Application of Thomas–Reiche–Kuhn Sum Rule to the Parametrization of JDOS of Hydrogenated Amorphous Carbon

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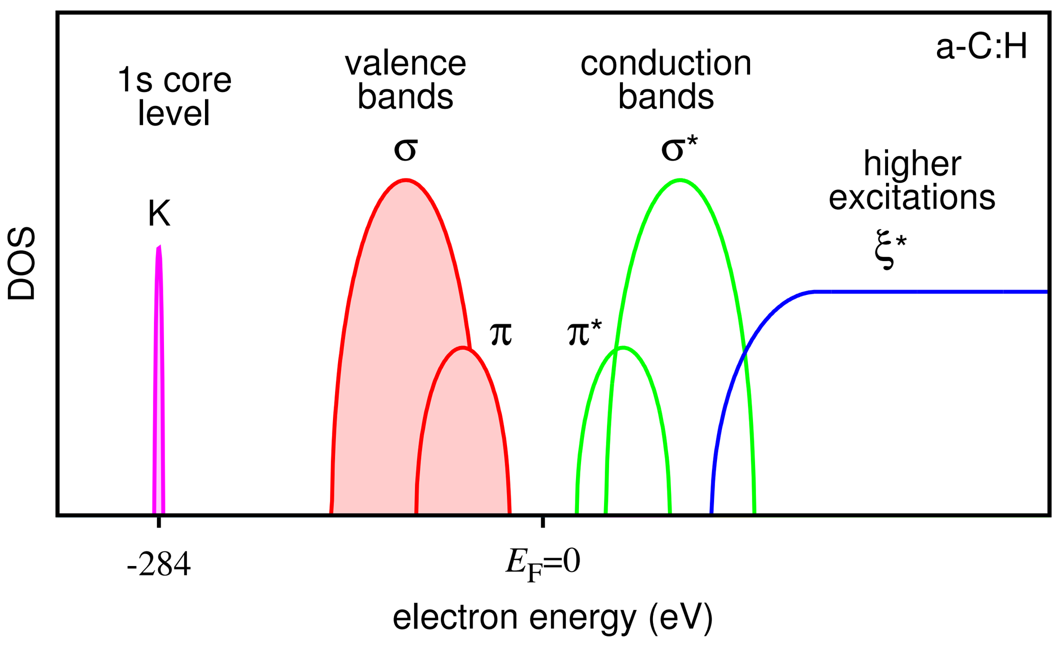
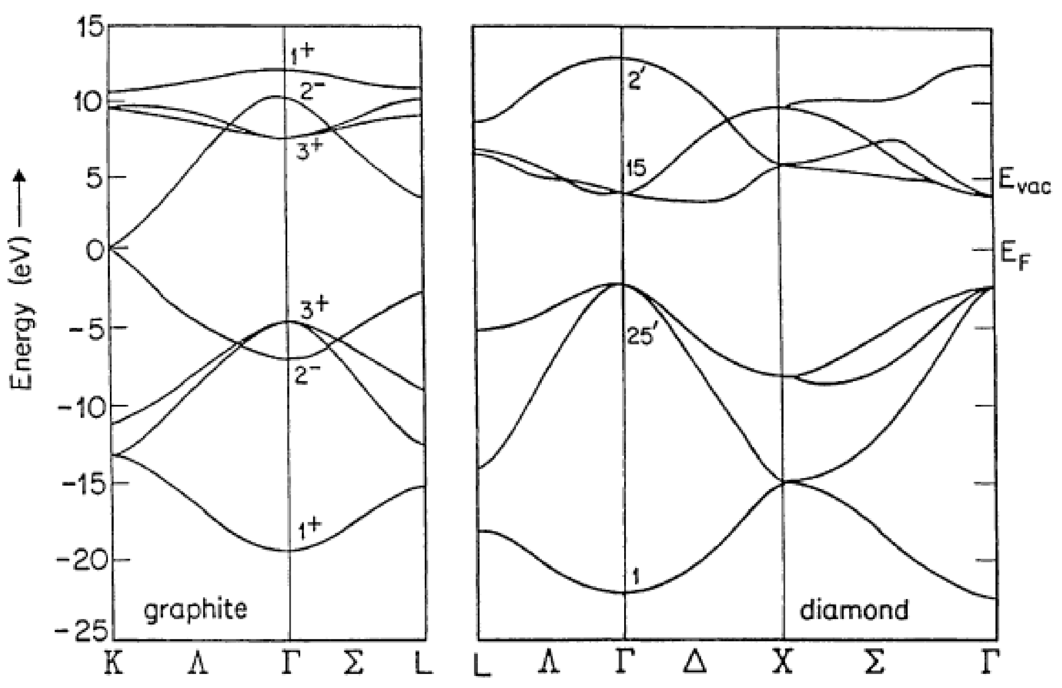
Electronic structure

	K	σ, π, π^*, σ^*	ξ^*
C	1s	2s, 2p	3s, 3p, 3d, 4s, 4p, …
H	–	1s	2s, 2p, 3s, …

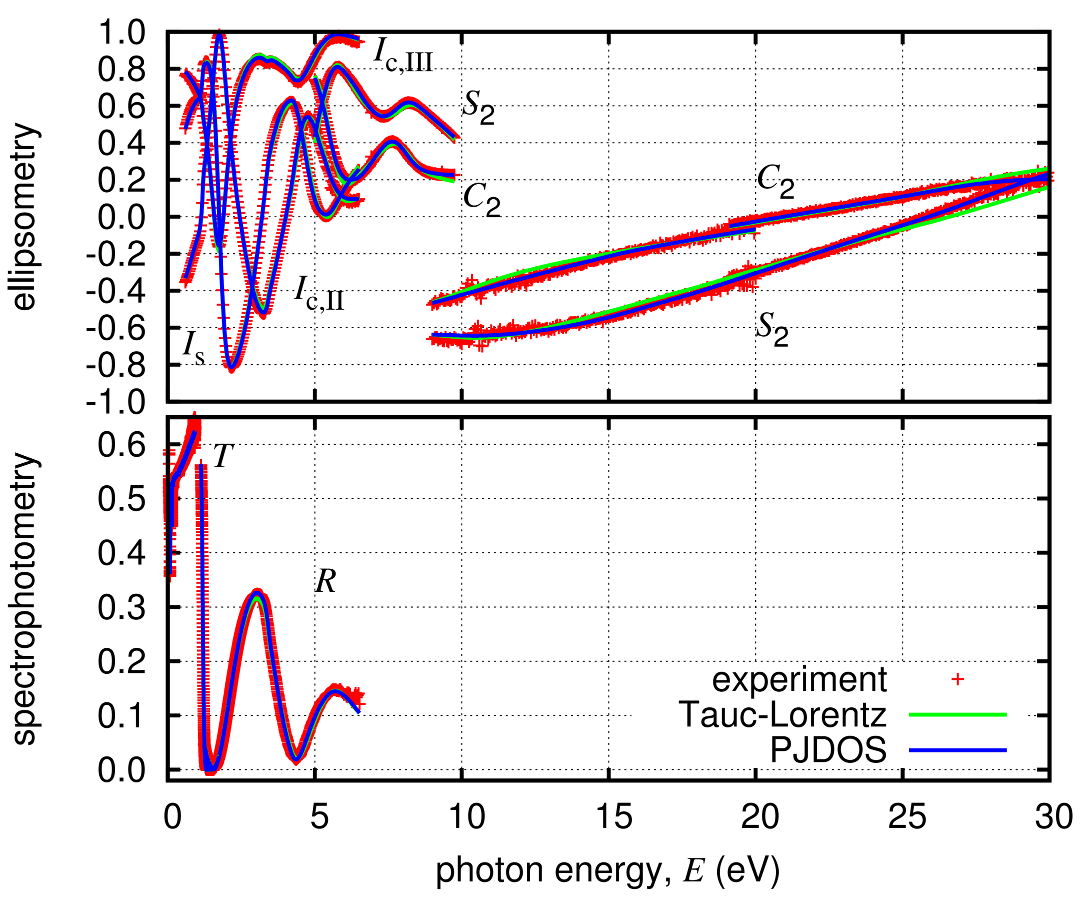


Schematic diagram of electronic structure of diamond-like carbon.



Electronic structure of graphite and diamond calculated using tight-binding method [1].

Experiment



Modeling

PJDOS model

The PJDOS model was constructed from following contributions

transitions	model	parameters
$\pi\to\pi^*$	IBTL5	$N_{\pi\pi}$, $E_{g\pi}$, $E_{c\pi}$, $E_{h\pi}$, $B_{c\pi}$
$\pi\to\xi^*$	HET2	$N_{\pi\xi}$, $E_{g\pi\xi}$
$\sigma\to\sigma^*$	IBTL5	$N_{\sigma\sigma}$, $E_{g\sigma}$, $E_{c\sigma}$, $E_{h\sigma}$, $B_{c\sigma}$
$\sigma\to\xi^*$	HET2	$N_{\sigma\sigma}$, $E_{g\sigma\xi}$
$\mathrm{K}\to\pi^*+\sigma^*+\xi^*$	CEE2	N_{K}, E_{K}
$\sigma\to\pi^*$, $\pi\to\sigma^*$	*considered negligible*	
phonon absorptions	16×GP3	

with following substitutions

$$N_{\pi\pi}=N_\pi(1-C_{\pi\xi}),\quad N_{\pi\xi}=N_\pi C_{\pi\xi},\quad E_{g\pi\xi}=E_\xi+E_{g\pi}/2$$

$$N_{\sigma\sigma}=N_\sigma(1-C_{\sigma\xi}),\quad N_{\sigma\xi}=N_\sigma C_{\sigma\xi},\quad E_{g\sigma\xi}=E_\xi+E_{g\sigma}/2$$

$$N_{\mathrm{K}}=2(N_\pi+N_\sigma)\frac{1-C_{\mathrm{H}}}{4-3C_{\mathrm{H}}}$$

For PJDOS models see poster devoted to a-Si:H.

Renormalized Tauc-Lorentz model ($\pi\to\pi^*+\xi^*$ and $\sigma\to\sigma^*+\xi^*$)

$$\varepsilon_i(E)=\frac{J(E)}{E^2}=\begin{cases}0 & \text{for } |E|\le E_g\\ \dfrac{N}{C}\dfrac{(|E|-E_g)^2}{ED(E)} & \text{for } |E|>E_g,\end{cases}$$

where

$$D(E)=(E^2-E_c^2)^2+B_c^2E^2$$

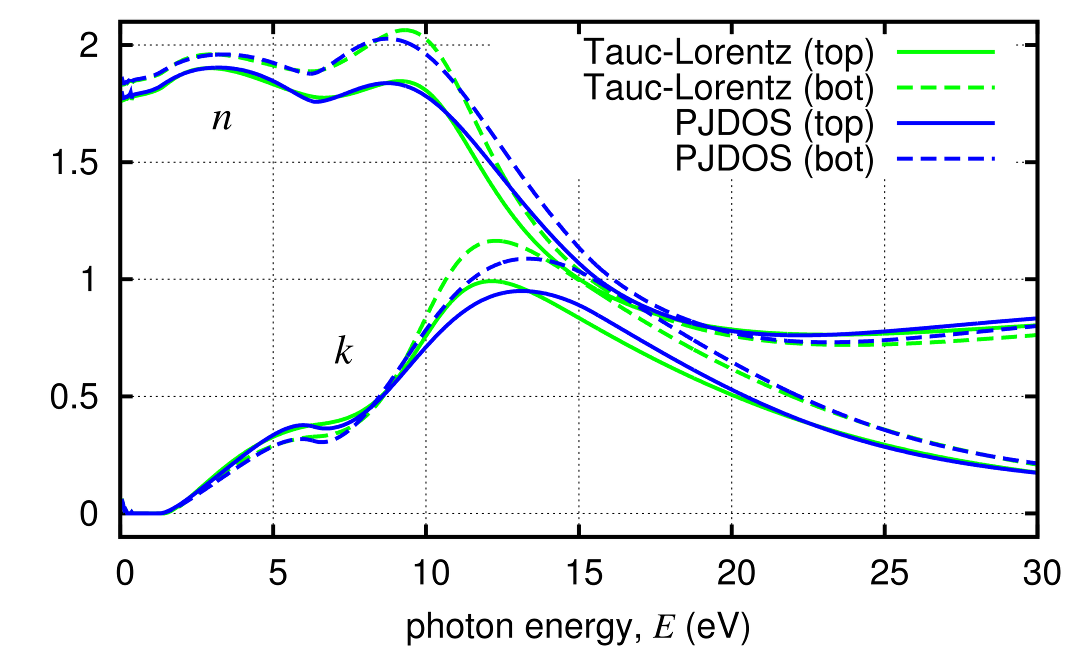
$$\varepsilon_r(E)-1=\frac{N_{j\xi}}{\pi C}\Big[a(E)\ln|E_g-E|+b(E)\ln|E_g+E|$$
$$+c(E)A_m+d(E)A_p+e(E)L_m+f(E)L_p+g(E)\Big]$$

where N, E_g, E_c, B_c are fitting parameters, $a(E)$, $b(E)$, … $g(E)$ are rational functions and C, A_m, … L_p are parameter-dependent constants. The complete model contains two Tauc-Lorentz contributions representing $\pi\to\pi^*+\xi^*$ and $\sigma\to\sigma^*+\xi^*$ transtions. Moreover, this model contains also contributions representing excitations of core electrons $\mathrm{K}\to\sigma^*+\xi^*$ and phonon absorption calculated by PJDOS models.

Inhomogeneous layer (refractive index profile)

We assumed linear profiles of parameters N_π and N_σ. Remaining parameters of dispersion model were constant.

Results



Optical constants of DLC film determined using different models on the top and bottom of the film.

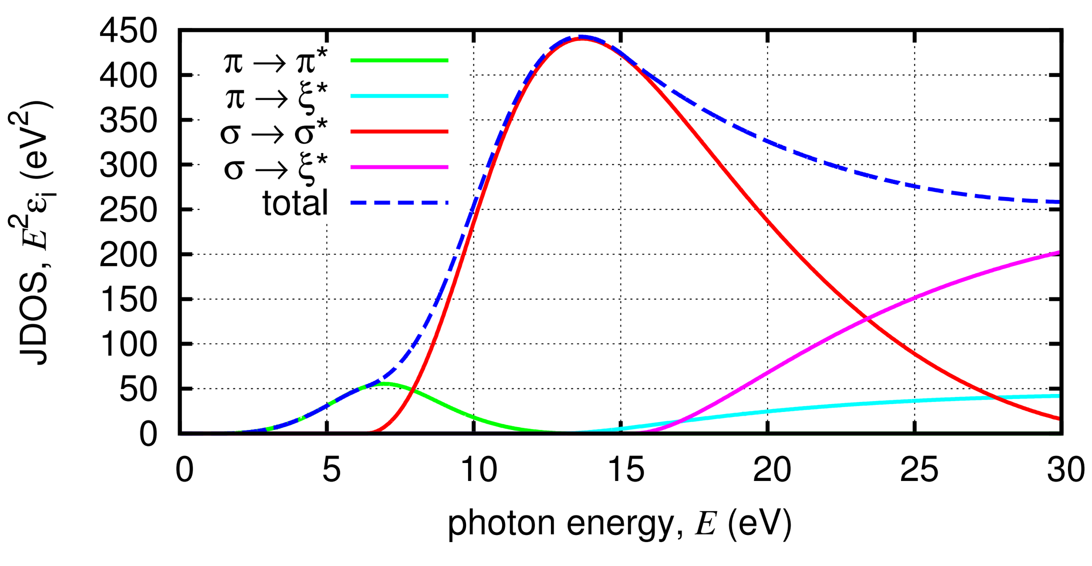
model	$E_{g\pi}$ (eV)	$E_{c\pi}$ (eV)	$E_{h\pi}$ (eV)	$B_{c\pi}$ (eV)	$E_{g\sigma}$ (eV)	$E_{c\sigma}$ (eV)	$E_{h\sigma}$ (eV)	$B_{c\sigma}$ (eV)
Tauc–Lorentz	1.359	9.45	–	20.34	6.42	10.59	–	5.39
$PJDOS_1$	1.241	7.42	13.39	6.44	6.32	11.09	33.9	11.76
$PJDOS_2$	1.242	7.42	13.51	6.50	6.32	11.09	34.0	11.59

	top		bottom				
model	N_π (eV^2)	N_σ (eV^2)	N_π (eV^2)	N_σ (eV^2)	$C_{\pi\xi}$	$C_{\sigma\xi}$	E_ξ (eV)
Tauc–Lorentz	425.4	317.3	391.9	469.5	–	–	–
$PJDOS_1$	39.7	989.0	35.4	1216.2	0*	0.663	11.93
$PJDOS_2$	140.2	886.4	125.2	1097.8	0.714†	0.627	12.24

model	E_{K} (eV)	C_{H}	χ
Tauc–Lorentz	284*	0.34*	3.545
$PJDOS_1$	284*	0.34*	1.392
$PJDOS_2$	284*	0.34*	1.391

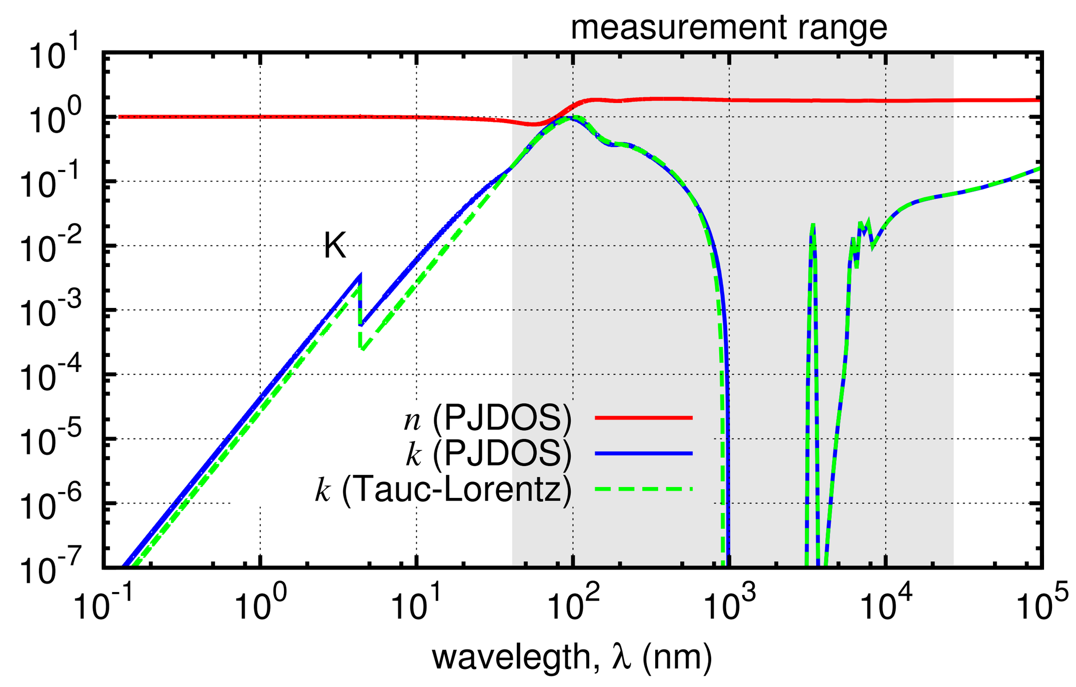
* Fixed parameter.
† Fit is almost independent on this parameter due to the impossibility to separate $\pi\to\xi^*$ and $\sigma\to\xi^*$ transitions. See the quantity χ characterizing the disagreement between theoretical and experimental data (1 is optimum).

Separation of individual contributions



Separation of individual contributions of PJDOS model.

Optical constants in wide spectral range



Log–log plot of optical constants of DLC.

Density of the electrons

$$N_e=N_v+N_K=(N_\pi+N_\sigma)\frac{6-5C_{\mathrm{H}}}{4-3C_{\mathrm{H}}}\quad(\mathrm{eV}^2)$$

$$\mathcal{N}_e=4.617\cdot10^{26}N_e\quad(1/\mathrm{m}^3)$$

Density of the DLC

$$\varrho=\mathcal{N}_a\Big[A_{\mathrm{C}}(1-C_{\mathrm{H}})+A_{\mathrm{H}}C_{\mathrm{H}}\Big]u\quad(\mathrm{Kg/m^3})$$

$$\mathcal{N}_a=\frac{\mathcal{N}_e}{6-5C_{\mathrm{H}}}\quad(1/\mathrm{m}^3)$$

- $\mathcal{N}_a$ density of atoms ($1/m^3$)
- A_{C} carbon atomic weight (12.01 g/mol)
- A_{H} hydrogen atomic weight (1.008 g/mol)
- u atomic mass unit ($1.6605\cdot10^{-27}$ Kg)

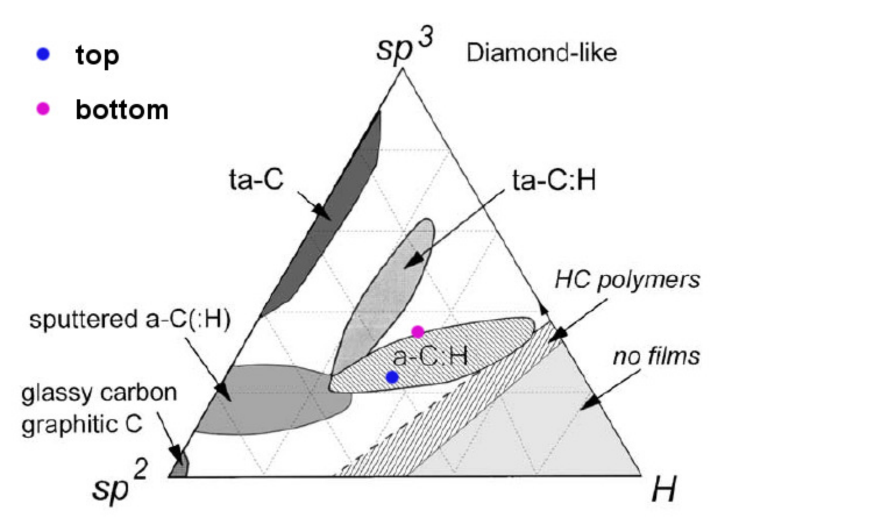
Hardness of DLC: $H_{IT}=21.7$ GPa

sp^3/sp^2 ratio

$$\frac{\mathcal{N}_{sp3}}{\mathcal{N}_{sp2}}=\frac{(1-3N_\pi/N_\sigma)-C_{\mathrm{H}}(1-2N_\pi/N_\sigma)}{N_\pi/N_\sigma(4-3C_{\mathrm{H}})}$$

model	N_v (eV^2)	N_e (eV^2)	$\mathcal{N}_e$ ($1/m^3$)	ϱ (Kg/m^3)	$\mathcal{N}_{sp3}/\mathcal{N}_{sp2}$
top of the DLC film					
Tauc–Lorentz	742.7	1072	$4.948\cdot10^{29}$	1580	-0.613
$PJDOS_1$	1028.7	1484	$6.853\cdot10^{29}$	2188	4.74
$PJDOS_2$	1026.6	1481	$6.839\cdot10^{29}$	2185	0.622
bottom of the DLC film					
Tauc–Lorentz	861.4	1243	$5.739\cdot10^{29}$	1833	-0.513
$PJDOS_1$	1247.6	1800	$8.312\cdot10^{29}$	2654	6.83
$PJDOS_2$	1223.0	1765	$8.148\cdot10^{29}$	2602	1.16

Comparison with parameters presented in [1]



	sp^3 (%)	H (%)	Density (g cm^{-3})	Gap (eV)	Hardness (GPa)
Diamond	100	0	3.515	55	100
Graphite	0	0	2.267	0	
C_{60}	0	0		1.6	
Glassy C	0	0	1.3–1.55	0.01	3
Evaporated C	0	0	1.9	0.4–0.7	3
Sputtered C	5	0	2.2	0.5	
ta-C	80–88	0	3.1	2.5	80
a-C:H hard	40	30–40	1.6–2.2	1.1–1.7	10–20
a-C:H soft	60	40–50	1.2–1.6	1.7–4	<10
ta-C:H	70	30	2.4	2.0–2.5	50
Polyethylene	100	67	0.92	6	0.01

Note that sp^3=40 % corresponds to $\mathcal{N}_{sp3}/\mathcal{N}_{sp2}=40/60=0.667$.

Acknowledgements

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References

[1] J. Robertson, Mater. Sci. Eng. R 37 (2002) 129–281.