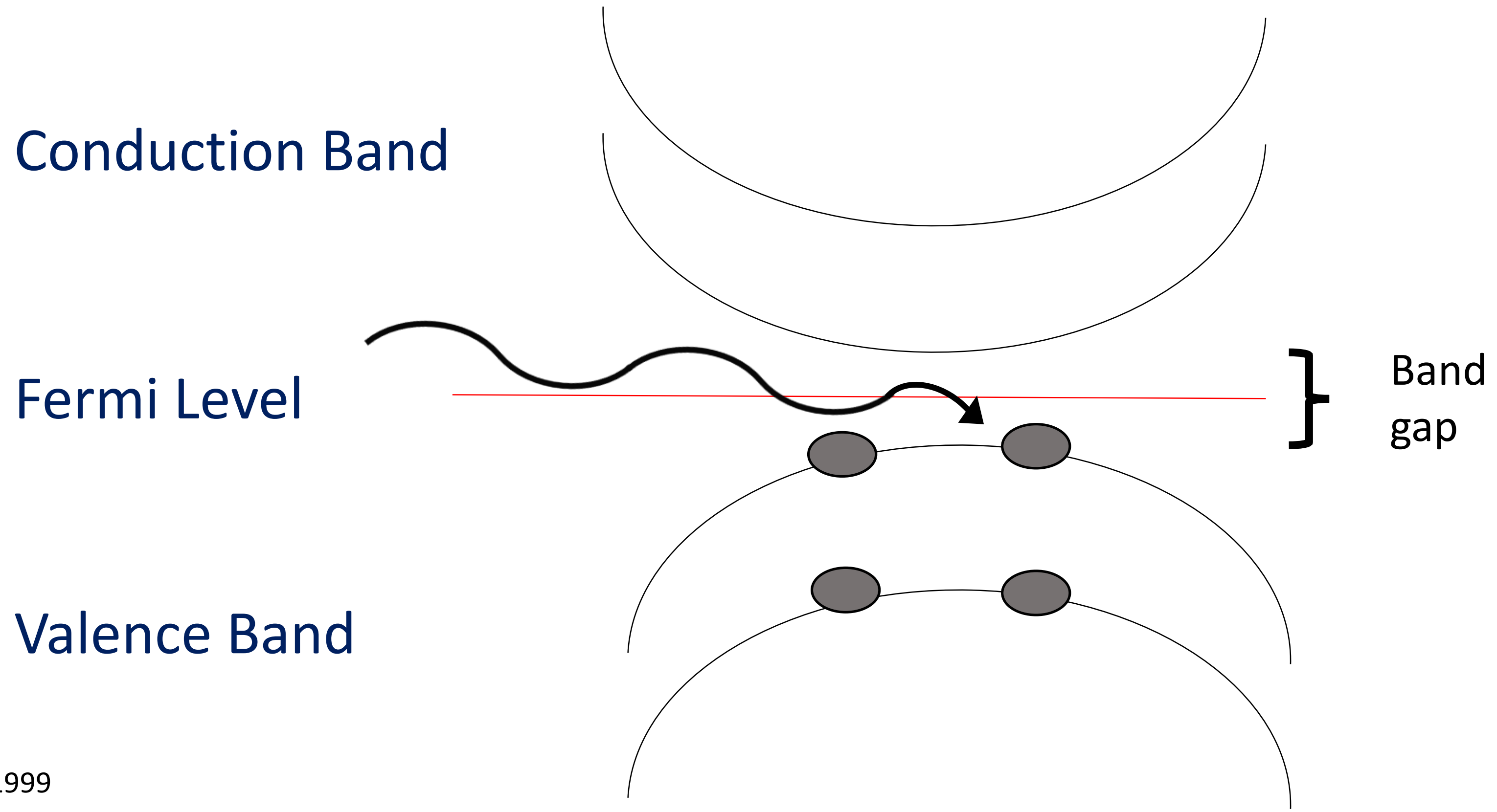
Fermi Level

Valence Band



L. X. Benedict and E. L. Shirley, Phys. Rev. B **59**, 5441 1999

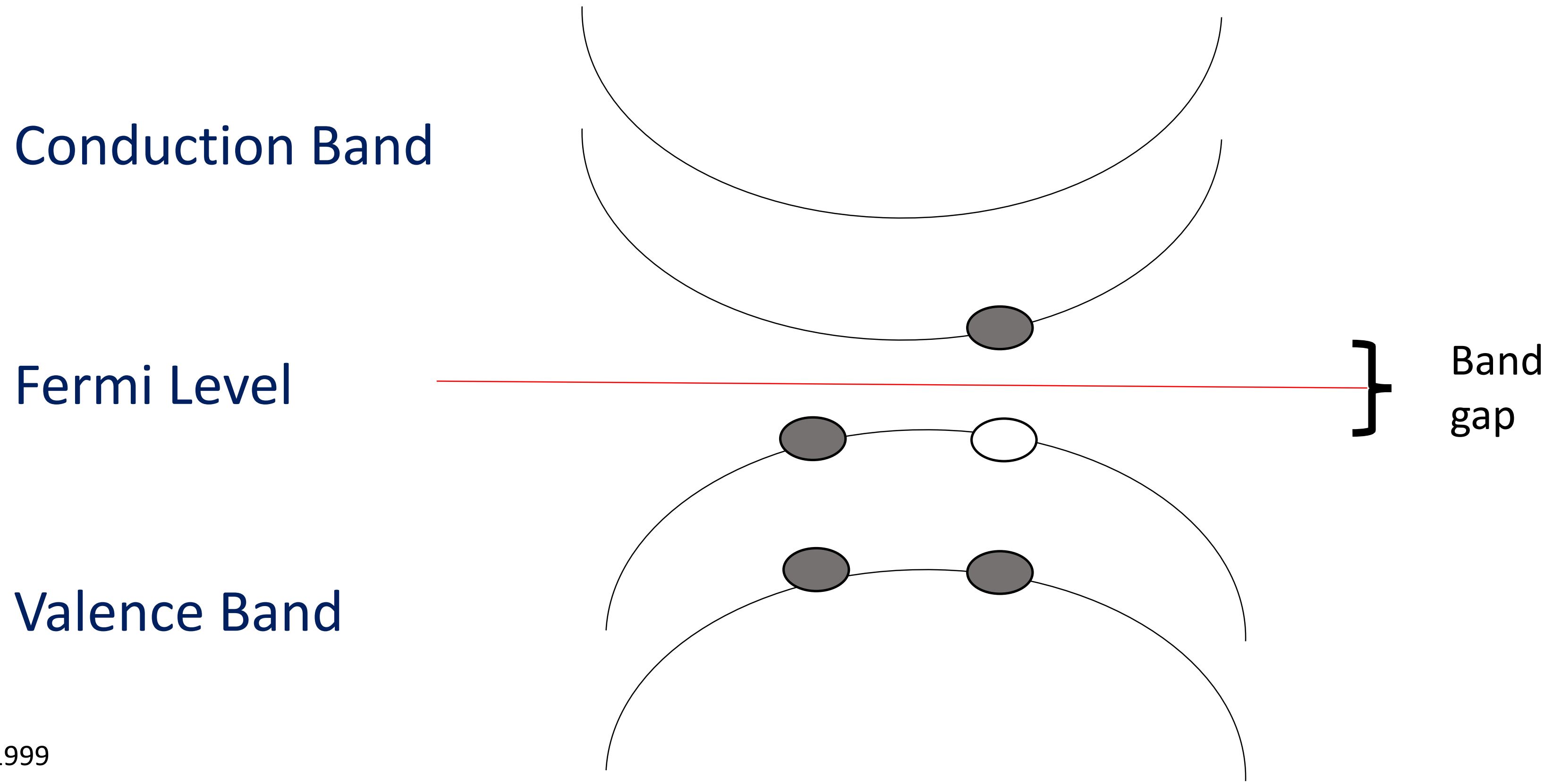
NBSE – Optical Response



L. X. Benedict and E. L. Shirley, Phys. Rev. B **59**, 5441 1999

NBSE – Optical Response

- Considers electron-hole interaction and screened Coulomb interaction



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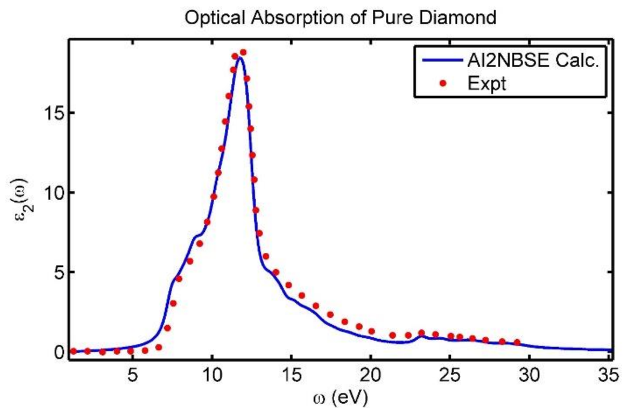

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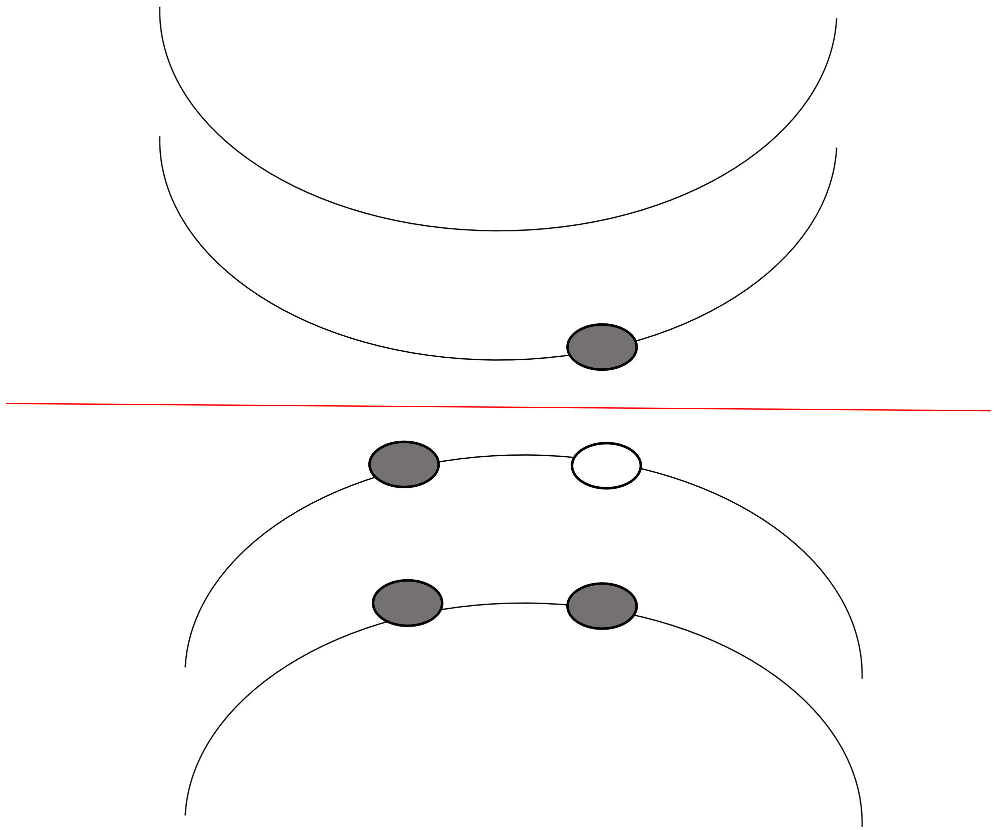


L. X. Benedict and E. L. Shirley, Phys. Rev. B **59**, 5441 1999

Structures

We know…

- Nitrogen exists in yellow-colored diamond

We are not sure…

- About the structure of yellow colored diamond

Candidate structures mentioned in literature are…

- N3 center (N3-V1) and N2 (N2-V0) defects (this study)

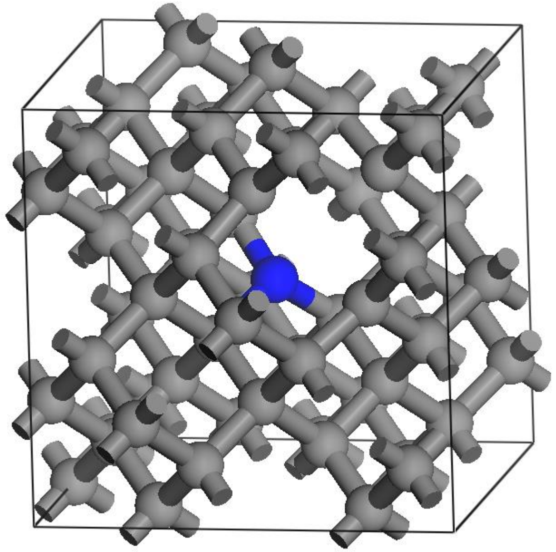
A. T. Collins, K. Mohammed 1982 J. Phys. C: Solid State Phys. 15 147 doi:10.1088/0022-3719/15/1/012

Future Work

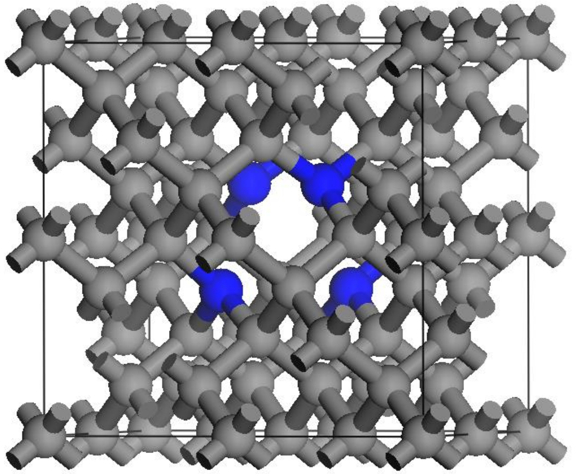
- N1-V0 and N0-V1

A. T. Collins 1982 *J. Phys. D: Appl. Phys.* **15** 1431 doi:10.1088/0022-3727/15/8/014
A. T. Collins, Diamond Related Materials Volume 8 Issues 8-9 (1455-1462), (1999)

Calculations -Structures

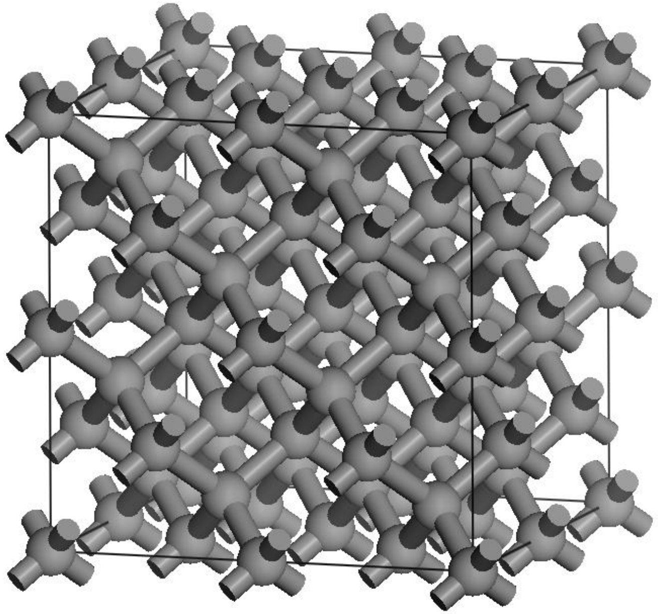


N1-V1



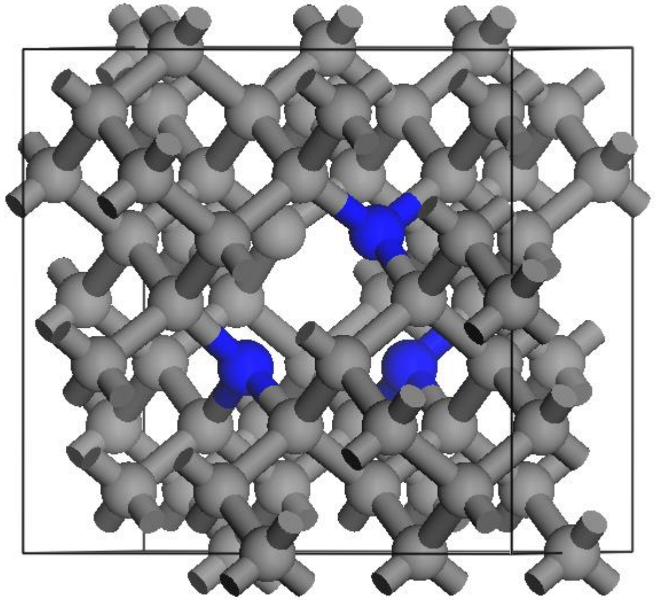
N4-V1

Pure Diamond

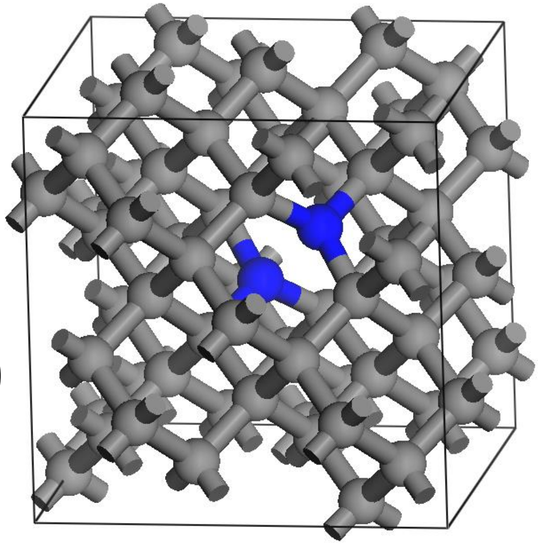


VASP: G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996)

N3-V1 (N3-center)

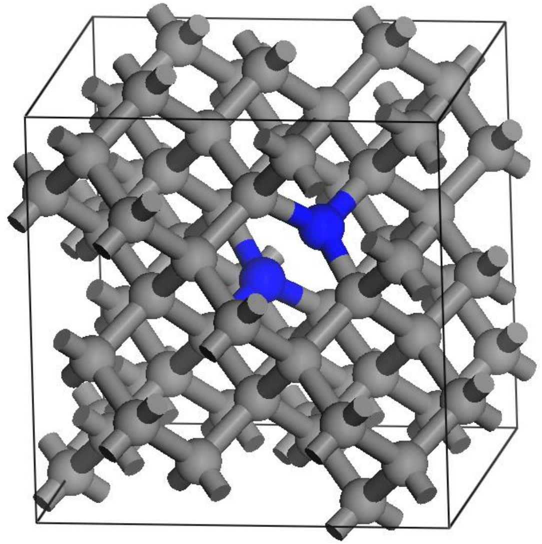


N2-V0 (N2 defect)



Optimized N-Defect Structures

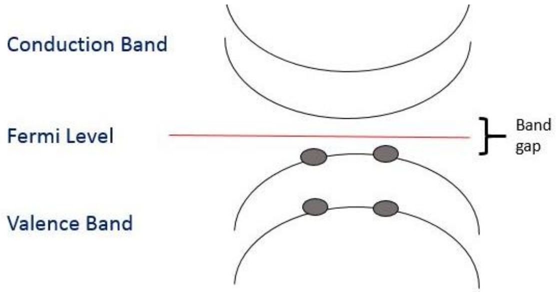
Structure	Bond	Bond Length (Ang.)	Deviation (Ang.)
Pure Dia.	C-C	1.544	0
N1-V1	C-N	1.481	-0.063
	C-C(N)	1.554	+0.010
	C-C(N)	1.536	-0.008
	C-C(V)	1.486	-0.058
	C-C(V)	1.502	-0.042
N3-V1	C-N	1.478	-0.066
	C-N	1.485	-0.059
	C-C(N)	1.547	+0.003
	C-C(N)	1.552	+0.008
	C-C(V)	1.486	-0.058
N4-V1	C-N	1.476	-0.068
	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

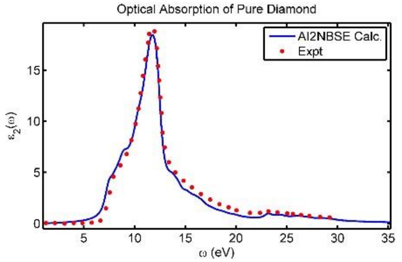


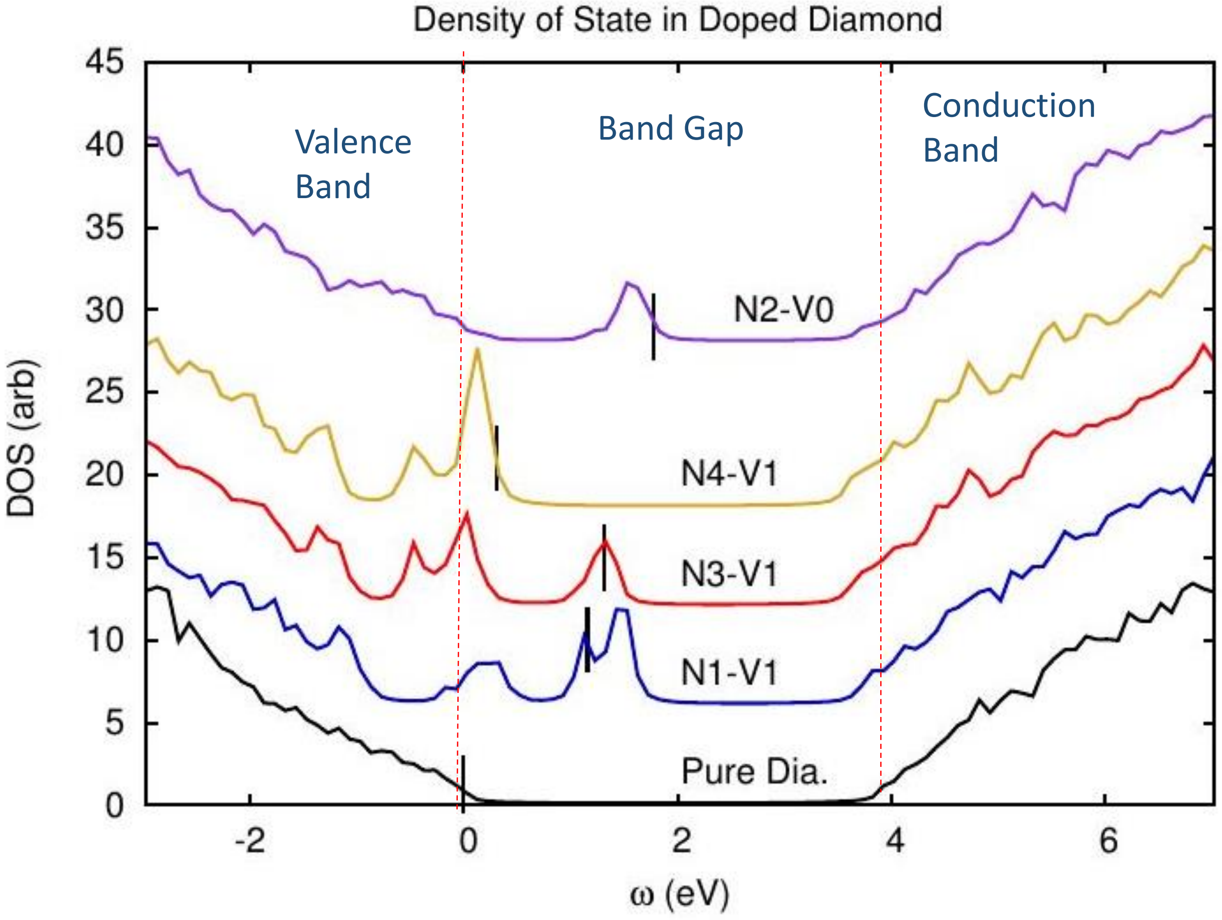
N2-V0

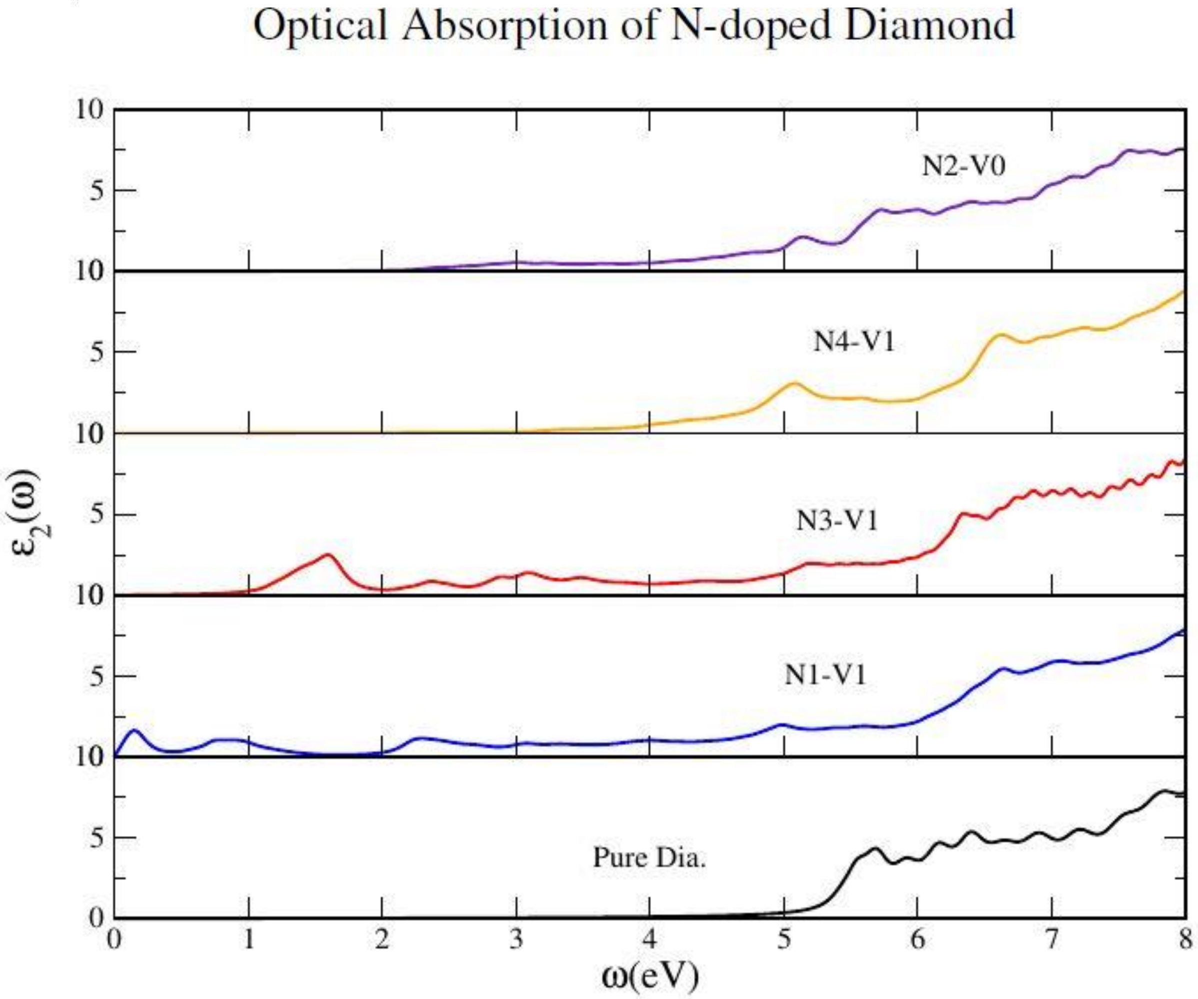
These defected structure only affected the bond length up to two shells.

Results





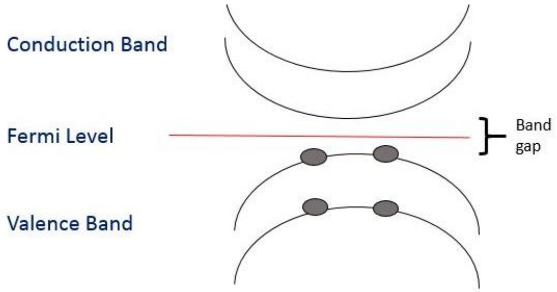


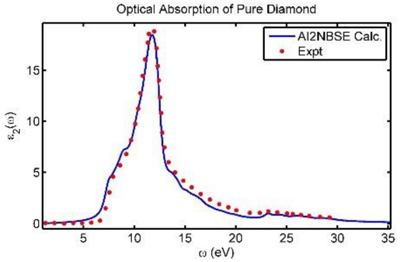


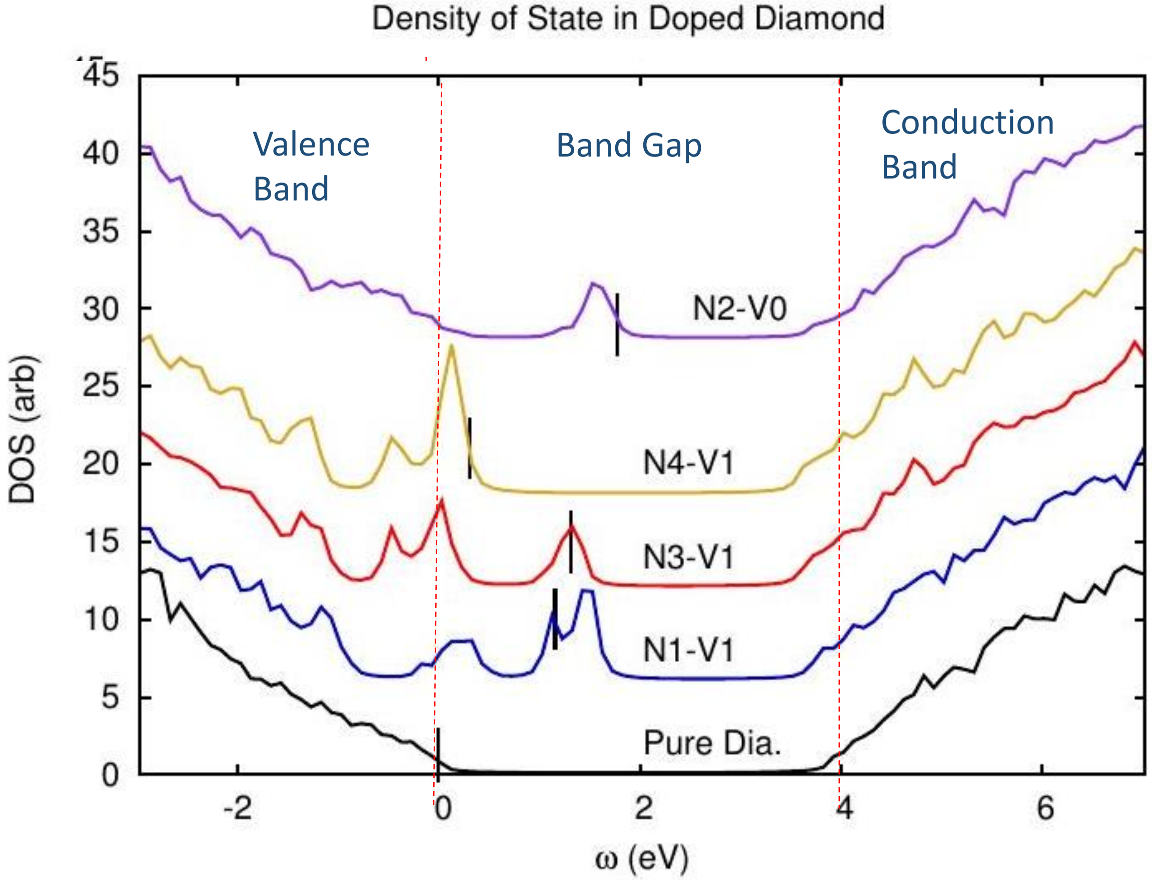
Density of state: # of states available at an interval of energy.

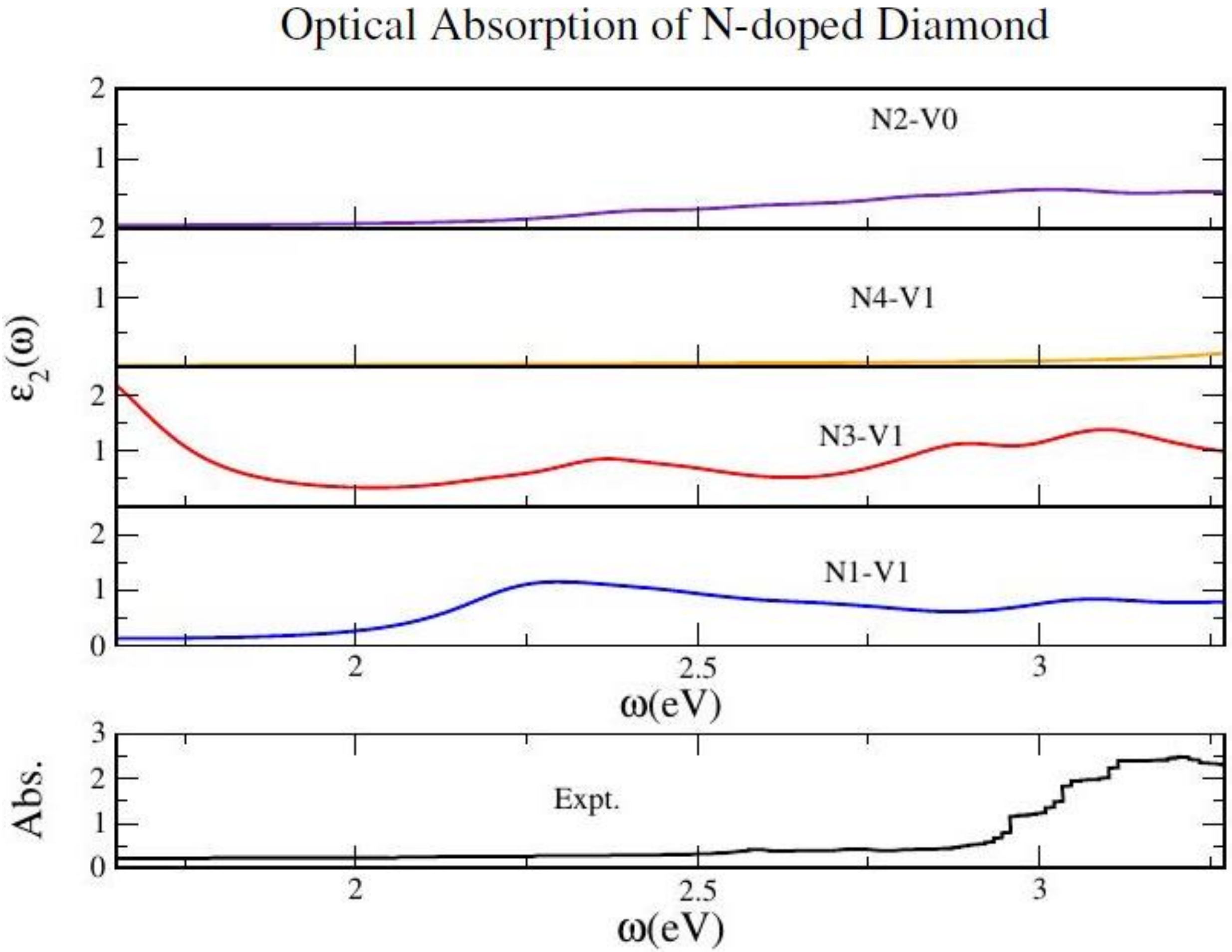
H. M. Lawler, J. J. Rehr, F. Vila, S. D. Dalosto, E. L. Shirley and Z. H. Levine, Phys. Rev. B 78, 205108 (2008).

Results









H. M. Lawler, J. J. Rehr, F. Vila, S. D. Dalosto, E. L. Shirley and Z. H. Levine, Phys. Rev. B 78, 205108 (2008).

Color Simulation

N1-V1

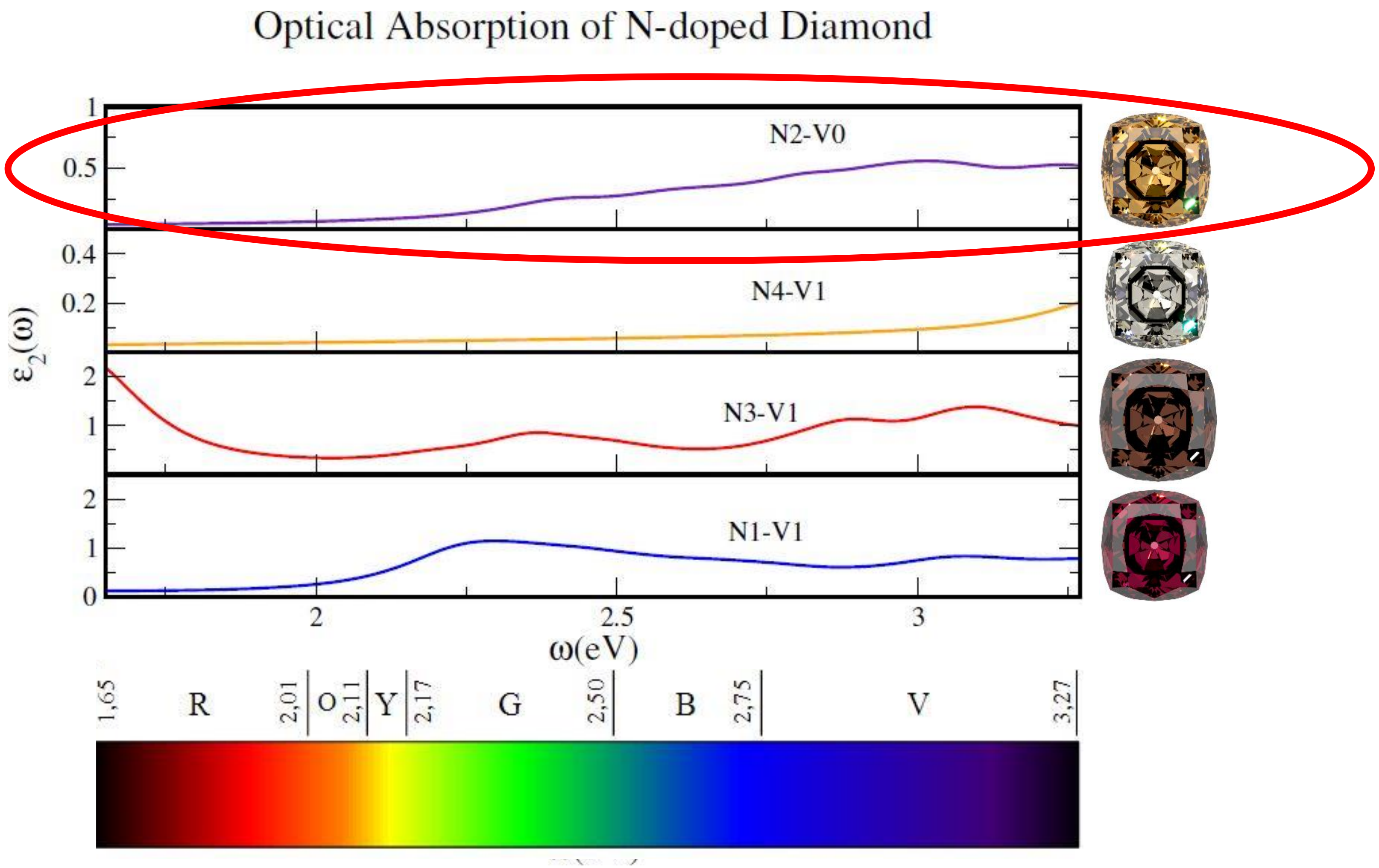
N2-V0

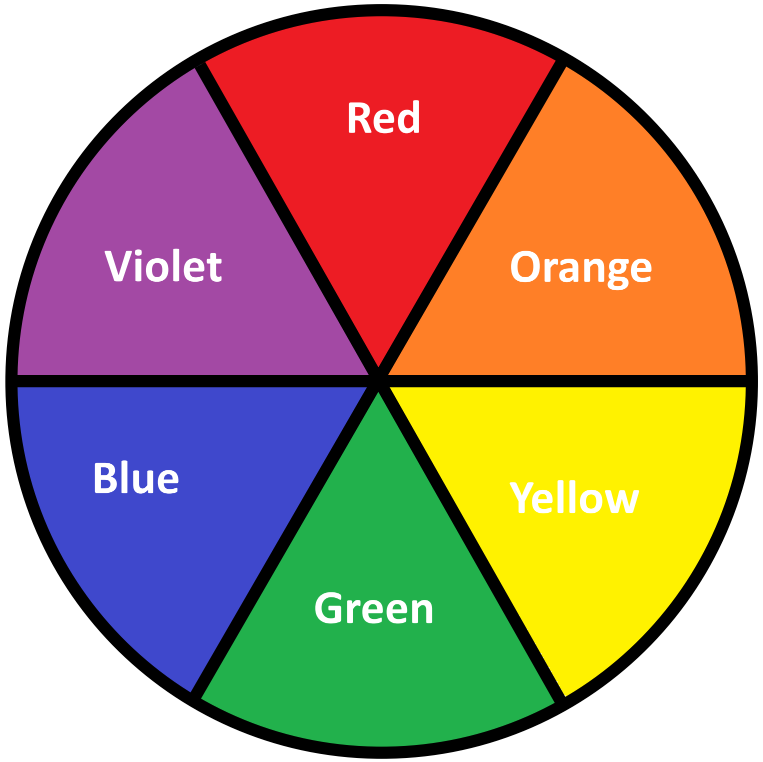
N4-V1

N3-V1

Diamond Simulations : F. Farges, Personal Contact

Color Simulation





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G. R. Rossman, Mineral Spectroscopy Server, California Institute of Technology

Diamond Simulations : F. Farges, Personal Contact
Figure: https://www.wou.edu/las/physics/ch462/tmcolors.htm

Conclusion

- Color is sensitive to impurities.
- Our simulation suggest that N2-V0 structure can produce a yellow colored diamond.
- AI2NBSE calculations of optimized defect structures are a promising tool for the study of optical spectra and color properties of diamonds.

Acknowledgement

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  - Prof. John J. Rehr
  - Dr. Fernando Vila
  - Dr. Joshua Kas
- Diamond Simulations
  - Prof. Francois Farges
- Rehr Group
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  - Egor Clevac
- REU Staff
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- This project was funded by NSF.

Questions?

ABINIT - SCF

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

$$G[n] \equiv T_s[n] + E_{xc}[n]$$

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

ABINIT - SCF

$$\int \delta n(\mathbf{r}) d\mathbf{r} = 0$$

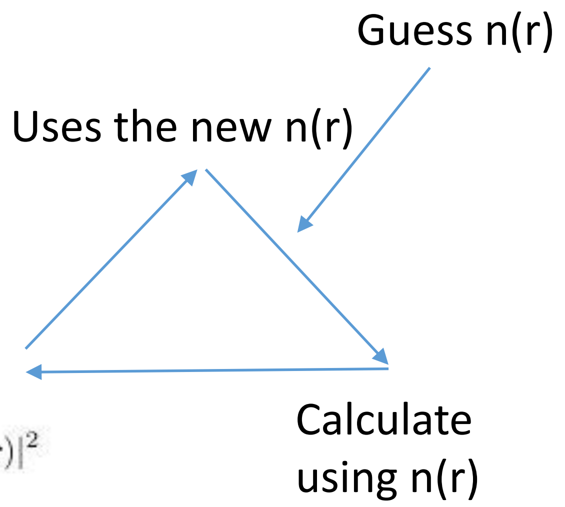
$$\int \delta n(\mathbf{r}) \left\{ \varphi(r) + \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \mu_{xc}(n(\mathbf{r})) \right\} d\mathbf{r} = 0$$

$$\varphi(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \qquad \mu_{xc}(n) = d(n\epsilon_{xc}(n))/dn$$

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

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

$$E = \sum_i^N \epsilon_i - \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} |d\mathbf{r} d\mathbf{r}' + \int n(\mathbf{r})[\epsilon_{xc}(n(\mathbf{r})) - \mu_{xc} n(\mathbf{r})] d\mathbf{r}$$



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

NBSE

- Considers electron-hole interaction and screened Coulomb interaction
- Calculates ε_2

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

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

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

Equations obtained from: L. X. Benedict, E. L. Shirley, Phys. Rev. B 58, (1999)

Result / Analysis

$\epsilon(\omega)$: dielectric const.

i_T : intensity

$r(\omega)$: reflectivity

$\mu(\omega)$: photon absorption coef.

$\kappa(\omega)$: imaginary part of index of refraction

$n(\omega)$: index of refraction

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

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

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

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

$$i_T = (1 - r(\omega))e^{-2\frac{\omega}{c}Im(\epsilon(\omega)^{\frac{1}{2}})D}$$

M. P. Prange, J. J. Rehr, G. Rivas, J. J. Kas, and John W. Lawson, Phys. Rev. B 80, 155110 (2009).

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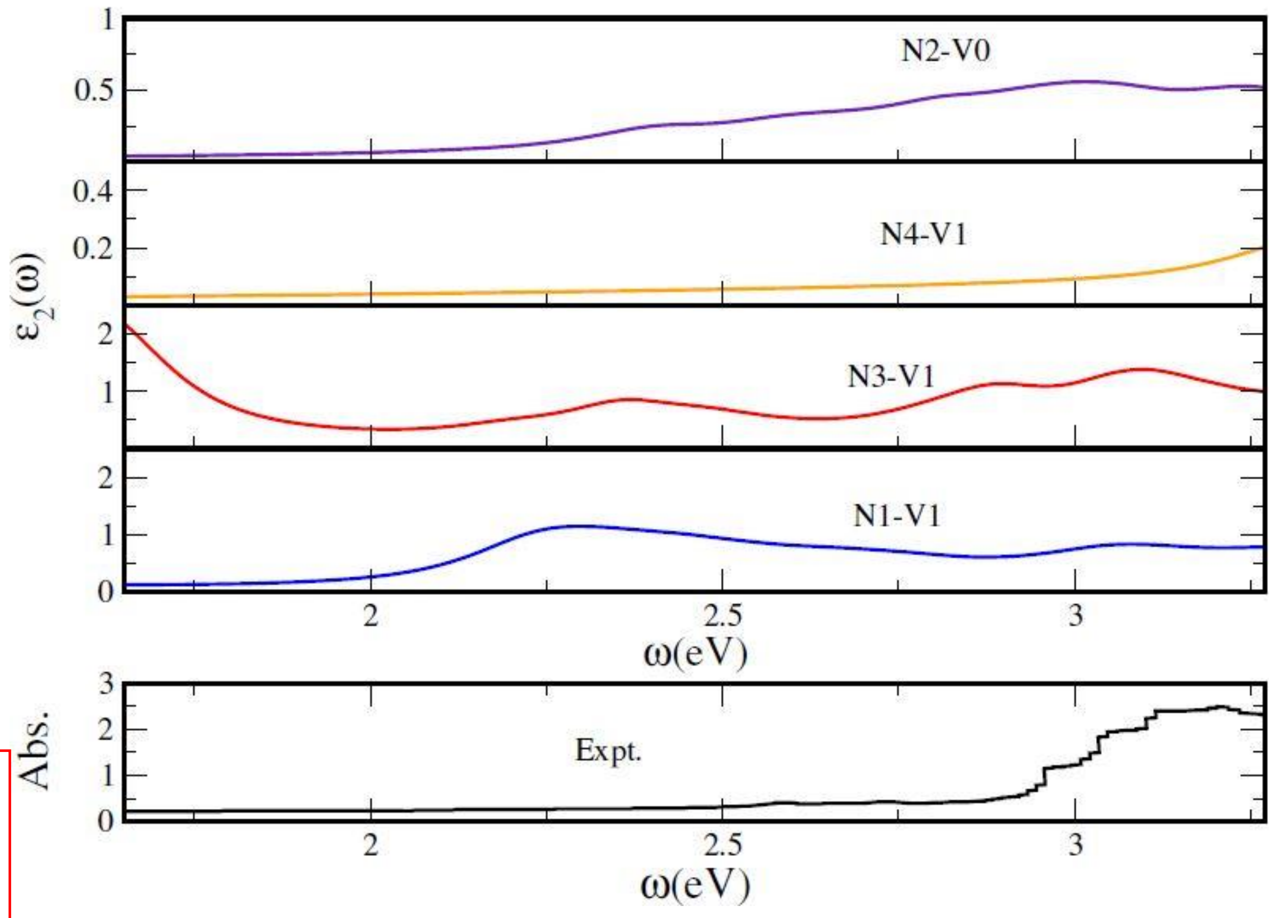

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G. R. Rossman, Mineral Spectroscopy Server, California Institute of Technology

Result / Analysis

- Color Rendering (Intensity Spectrum to RGB)

$$X = k \int i(\lambda)\bar{x}d\lambda$$

$$Y = k \int i(\lambda)\bar{y}d\lambda$$

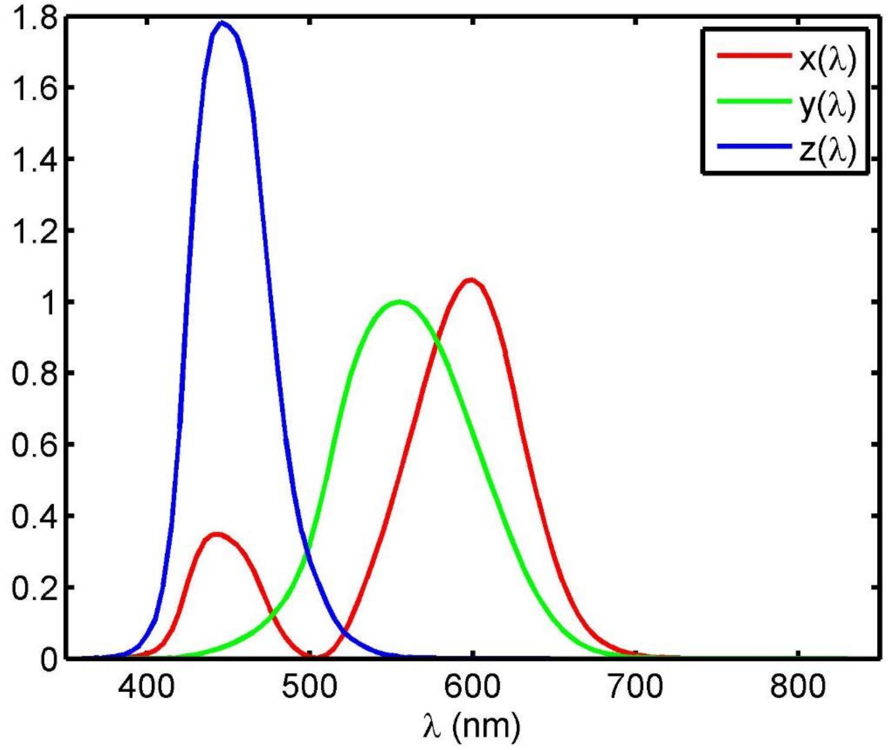
$$Z = k \int i(\lambda)\bar{z}d\lambda$$

F. W. Billmeyer, Jr., M. Saltzman. *Principles of Color Technology*, 2nd edition, John Wiley & Sons, Inc., New York, 1981.

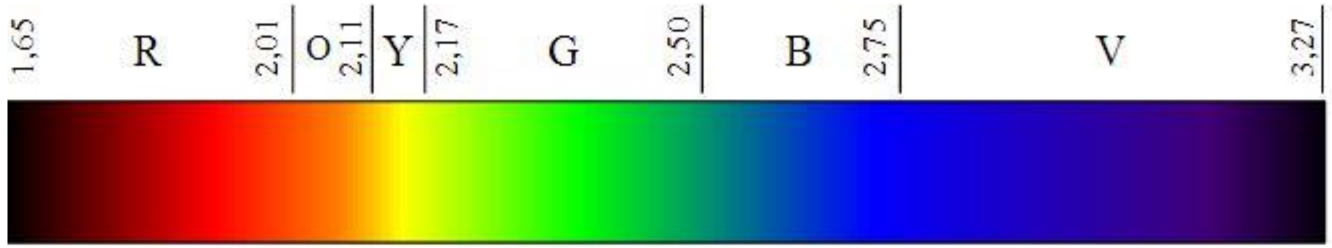
```
[ R ]     [  3.240479 -1.537150 -0.498535 ]   [ X ]
[ G ] = [ -0.969256  1.875992  0.041556 ] * [ Y ]
[ B ]     [  0.055648 -0.204043  1.057311 ]   [ Z ].
```

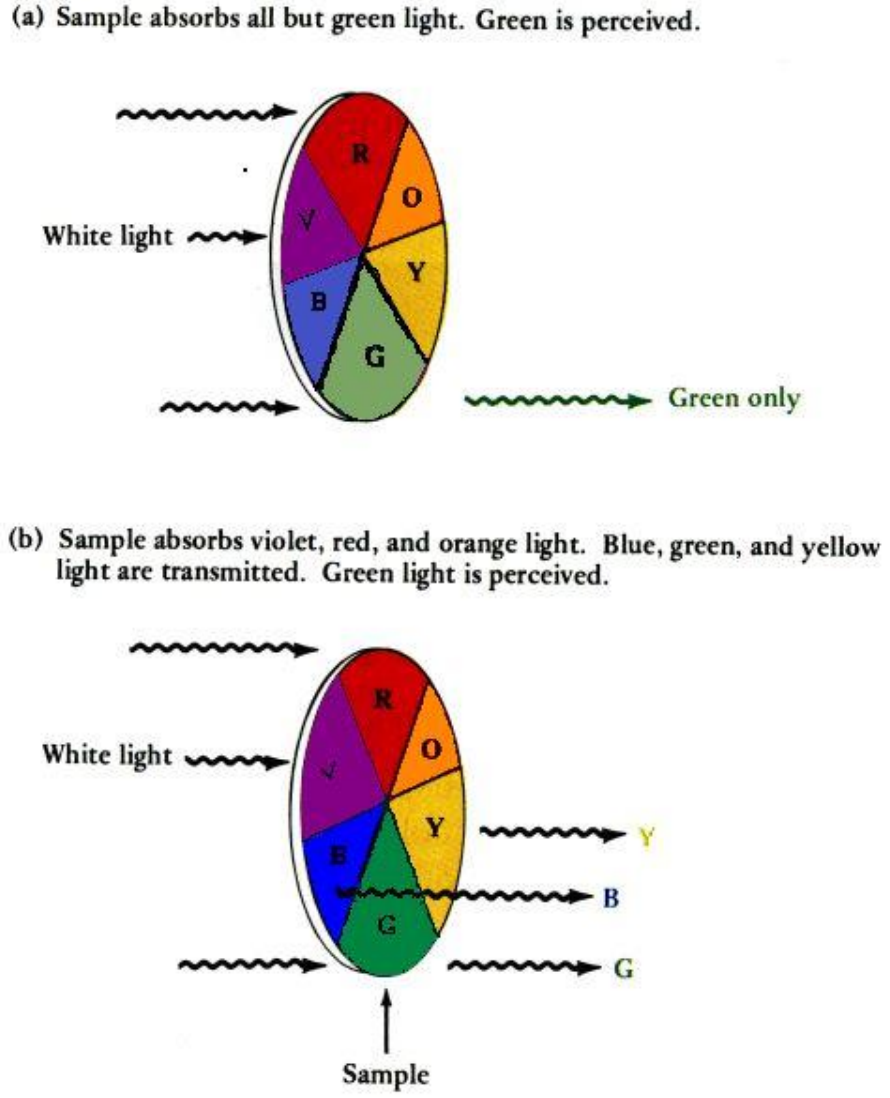
CIE 1971, International Commission on Illumination. *Colorimetry: Official Recommendations of the International Commission on Illumination*. Publication CIE No. 15 (E-1.3.1) 1971, Bureau Central de la CIE, Paris, 1971.

http://www.cs.rit.edu/~ncs/color/t_spectr.html



Colors





Spectrum from :
http://upload.wikimedia.org/wikipedia/commons/7/7f/Colors_in_eV.svg

Figure Obtained at:
https://www.wou.edu/las/physics/ch462/tmcolors.htm