Bound small hole polaron in oxides and related materials:

*strong colorations and high ionization energies*

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central example: acceptor $\text{Li}^{+}_{\text{Zn}}$ in ZnO
• Small polaron: carrier localized at one of several equivalent sites - here: hole–polaron bound to acceptor
  
  o Large polaron: usually delocalized over many equivalent sites

• Localization by short range carrier – lattice coupling
  
  o Coupling by long range Coulomb interaction (Fröhlich-coupling)

• Transport from a site to a neighbouring one by thermally activated hopping (incoherent)
  
  o Transport by coherent bandlike tunneling
Evidence by:

1) Paramagnetic resonance of unpaired spins:

2) Typical optical absorption:

3) Theoretical reproduction of structure and energy levels:
Carriers are provided by:

1) doping

2) optical irradiation
Summarizing overviews:


Menu:

1) Formation of small polarons, their optical absorptions and their energies of ionization

2) Basic features of the theoretical reproduction of bound small polarons

3) Luminescence accompanying recombination with bound small polarons

4) Examples of bound small polarons in 'semiconductor' (high gap) materials
Bound small polarons:

Typical features of

• their optical absorptions

• their energies of ionization
Optical absorption  Most simple example: **2 equivalent sites**  
(localization of a hole at one of 2 equivalent sites)
\[ H = J \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + VQ \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + KQ^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \] operating on \( \begin{pmatrix} R \\ L \end{pmatrix} \)

\[ H = \begin{pmatrix} VQ + KQ^2 & J \\ J & -VQ + KQ^2 \end{pmatrix} \]

\[ E_p = \frac{V^2}{4K} \quad \text{minimal energy at} \quad Q_{\min} = \pm \frac{V}{2K} \]
Optical absorption:

O^- - O^2^- charge transfer under Franck – Condon conditions

\[ \alpha(\omega) \propto \left( \frac{J^2 d^2}{\hbar \omega} \right) \exp(-w(\hbar \omega - 4E_p)^2) \]

\[ w = 1/(8E_p \hbar \omega_0) \]

a) high oscillator strength

b) largest possible width of an absorption band for given peak energy.

c) characteristic fingerprint, indep. of \( E_p \):
\[ W^2/M = \ln 2 \times 8E_p \hbar \omega_0 / 4E_p \sim 0.14 \text{ eV} \]

d) width of the 'zero-phonon band' :
\[ \propto 2J \times \exp(-4E_p / \hbar \omega_0) \]
2-well small polaron absorption

\[ M \sim 4 \, E_p \]

\[ W \]

\[ \text{absorptivity [arb. u.]} \]

\[ \text{photon energy [eV]} \]
Tetrahedral symmetry: ZnO:Li, BeO:Li

\[
H = \begin{pmatrix}
VQ_{111} + KQ^2 & J & J & J \\
J & VQ_{-111} + KQ^2 & J & J \\
J & J & VQ_{-1-1} + KQ^2 & J \\
J & J & J & VQ_{1-1} + KQ^2
\end{pmatrix}
\]

operating on \[\begin{pmatrix}
1 \\
2 \\
3 \\
4
\end{pmatrix}\]
\[ \alpha_\parallel \propto (Jd_\parallel)^2 / \omega \exp(-w(\hbar \omega - 8/3E_p + J)^2) \]
\[ \alpha_\perp \propto (Jd_\perp)^2 / \omega \exp(-w(\hbar \omega - 8/3E_p - 2J)^2) \]
\[ w^{-1} = (16/3)E_p \hbar \omega_0 \]
\[ J = 0.18 \text{ eV}, \quad E_P = 1.18 \text{ eV}, \quad W^2/M = 0.17 \text{ eV} \]
Energy of ionization, $E_{th}$:

Contributions to energy of carrier:

1) Stabilization by lattice distortion, parameter $E_p$
2) Stabilization by Coulomb potential of acceptor, parameter $E_d$
3) Destabilization by rise of kinetic energy, typically $W/2$
lattice distortion, parameter $E_p$

Coulomb potential of acceptor, parameter $E_d$

rise of kinetic energy, typically $W/2$

$$E_{th} = E_p + E_d - \frac{W_b}{2}$$

$$E_{opt} = \frac{8}{3} E_p \pm a J$$
Concerning the theoretical treatment of bound small polarons: structure and energy levels

ZnO:Li_{Zn}

\[ \text{CB} \]

\[ \begin{array}{c}
\sim 0.7 \text{ eV} \\
\text{O}^2-/O^- \\
\text{O}^2-/O^-
\end{array} \]

\[ \text{VB} \]

\[ \text{DFT (LDA)} \]

0.09 – 0.2 eV

experiment

acceptor deep
hole localised

theory

acceptor shallow
hole delocalised

S. Lany (2011)
Predicting polaronic defect states by means of generalized Koopmans density functional calculations

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In order to calculate the properties of a bound polaron the environment of the binding defect, consisting of hundreds of ions, must be included. This implies a corresponding high number of electrons.

This Many-Electron-Problem can be tackled by using 'density functional theory (DFT)' (W. Kohn, Nobel prize 1998). For instance, the energy is described as a functional of the electron density:

\[ E[\rho] = T[\rho] + V[\rho] + E_{xc}[\rho] + \ldots \]

\[ \rho = \ldots \rho_i + \rho_j + \ldots \]

\[ V[\rho] = \int \int \frac{1}{(\text{dist. bet. each two elec.})} (\ldots \rho_i + \rho_j + \ldots)(\ldots \rho_i + \rho_j + \ldots) \, d(\text{all. elec.}) \]

Coulomb-interaction of the electrons; contains also the self-interaction of single electrons, e.g. \( \rho_i \rho_i \).
This is not correct physically: there is no self-interaction. Consequence: The electron-electron repulsion is underestimated. Therefore it costs less energy to put an additional electron into the system, as compared to the 'correct' description.

The energy distance to the excited states is too low: If the next higher state is not populated, this corresponds to a hole with a low ionization energy. Since recently there are tricks by which the compensation of the erroneous self-interaction can be described exactly.

One adds a repulsive additional potential, which strongly raises energy of next electron. A hole, captured in the corresponding level, then has a high ionization energy with respect to the occupied states.
Since the hole is expected to be localized at an O$^{2-}$ ion, the electron potential at this ion is raised correspondingly:

\[ V_{hs} = \lambda_{hs} \left(1 - n_{m,\sigma}/n_{\text{host}}\right) \]

This raises the ionization energy of the hole.

The strength of the potential is not arbitrary, however. The parameter $\lambda_{hs}$ is chosen in such a way, that all effects of self-interaction are removed. This leads to exact solution of the problem.

In addition there are a series of approximation procedures, which have a good predictive power.

Result: hole localized as O$^-$. Minimization of energy also with respect to lattice distortion yields polaronic state and ionization energy.
Luminescence: recombination of electron with bound polaron

So far: Transitions within hole polaron system with fixed charge state \((\text{Li}_\text{Zn}^0 (\text{h}))\).

When recombining with an electron the charge state changes: \((e + h)\). What is the corresponding complete level scheme?
$E_{\text{max}} = 1.95 \text{ eV}$

D. Zwingel, J. Luminescence (1972)

$E_{\text{max}} = E_{\text{gap}} - 2 E_{\text{ion}}$

$\rightarrow E_{\text{ion}} \approx 0.7 \text{ eV}$
Examples of bound small polarons in semiconductor (or insulating) materials:

*Identification by:*

- EPR
- Optical absorption
- Theoretical simulation
Oxides - acceptor defects binding small hole polarons:

**Tetrahedral coordination (4 O neighbors)**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Li&lt;sub&gt;Zn&lt;/sub&gt;</th>
<th>Na&lt;sub&gt;Zn&lt;/sub&gt;</th>
<th>V&lt;sub&gt;Zn&lt;/sub&gt;</th>
<th>N&lt;sub&gt;O&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Li&lt;sub&gt;Be&lt;/sub&gt;</td>
<td></td>
<td>V&lt;sub&gt;Be&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>BeO</td>
<td></td>
<td>Na&lt;sub&gt;Zn&lt;/sub&gt;</td>
<td>V&lt;sub&gt;Zn&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Al&lt;sub&gt;Si&lt;/sub&gt;</td>
<td>Ge&lt;sub&gt;Si&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi&lt;sub&gt;12&lt;/sub&gt;M&lt;sub&gt;20&lt;/sub&gt; (M = Ti or Si or Ge)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi&lt;sub&gt;M&lt;/sub&gt; (antisite defect)</td>
<td></td>
<td></td>
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</table>
ZnO:Li$_{Zn}$ $E_{\text{ionization}} = 0.64$ eV \hspace{1cm} \text{(Lany 2009)}
\[ \text{ZnO:Na}_{\text{Zn}} \quad E_{\text{ion}} = 0.79 \text{ eV} \quad (\text{Lany 2009}) \]

\[ \text{ZnO:V}_{\text{Zn}} \quad E_{\text{ion}} = 0.95 \text{ eV} \quad (\text{Chan, Lany, Zunger 2009}) \]

\[ \text{ZnO:NO} \quad E_{\text{ion}} = 1.62 \text{ eV} \quad (\text{Lany 2011}) \]
SiO₂ : Al  (smoky quartz)  - Gillen, Robertson 2012

E_{ion} = 2.5 \text{ eV}
For comparison: oxygen vacancy, $V_\text{O}$, in ZnO Clark et al. 2011

Electron(s): widely extended (no small polaron)
Further example for tetrahedral coordination

\[ \text{Bi}_{12}\text{TiO}_{20} \quad \text{Bi}_{\text{Ti}} \]
Oxides

*Octahedral coordination (6 O neighbors):*

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ionic Substitution</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Li&lt;sub&gt;Mg&lt;/sub&gt;</td>
</tr>
<tr>
<td>CaO</td>
<td>Li&lt;sub&gt;Ca&lt;/sub&gt;</td>
</tr>
<tr>
<td>SrO</td>
<td>Li&lt;sub&gt;Sr&lt;/sub&gt;</td>
</tr>
<tr>
<td>LiNbO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>V&lt;sub&gt;Li&lt;/sub&gt;</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Mg&lt;sub&gt;Al&lt;/sub&gt;</td>
</tr>
<tr>
<td>CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>La&lt;sub&gt;Ce&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>V&lt;sub&gt;Cu&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
oxides

perovskites

BaTiO$_3$ : Na$_{Ba}$, Ca$_{Ti}$

SrTiO$_3$ : Fe$_{Ti}$, Al$_{Ti}$

CaTiO$_3$ : V$_{ti}$

LaMnO$_3$ : Sr$_{La}$
Tellurides, selenides, sulfides:

*Tetrahedral coordination*

ZnTe, ZnSe: $V_{\text{Zn}}$

Nitrides

*Tetrahedral coordination*

GaN: $\text{Mg}_{\text{Ga}}$, $\text{Be}_{\text{Ga}}$, $\text{Zn}_{\text{Ga}}$
GaN:Mg  deep: $E_{\text{ion}} = 0.18$ eV (Lany, Zunger 2010)

- polaronic
- responsible for blue luminescence of GaN  (LED !!)

GaN:Mg  shallow: $E_{\text{ion}} = 0.15$ eV (Lany, Zunger 2010)
<table>
<thead>
<tr>
<th></th>
<th>deep</th>
<th>shallow</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN:Be</td>
<td>0.45 eV</td>
<td>0.15 eV</td>
<td>(Lany, Zunger 2010)</td>
</tr>
<tr>
<td>GaN:Zn</td>
<td>0.32 eV</td>
<td>0.25 eV</td>
<td>(Lany, Zunger 2010)</td>
</tr>
</tbody>
</table>
Bound small $O^-$ polaron also in topaz:
Summary:

• Small (hole) polarons bound to acceptor defects are often found in semiconductor (or high gap) materials.

• Such polarons are characterized by intense wide absorption and luminescence bands with maxima in the visible spectral range.

• The interaction with the lattice is rather strong; $E_p$ (typ.) $\sim 1$ eV

• This implies high ionization energies and low p-conductivity

• Reliable ab-initio predictions of the features of bound small polarons have become possible recently
Holes 'self-trapped', without attraction by acceptor:

Theory: van de Walle et al. (Phys. Rev. B 85, 081109 (2012))

$\text{TiO}_2$
$\text{Al}_2\text{O}_3$
$\text{Ga}_2\text{O}_3$
$\text{In}_2\text{O}_3$

$\text{a-SiO}_2$ O- hole small polaron, self-trapped

No 'self-trapped' holes in ZnO, crystalline SiO$_2$