Exciton-Phonon coupling in the finite temperature optical absorption of semiconductor

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Do we need exciton-phonon coupling?

**Temperature dependence of the dielectric function and interband critical points in silicon**

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The complex dielectric function $\varepsilon(\omega)$ of Si was measured ellipsometrically in the 1.7–5.7-eV photon-energy range at temperatures between 30 and 820 K. The observed structures are analyzed by fitting the second-derivative spectrum $d^2\varepsilon/d\omega^2$ with analytic critical-point line shapes. Results for the temperature dependence of the parameters of these critical points, labeled $E'_0$, $E_1$, $E_2$, and $E'_1$, are presented. The data show good agreement with microscopic calculations for the energy shift and the broadening of interband transitions with temperature based on the electron-phonon interaction. The character of the $E_1$ transitions in semiconductors is analyzed. We find that for Si and light III-V or II-VI compounds an excitonic line shape represents best the experimental data, whereas for Ge, $\alpha$-Sn, and heavy III-V or II-VI compounds a two-dimensional critical point yields the best representation.

Debye Temperatures

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>426</td>
</tr>
<tr>
<td>Cadmium</td>
<td>186</td>
</tr>
<tr>
<td>Chromium</td>
<td>610</td>
</tr>
<tr>
<td>Copper</td>
<td>344.5</td>
</tr>
<tr>
<td>Gold</td>
<td>165</td>
</tr>
<tr>
<td>$\alpha$-Iron</td>
<td>464</td>
</tr>
<tr>
<td>Lead</td>
<td>96</td>
</tr>
<tr>
<td>$\alpha$-Manganese</td>
<td>476</td>
</tr>
<tr>
<td>Nickel</td>
<td>440</td>
</tr>
<tr>
<td>Platinum</td>
<td>240</td>
</tr>
<tr>
<td>Silicon</td>
<td>640</td>
</tr>
<tr>
<td>Silver</td>
<td>225</td>
</tr>
<tr>
<td>Tantalum</td>
<td>240</td>
</tr>
<tr>
<td>Tin (white)</td>
<td>195</td>
</tr>
<tr>
<td>Titanium</td>
<td>420</td>
</tr>
<tr>
<td>Tungsten</td>
<td>405</td>
</tr>
<tr>
<td>Zinc</td>
<td>300</td>
</tr>
<tr>
<td>Diamond</td>
<td>2200</td>
</tr>
<tr>
<td>Ice</td>
<td>192</td>
</tr>
</tbody>
</table>

793 K = 68 meV
QP gap is 1200 meV
At the absorption treshold the QP lifetime is EXACTLY infinite

YES ! At least we do need phonons.
Are you sure we need exciton-phonon coupling?

YES! Because it is possible to observe phonon sidebands.

YES! Because phonons are responsible for the low-temperature saturation of the excitonic lifetime.

YES! Because there are many different “flavours” of excitons: polaritons, polaronic excitons, ...

PRL 95, 247401 (2005)
PRL 95, 197401 (2005)
Outline

Polarons (I): Cardona-Allen approach

1

Polarons (II): Silicon and Diamond

2

Finite temperature optics in the polaronic approximation

3

Dynamical BSE: the exciton phononic self-energy
Polarons
the Cardona-Allen approach
PRB 23, 1495 (1981)

\[ H = T + V_{SCF}(\{R_{Is}\}) \]
\[ R_{Is} = R_{Is} + u_{Is} \]

Using standard 1\textsuperscript{st} and 2\textsuperscript{nd} order perturbation theory and the fact that

\[ E_{nk} = \langle n|k|H|n,k \rangle \]

\[ \delta H = \delta H^{(1)} + \delta H^{(2)} \]
\[ \delta H^{(1)} = \sum_{Is} \frac{\partial V_{SCF}}{\partial R_{Is}} u_{Is} \]
\[ \delta H^{(2)} = \frac{1}{2} \sum_{Is, Jt} \frac{\partial^2 V_{SCF}}{\partial R_{Is} \partial R_{Jt}} u_{Is} u_{Jt} \]

Cardona-Allen further impose an "acoustic sum rule"

\[ \delta E_{nk} \left[ \{ u_{Is} + v \} \right] = \delta E_{nk} \left[ \{ u_{Is} \} \right] \]

Finally

\[ \sum_{Is} u_{Is} \langle n'|k + q | \frac{\partial V_{SCF}}{\partial R_{Is}} | n,k \rangle = \sum_{q\lambda} g_{n'nk}^{q\lambda} \left( b_{q\lambda}^\dagger + b_{q\lambda} \right) \]

\[ \delta E_{nk} = \sum_{q\lambda m} \left[ \frac{|g_{n'nk}^{q\lambda}|^2}{E_{nk} - E_{mk+q}} - \frac{\Lambda_{n'nk}^{q\lambda}}{E_{nk} - E_{mk}} \right] \left( 2\langle N_{q\lambda} \rangle + 1 \right) \]

Clear dependence on the temperature
Polaron damping neglected
Polarons, Hedin's equations, and Density Functional Perturbation Theory


\[ \delta E_{nk} = \sum_{q\lambda m} \left[ \frac{|g_{n'n\kappa}|^2}{E_{nk} - E_{m\kappa+q}} - \frac{\Lambda_{n'n\kappa}^q}{E_{nk} - E_{m\kappa}} \right] (2\langle N_{q\lambda} \rangle + 1) \]

\[ H_{MB} + \int d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r}, t) \]

Hochstetter contribution to the screened interaction

\[ W_{ph}(\mathbf{r}_1, \mathbf{r}_2, i\omega) = \sum_{q\lambda} \frac{2\omega q_{\lambda}^q}{\omega^2 + \omega_{q\lambda}^2} g_{q\lambda}(\mathbf{r}_1, i\omega) g_{q\lambda}^*(\mathbf{r}_2, i\omega) \]

SC field

- The SC field is frequency dependent
- There is no coupled equation for the phonon propagator
- There is no need of an explicit el-ph term in the Hamiltonian (Frohlich-like)

We can use DFPT to describe phonons as it is "almost" consistent with MB (DFPT uses a static test-electron dielectric function to screen the ionic potential)
Polarons in silicon & diamond

Using finite temperature diagrammatic techniques the phononic GW self-energy is

\[ \Sigma_{n,k}^{FAN} (i\omega) = \sum_{\lambda} |g_{n',nk}^{q\lambda}|^2 \left[ \frac{\langle N_q\lambda \rangle + 1 - f_{mk-q}}{i\omega - E_{mk+q} - \omega_{q\lambda}} + \frac{\langle N_q\lambda \rangle + f_{mk-q}}{i\omega - E_{mk+q} + \omega_{q\lambda}} \right] \]

The FAN SE includes polaron dampings.

It reduces to the Cardona-Allen formulation in the “on mass-shell” approximation.

(... the zero-point renormalization vibration amplitude is responsible for energy renormalizations up to 200 meV, of the order of accuracy claimed for state-of-the-art ab initio calculations (...)

\[ E_g = 8.24 \text{ eV} \]

\[ E_g < 3.5 \text{ eV} \]
EXCITONS


In TDDFT: AM, R. Del Sole, A. Rubio PRL 91, 256402
In any ab initio calculation of the optical spectra (RPA or BSE) the electron-hole damping is used as a parameter, fitted to get the best agreement with the experiment. In all the present calculations the numerical damping is 0.1 meV. The real, physical, damping is due to the polaronic widths.
Exciton-phonon coupling state-of-the-art

Bosonic Hamiltonians

B. Segall, G.F. Mahan PR 171, 935 (1968)
A. Suna, PR 135, A111 (1964)

\[ H = \sum_{\lambda K} \epsilon_{\lambda K} n_{\lambda K}^{\text{exc}} + \sum_{\mathbf{q}} \omega_{\mathbf{q}} n_{\mathbf{q}}^{\text{ph}} + \sum_{\lambda \lambda' K \mathbf{q}} V(\mathbf{q})^{\lambda \lambda'} c_{\lambda K + \mathbf{q}}^{\dagger} c_{\lambda' K} (a_{\mathbf{q}} + a_{\mathbf{q}}^{\dagger}) \]

Easy interpretation

Impossible to do Ab-Initio: no idea how to evaluate the exc-ph coupling potential

"Interacting excitons should not be bosonized"

M. Combescot

Frohlich Hamiltonians

K. Hannewald and P. A. Bobbert, PRB 72, 113202 (2005)

Widely used

Phonon overscreening

[RvL, PRB 69, 115110 (2004)]
A correct derivation of the BSE from the generalized Hedin's equations yields an indirect (polaronic mediated) and a direct exciton-phonon coupling.

The dynamical BSE [AM, R. Del Sole, PRL 91, 176402 (2003)] was introduced to sum the frequency dependent Coulombic interaction.

\[
K \equiv (n_c, n_h, k) = L_{K_1}^{(0)} (\tau - \tau_1) + \Pi_{K_1, K_2}^{el} (\tau_1 - \tau_2) + L_{K_2}^{(0)} (\tau_2)
\]
The phononic kernel enhances the screening (like in the polaronic SE) reducing the electron-hole interaction.

The phonon frequencies in the DBSE kernel are responsible for the phonon sidebands (an additional contribution stem from the polaronic self-energy diagrams).
Similarly to the quasiparticle case the phononic and electronic parts can be summed separately

\[
\tilde{L}(i\omega) = \tilde{L}^{(0)}(i\omega) \left[ 1 - \tilde{L}^{(0)}(i\omega) W \right]^{-1} \left[ 1 - \tilde{L}^{(0)}(i\omega) \left[ 1 - \tilde{L}^{(0)}(i\omega) W \right]^{-1} \Pi^{ph}(i\omega) \right]^{-1}
\]

\[
\tilde{L}^c(i\omega) = \tilde{L}^{(0)}(i\omega) \left[ 1 - \tilde{L}^{(0)}(i\omega) W \right]^{-1}
\]

If we rotate in the excitonic basis

\[
|I\rangle = \sum_K \langle K|I\rangle
\]

\[
\langle I|\tilde{L}^c(i\omega)|J\rangle = -\delta_{IJ} (i\omega - E_I)^{-1}
\]

The excitonic self-energy implies all the physical consequences of the self-energy potential in any quasiparticle theory: damping, phonon replicas, fictitious exciton-phonon coupling potential. No bosonic Hamiltonians are needed.
Conclusions...

The finite temperature optical properties in presence of weak electron-phonon coupling can be described with the standard BSE in the polaronic picture.

The excitonic damping and zero-point motion effect are in excellent agreement with the experiment, being small in systems (like diamond) with large Debye energy.

In presence of STRONG electron-phonon coupling the dynamical extension of the BSE includes a phononic kernel that act to reduce the electron-hole interaction.

The DBSE can be reduced in the static excitons basis to yield a phononic self-energy WITHOUT ANY drastic assumption on the Hamiltonian.

...and...
About SELF

SELF is a FORTRAN/C code for Many-Body calculations in solid state physics. SELF relies on the Kohn-Sham wavefunctions generated by several DFT public codes. The code has been originally developed in the Condensed Matter Theoretical Group of the Physics Department at the university of Rome by Andrea Marini. See features for an extensive overview or enjoy the view of the developers' faces.

Please do not contact us to get SELF as the code is (still) not freely available.

Bethe-Salpeter.org

To have more informations about the Many-Body theory, and the Bethe-Salpeter equation visit the Bethe-Salpeter.org community.

News

The documentation is now online and SELF has its first tutorial.
“SELF, a shiny pot of fun and happiness”

[C. Hogan]

http://www.fisica.uniroma2.it/~marini
http://www.fisica.uniroma2.it/~self