Transition-Metal Solid-State Lasers

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Outline

• Motivation
• Early Transition Metal, Infrared Lasers
• Transition Metal Spectroscopy
• The Cr$^{2+}$ Revolution
  – No ESA
  – Low nonradiative relaxation rates
• Cr$^{2+}$ laser advances
• Fe$^{2+}$ laser advances
• TM laser issues
• Summary
Motivation for IR Lasers

- **Uses**
  - Remote Sensing
  - Spectroscopy
  - Medical
  - Target Designation / Recognition
  - IR Countermeasures

- **Requirements**
  - Rugged
  - Compact
  - Solid-State
  - Tunable
  - Low Cost
Available IR Sources

• **QCLs (4-12 µm), ICLs (2-4 µm)**
  - Direct electric pumping
  - Limited tuning for specific structure
  - Efficient
  - No energy storage

• **Rare Earth Lasers**
  - Specific wavelengths dependent on ion and host
  - High energy storage
  - Efficiency decreases as wavelength increases

• **Nonlinear frequency conversion, e.g. OPO**
  - Broadband tuning
  - Simultaneous multiple wavelengths
  - Conversion stage adds complexity and reduces efficiency

• **Transition Metal Lasers**
  - Broadband tuning
  - Easily optically pumped
  - CW, gain-switched and modelocked operation
Transition Metal Lasers

• not initially recognized as natural laser candidates
  • broad fluorescence lines in visible and IR between electronic d levels
  • easily substituted in large variety of host materials
  • ruby [the first laser] is an exception to the rule
• d levels strongly couple to crystal field (not shielded)

Important Transition Metal Lasers

\[ \begin{align*}
\text{Ti}^{3+} & \\
\text{Cr}^{2+}, \text{Cr}^{3+}, \text{Cr}^{4+} & \\
\text{Fe}^{2+} & \\
\text{Co}^{2+} & \\
\text{Ni}^{2+} & 
\end{align*} \]

• Cu and Au operate as metal vapor lasers but not as solid state lasers
Transition Metals vs. Rare Earths

d orbitals

f orbitals

$6s^2$
Early Transition Metal Lasers

- **Ruby laser [1960]**
  - First laser
  - Cr$^{3+}$ ions in Al$_2$O$_3$

- **Ni$^{2+}$, Co$^{2+}$ lasers [1980]**
  - Broadband tuning in the mid-IR but ESA present
  - Flashlamp pumped and cryogenically cooled
  - High nonradiative relaxation at 300K
  - Pulsed pumping makes RT operation possible

![Energy Level Diagram](image)
In 1996 LLNL researchers demonstrated Cr$^{2+}$ lasing in a II-VI semiconductor host
- small phonon energy $\rightarrow$ small nonradiative relaxation rate $\rightarrow$ RT operation
- widely tunable mid-IR wavelength tuning
- No ESA

Flurry of activity in many labs demonstrating new Cr$^{2+}$ lasers (ZnS, CdSe, CdMnTe)

Fe$^{2+}$ lasing – 1983 (Fe$^{3+}$ false start) rediscovered 1999
Optical Spectroscopy of Inorganic Solids

B. Henderson and G. F. Imbush
ISBN 0-19-851372-0
Oxford University Press 1989

Chapter 5 Vibrating Crystal Environment
Chapter 9 Transition Metal Ions in Solids
We can treat isolated atoms with a free ion Hamiltonian – spectra are sharp transitions between **hydrogen-like Hamiltonian levels**

For a gas we add the **inter-atom potential** and treat the potential as radially symmetric

\[
V(r) \propto \frac{1}{r^m} \left[ 1 - \left( \frac{m}{n} \frac{r_o}{r} \right)^{n-m} \right]
\]

\(m\) and \(n\) can be adjusted to model different situations; \(r_o\) is the equilibrium separation

A liquid is basically a denser gas

A **solid breaks the radial symmetry**. A particular ion or atom is in a lattice with a particular local symmetry determined by the crystal structure. What does that do to the electronic energy level structure of an ion? This is what crystal field or ligand field theory addresses.
Full Hamiltonian \[ H = H_{FI}(r_i) + H_c(r_i, R_l) + V_l(R_l) + \sum_l \frac{p_i^2}{2M_l} \]

\( H_{FI} \) [Free ion Hamiltonian]: closed shell Hamiltonian + Coulomb interaction of outer electrons + spin-orbit coupling. \( r = \) electron position, \( R = \) ligand ion position, \( L = \) ligand

\( H_c(r_i, R_l) \): crystal field

\( V_l \): inter-ion potential energy

Last term: kinetic energy of lattice ions

\[ H_{FI} = H_o + H' + H_{so} \]

\( H_o = \sum_i \left( \frac{p_i^2}{2m} + V'(r_i) \right) \)  \textit{Free Ion Hamiltonian}

Kinetic energy of the electrons outside closed shells + \( V' \), the central potential of the nucleus and inner closed shell electrons

\( H' = \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \)  \text{Coulomb interaction between outer electrons}

\( H_{so} = \sum_i \zeta(r_i) \hat{\mathbf{l}}_i \cdot \mathbf{s}_i \)  \text{Spin-orbit coupling}
(np)² Splitting Example

Configuration designation:

\((2S+1)L_J\)

S: total spin
L: total orbital momentum
J: total angular momentum

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹S</td>
<td>¹S₀</td>
</tr>
<tr>
<td>¹D</td>
<td>¹D₂</td>
</tr>
<tr>
<td>³P</td>
<td>³P₀  ³P₁  ³P₂</td>
</tr>
</tbody>
</table>

H₀, H₀ + H', H₀ + H' + H_{so}

Coulomb splitting
Spin-Orbit splitting
Crystal Field Hamiltonian \([H_c]\)

\[
H_c = \sum_i (-e)\phi(r_i) = \frac{1}{4\pi\varepsilon_o} \sum_i \sum_l \frac{Z_i e^2}{|R_l - r_i|}
\]

Transition metal ions have electrons that can ‘see’ the surrounding ion charges in a crystal. Note that the crystal field term couples the electronic motion \([r_i]\) with the motion [vibrations] of the lattice (or ligand) ions \([R_l]\). The crystal field also has a spatial symmetry which determines how the degenerate electronic energy levels (e.g. 5d levels) will split.

We will temporarily ignore the ionic kinetic energy term [assume the ions are stationary since electrons move much faster] and write the static lattice Hamiltonian \([R_l \text{ is a constant}]\)

\[
H_o = H_{Fl}(r_i) + H_c(r_i, R_l) + V_l(R_l)
\]

\[
= H_e(r_i, R_l) + V_l(R_l)
\]

electronic Hamiltonian + potential due to surrounding ions
We write the eigenfunctions of $H_o$ as $\psi_a(r_i, R_l)$ static eigenfunctions

$$H_o \psi_a(r_i, R_l) = E^{(a)}(R_l) \psi_a(r_i, R_l)$$

static eigenenergies

The subscript $a$ refers to a particular electronic state of an optically active ion.

Now we return to the dynamic lattice [let ions move again] and the Schrödinger equation is

$$\left[ H_o + \sum_l \frac{P_l^2}{2M_l} \right] \psi_a(r_i, R_l) \chi_a(R_l) = E \psi_a(r_i, R_l) \chi_a(R_l)$$

where $\psi_a$ is an eigenfunction of $H_o$ and $\chi_a$ is a function of the ligand positions.

Write $P_l = -i\hbar \nabla_l$ (lattice state)

$$\frac{P_l^2}{2M_l} \psi_a \chi_a = -\frac{\hbar^2}{2M_l} \left[ \chi_a \nabla_l^2 \psi_a + 2(\nabla_l \chi_a)(\nabla_l \psi_a) + \psi_a \nabla_l^2 \chi_a \right]$$
The approximation where we ignore the first two terms above is called the **Born-Oppenheimer (or adiabatic) approximation**. It implies that we are assuming the electrons move much faster than the ions and that they adiabatically adjust to the varying ionic positions. It also implies that the electrons do not change their electronic state when the ionic positions change. One can add the terms back as a perturbation which will mix $\psi_a \chi_a$ with other $\psi_b \chi_b$ states but the mixing will be small if the energy separation is large.

The adiabatic theorem is an important theorem in quantum mechanics which provides the foundation for perturbative quantum field theory.

There are different versions of this theorem. Max Born and V. A. Fock proved the original version in 1928:

A physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum.

The ion-plus-lattice eigenstates $\psi_a(r_i, R_l) \chi_a(R_l)$ are known as Born-Oppenheimer states.
The remaining term of the dynamic Hamiltonian no longer operates on $\psi_a$ so it reduces to

$$\frac{p_i^2}{2M_i} \psi_a \chi_a = -\frac{\hbar^2}{2M_i} \left[ \psi_a \nabla_i^2 \chi_a \right]$$

The Schrödinger equation becomes

$$\left[ \sum_l -\frac{\hbar^2}{2M_l} \nabla_l^2 + E^{(a)}(R_l) \right] \chi_a(R_l) = E \chi_a(R_l)$$

The $l$th ion oscillates about some equilibrium position $R_l^{(a)}(0)$ when the system is in electronic state $a$. So we can write:

$$R_l = R_l^{(a)}(0) + q_l^{(a)}$$

where $q_l^{(a)}$ is the displacement of the ion from its equilibrium position.
The electronic energy term can be written: 
\[ H_e^{(a)}(R_l) = H_e^{(a)}(R_l^{(a)}(0)) + V_e^{(a)}(q_l^{(a)}) \]

The inter-ion potential term can be written: 
\[ V_I^{(a)}(R_l) = V_I^{(a)}(R_l^q(0)) + V_I^{(a)}(q_l^{(a)}) \]

The rigid lattice energy [all ions at their equilibrium positions] is: 
\[ E_o^{(a)}(R_l) = H_e^{(a)}(R_l^{(a)}(0)) + V_I^{(a)}(R_l^q(0)) \]

The ionic potential energy becomes: 
\[ E^{(a)}(R_l) = E_o^{(a)}(R_l) + V_e^{(a)}(q_l^{(a)}) + V_I^{(a)}(q_l^{(a)}) \]

Effect of lattice distortion on the electronic energy
Effect of lattice distortion on inter-ionic potential energy

The lattice state Schrödinger equation can be written

\[ \sum_l \left[ \frac{P_l^2}{2M_l} + \left( V_e^{(a)}(q_l^{(a)}) + V_I^{(a)}(q_l^{(a)}) \right) \right] \chi^{(a)}(q_l^{(a)}) = \left( E - E_o^{(a)} \right) \chi^{(a)}(q_l^{(a)}) \]

But now we are left with a problem. We cannot decouple the electronic and ionic \( V \)'s because they are both functions of the same variable \( q_l^{(a)} \). The dynamic lattice is a coupled system. The solution is to switch to a description in terms of \textbf{normal coordinates} (\( Q_k \)) of the complex of ions.
A quick hand-waving description of normal modes. The mode coordinates describe characteristic modes of vibration. For example, you may have seen a derivation of modes of vibration for a line of atoms, or modes of vibration for a molecule like CO₂.

O=C=O has modes of vibration that describe positions of the atoms. One mode involves the C atom being stationary and the O atoms vibrating in and out but 180° out of phase (breathing mode). Another mode has the C atom oscillating back and forth between the two O atoms while the O atoms oscillate in phase with each other but 180° out of phase with the C atom.

\[
\begin{align*}
Q_1 &= x(O_{(1)}) - x(O_{(2)}) \\
Q_2 &= x(O_{(1)}) + x(O_{(2)}) - x(C)
\end{align*}
\]

We will now write our lattice states as eigenfunctions of the normal mode coordinates of our ionic complex \( \chi_a(Q_k) \). If the \( V^{(a)} \) potential is harmonic in the normal mode coordinates, then the lattice eigenstates are products of linear harmonic oscillator functions, one for each normal mode \( k \).

\[
\chi_a = \prod_k \mid n_k \rangle
\]
The energy associated with a harmonic oscillator via quantum mechanics arguments is

\[ H_{HO} |n\rangle = \left( \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \right) |n\rangle = \hbar \omega (n + \frac{1}{2}) |n\rangle \]

For \( \chi_a = \prod_k |n_k\rangle \quad E = E_o^{(a)} + \sum_k \hbar \omega_k^{(a)} \left(n_k + \frac{1}{2} \right) \)

The summation term: is basically (1) a count of the number of phonons [vibrational quanta] present in each normal mode \( k \times (2) \) the energy of each phonon [\( \hbar \omega \)] plus the 1/2 [\( \hbar \omega \)] term that comes from the zero-phonon ground state.

At temperature \( T \) the average value of \( n_k \) is given by Bose-Einstein statistics [since phonons like photons are bosons]:

\[ < n_k > = \frac{1}{\exp\left(\frac{\hbar \omega}{kT}\right) - 1} \]

In review, \( \psi_a(r_i, R_l) \) is the electronic eigenstate of \( H_0 \) with energy \( E^{(a)}(R_l(0)) \)

\( \chi_a(Q_k) \) is the lattice state with the additional energy shown above.
There are many normal modes of vibration, \( k \), which must be taken into account. We will now make the **simplifying assumption** that we can confine our attention to **one representative mode** only. It is conceptually useful to consider this the breathing mode with the distance from the central optically active ion to the first shell of neighboring ions labeled as \( Q \). In the single configuration coordinate [SCC] model, \( Q \) oscillates about its equilibrium value \( Q_0^{(a)} \). The Born-Oppenheimer wavefunction can be written as

\[
\psi_a(r, Q_0^{(a)}) \chi_a(Q)
\]

The ionic potential energy can be written as

\[
E^{(a)}(Q) = E_0^{(a)} + V^{(a)}(Q)
\]

The general potential above is approximated by a harmonic oscillator potential. The lattice state \( \chi(Q) \) can be written as \( |n> \) where \( n \) is the number of vibrational quanta above the zero-point energy.

When the system changes to another electronic state \( b \), the electronic wavefunction changes to \( \psi_b \) with new equilibrium positions for the surrounding ions and \( Q \) oscillates about a new equilibrium value. The excited state \( b \) ionic potential energy becomes a new harmonic oscillator state.
Ionic Potential Energy Curves of SCC Model

Electronic state b

Electronic state a

Phonon states $n^{(b)}$

$E_o^{(b)}$

$E_o^{(a)}$

Q

Q

Configuration Coordinate

$\left( n^{(b)} + \frac{1}{2} \right) \hbar \omega^{(b)}$

$\left( n^{(a)} + \frac{1}{2} \right) \hbar \omega^{(a)}$

$Q_o^{(a)}$

$Q_o^{(b)}$
SCCM Radiative Transitions

Consider a radiative transition between electronic states \( a \) and \( b \) on an optically active ion in a vibrating lattice. We will use the harmonic oscillator approximation. We will also assume that the vibrational frequencies are the same in the two electronic states but we will allow the equilibrium position to differ. The difference in equilibrium position arises because of the difference in coupling between the optically active electron(s) and the lattice [electron-lattice coupling] in states \( a \) and \( b \).

Let \( M \) be some effective ion mass and \( \omega \) be the frequency of the vibrational mode. Then the classical oscillator potential energy in the ground state is:

\[
E^{(a)}(Q) = E^{(a)}_o + \frac{1}{2} M \omega^2 \left( Q - Q^{(a)}_o \right)^2
\]

2\(^{nd}\) term comes from energy of a harmonic oscillator

\[
E = K + U = \frac{1}{2} m v^2 + \frac{1}{2} k x^2 = \frac{1}{2} m \omega x_{\text{max}}^2
\]

The energy of the excited state \( b \) is:

\[
E^{(b)}(Q') = E_{ab} - \frac{1}{2} M \omega^2 \left( Q^{(b)}_o - Q^{(a)}_o \right)^2 + \frac{1}{2} M \omega^2 \left( Q' - Q^{(b)}_o \right)^2
\]

\( E_{ab} \) is defined because it is a measurable absorption energy, \( \omega_a = \omega_b \)
We can re-arrange the terms to also write

\[ E^{(b)}(Q') = E_{ab} + \frac{1}{2} M \omega^2 (Q' - Q_o^{(a)})^2 - M \omega^2 (Q_o^{(b)} - Q_o^{(a)}) (Q' - Q_o^{(a)}) \]

Substituting for \( E^{(a)}(Q') \)

\[ E^{(b)}(Q') - E^{(a)}(Q') = E_{ab} - M \omega^2 (Q_o^{(b)} - Q_o^{(a)}) (Q' - Q_o^{(a)}) \]

Note that the difference in energy between the two electronic states for any value of \( Q' \) is proportional to \( Q' - Q_o^{(a)} \). This is referred to as the linear coupling case.

It is usual to characterize the difference in electron-lattice coupling as a dimensionless constant, the **Huang-Rhys parameter**, \( S \), defined as

\[
S \equiv \frac{E_{\text{dis}}}{\hbar \omega} = \frac{1}{2} \frac{M \omega^2}{\hbar \omega} \left( Q_o^{(b)} - Q_o^{(a)} \right)^2
\]

Also, \( E_{\text{dis}} = \left( m' + \frac{1}{2} \right) \hbar \omega = S \hbar \omega \)

where \( |m'\rangle \) is the state with \( m' \) phonons present

Note that \( S \) increases quadratically as the offset of the upper and lower parabolas increases
Absorption Transitions

Probability of a photon absorption transition from electron-vibration state $|a,n\rangle$ to electron-vibration state $|b,m\rangle$ is proportional to:

$$\left| \langle \psi_b(r,Q) \chi_b(m) | \mu | \psi_a(r,Q) \chi_a(n) \rangle \right|^2$$

where $\mu$ is the appropriate electronic dipole operator

The lattice states, $\chi$, do not depend upon $\mu$ so we can separate the matrix element evaluation [Condon approximation]. The transition probability is then:

$$W_{an-bm} = P_{ab} \left| \langle \chi_b(m) | \chi_a(n) \rangle \right|^2$$

Where $P_{ab}$ is the **purely electronic transition probability** and is the same for all $n$ and $m$.

The $\chi$’s are the harmonic oscillator eigenfunctions but defined with **different equilibrium points** so the **overlap integrals** [matrix elements] are in general not zero.

What happens if the equilibrium points are the same? The $m^{th}$ and the $n^{th}$ $\chi$ eigenfunctions are orthogonal and the matrix element becomes zero unless $n = m$ where the matrix element becomes 1. We have uncoupled the electrons from the lattice vibrations. Rare earth ion transitions act this way because the f orbitals are shielded from the crystal field of the ligand ions.
Overlap Integrals

The overlap integral can be expressed in closed form as:

\[
\langle \chi_b(m)\|\chi_a(n) \rangle = \exp[-S/2]\sqrt{n!/m!(\sqrt{S})^{m-n}} L_{n-m}^{m-n}(S)
\]

where \(S\) is the Huang-Rhys parameter \(L_{n-m}^{m-n}\) is an associated Laguerre polynomial and \(L_0^m(x) = 1\)

Associated Laguerre polynomials also show up in radial eigenfunction solutions to the Coulomb potential.

\[
\begin{align*}
L_0^k(x) &= 1 \\
L_1^k(x) &= -x + k + 1 \\
L_2^k(x) &= \frac{1}{2}[x^2 - 2(k + 2)x + (k + 1)(k + 2)] \\
L_3^k(x) &= \frac{1}{6}[-x^3 + 3(k + 3)x^2 - 3(k + 2)(k + 3)x + (k + 1)(k + 2)(k + 3)].
\end{align*}
\]

\(k = m - n\)
Franck-Condon Factor

At $T = 0$ K only the $n = 0$ vibrational state is occupied so the matrix elements become

$$F_m(0) = \left| \langle \chi_b(m) | \chi_a(0) \rangle \right|^2 = \frac{\exp[-S]S^m}{m!} \quad \text{[Zero-temperature Franck-Condon factor]}$$

So at $T = 0$ K, the absorption bandshape will be

$$I_{ab}(E) = I_o \sum_m \frac{\exp[-S]S^m}{m!} \delta(E_{bm} - E_{a0} - E)$$

where $\delta(\ )$ is a delta function.

The energy between the zero vibrational levels of the initial and final states is

$$E_o \equiv E_{b0} - E_{a0}$$

This is the energy difference between the bottoms of the two parabolas in the SCCM diagram and is called the zero phonon line since no phonons are created or destroyed.
Using the definition of $E_o$ we can also write the absorption bandshape as

$$I_{ab}(E) = I_o \sum_m \frac{\exp[-S]}{m!} \delta(E_o + m\hbar\omega - E)$$
Since $\sum_m |\langle \chi_b(m) | \chi_a(n) \rangle|^2 = 1$ the intensity of the full band is $I_0$ and is independent of $S$. This also means that the intensity is independent of temperature.

Intensity of the zero phonon line [$m = 0$]: $I_{ab}(E_o) = I_o e^{-S}$

If $S = 0$, then all of the intensity is contained in the zero-phonon line and there is no lateral displacement of the harmonic oscillator parabolae, i.e. $Q_o^{(a)} = Q_o^{(b)}$. As $S$ increases, the intensity in the zero-phonon line decreases but this is compensated for by the appearance of vibrational sidebands observed at energies $m\hbar\omega$.

Predicted bandshapes for different values of $S$. Note that the most likely transition is at an energy $(S-1/2)\hbar\omega$ above the zero phonon line for $S \geq 1$ and $S\hbar\omega$ above the bottom of the excited state parabola. The zero phonon line rapidly gets small as $S$ increases.
δ function representation is not valid for a real system. Lattice vibration has many modes not just one. Assume a sideband at energy $m\hbar\omega$ has a width of $m\hbar\omega$. This gives a bandshape like the one on the left for

$$S = 7 \quad \hbar\omega = 250 \text{ cm}^{-1}$$

Observed absorption spectrum of ruby at 77 K.
Franck-Condon Principle: The maximum probability absorption transition is indicated by the vertical line drawn from the center of the initial parabola to the point where it intersects the upper level parabola. Quantum mechanically this is true because the overlap integral is the largest there. We also saw this in our $\delta$-function band shape spectra.

(semi-classical explanation)
The harmonic oscillator spends most of its time at the ends of the oscillation and so that is where the transition is most likely to occur.

Fig. 5.9. $\chi_d(0)$ and $\chi_b(m')$ have maximum amplitudes at the same value of the configurational coordinate, $Q_0^{(\theta)}$. 
Lineshapes

Lineshape depends on size of $S$. For large $S$ the parabola has nearly constant slope and the spectrum is a nearly symmetric Gaussian and is broad. For small $S$ the spectrum is not symmetric and has a Pekarian shape with narrower bandwidth.

From this curve let us now calculate a linewidth. The zero vibrational level involves a variation $\Delta_0$ about $Q_0^{(a)}$. The energy at the zero-point level is

$$\frac{1}{2} M \omega^2 \Delta_0^2 = \frac{1}{2} \hbar \omega$$

$$m \quad \frac{1}{2} M \omega^2 (Q_0^{(b)} - Q_0^{(a)})^2 = (m + \frac{1}{2}) \hbar \omega$$

$$m - \Delta m \quad \frac{1}{2} M \omega^2 (Q_0^{(b)} - Q_0^{(a)} - \Delta_0)^2 = (m - \Delta m + \frac{1}{2}) \hbar \omega$$

$$m + \Delta m' \quad \frac{1}{2} M \omega^2 (Q_0^{(b)} - Q_0^{(a)} + \Delta_0)^2 = (m + \Delta m' + \frac{1}{2}) \hbar \omega$$

Spectrum asymmetry requires using $\Delta m \neq \Delta m'$

But we will now approximate them to be equal.
Assuming $\Delta \ll Q_0^{(b)} - Q_0^{(a)}$

$$M\omega^2(Q_0^{(b)} - Q_0^{(a)})\Delta_o \approx \Delta m\hbar\omega \approx \Delta m'\hbar\omega$$

At $T = 0$, the **bandwidth** $\Gamma$ is

$$\Gamma(0) \approx (\Delta m + \Delta m')\hbar\omega \approx 2M\omega^2(Q_0^{(b)} - Q_0^{(a)})\Delta_o$$

From the definition of the Huang-Rhys parameter and the zero point energy

$$S \equiv \frac{E_{dis}}{\hbar\omega} = \frac{1}{2} \frac{M\omega^2}{\hbar\omega} (Q_o^{(b)} - Q_o^{(a)})^2 \Rightarrow \frac{1}{2} M\omega^2\Delta_o^2 = \frac{1}{2} \hbar\omega$$

$$\Gamma(0) = 2\hbar\omega(2S)^{\frac{1}{2}}$$

An exact calculation of the 2nd moment of a Pekarian lineshape gives

$$\Gamma(0) = 2.36\hbar\omega(S)^{\frac{1}{2}}$$

[Remember this is a calculation for $T = 0$.]
The bandshape for temperatures above zero is calculated by carrying out a thermal average over the initial vibration states. This can be shown to result in

\[
I_{ab}(E) = I_o \sum_{p=-\infty}^{\infty} \exp\left[-S(1+2\langle n \rangle)\right]\left(1+\frac{\langle n \rangle}{\langle \rangle}\right)^{p/2} I_p\left(2S\sqrt{\langle n \rangle(\langle n \rangle+1)}\right)\delta(E_o + p\hbar\omega - E)
\]

where \( \langle n \rangle = \frac{1}{\exp(h\omega / kT) - 1} \) and \( I_p \) is the modified Bessel function.

\(<n>\) is the mean thermal occupancy of the vibrational mode

The zero-temperature lineshape is shown below again for comparison.

\[
I_{ab}(E) = I_o \sum_m \frac{\exp[-S] S^m}{m!} \delta(E_o + m\hbar\omega - E)
\]
• The term $S(1+2\langle n \rangle)$ is sometimes called the **effective Huang-Rhys parameter** at high temperatures.

• At $T > 0$ there can be vibrational components with negative values of $p$. So there is vibrational absorption on the high-energy side of the zero-phonon line. These are called anti-Stokes side bands.

• The total intensity of the transition remains constant.

• The intensity of the zero phonon line as a function of temperature is

$$I_o \exp[-S(1+2\langle n \rangle)]$$

which decreases with increasing temperature.
Bandwidth vs Temperature

For $T=0$ we already had

$$\Gamma(0) \approx 2M\omega^2(\mathcal{Q}_0^{(b)} - \mathcal{Q}_0^{(a)})\Delta_o$$

We can analogously write

$$\Gamma(T) \approx 2M\omega^2(\mathcal{Q}_0^{(b)} - \mathcal{Q}_0^{(a)})(\text{mean}(\Delta_n^2))^{\frac{1}{2}}$$

where $\Delta_n$ is the amplitude of the breathing mode oscillating in the $n^{th}$ vibrational level and $\Delta_n^2 = \Delta_0^2(1 + 2n)$

$$\therefore \text{mean}(\Delta_n^2) = \sum_n \frac{\Delta_n^2}{\sum_m \exp\left[-m\hbar\omega/kT\right]} \exp\left[-n\hbar\omega/kT\right]$$

$$= \Delta_0^2 \coth \frac{\hbar\omega}{2kT}$$

$$\Gamma(T) = \Gamma(0)\sqrt{\coth \frac{\hbar\omega}{2kT}}$$

T in units of phonon energy
Emission Transitions

At $T = 0$ emission is

$$I_{ba}(E) = I_o \sum_n \frac{\exp(-S)S^n}{n!} \delta(E_o - n\hbar\omega - E)$$

The emission band is a mirror image of the absorption band if the $a$ and $b$ state parabolas are equal. The shift in energy is known as the Stokes shift.

$$(2S - 1)\hbar\omega$$
Ti$^{3+}$ Crystal Field Example
Crystal Field of a single 3d electron in an octahedral field, (e.g. Ti$^{3+}$)

Electrostatic potential energy is

\[ V_x = \frac{-Ze}{4\pi \varepsilon_o} \left[ \frac{1}{\sqrt{r^2 + a^2 - 2ax}} + \frac{1}{\sqrt{r^2 + a^2 + 2ax}} \right] \]

via law of cosines

\[ V = V_x + V_y + V_z \]

6 negative ions at cube faces distance \( a \) away from positive ion

\[ r^2 = x^2 + y^2 + z^2 \]

3d electron position

\[ H_c^{O_h} = -eV \]

After some algebra and expanding in terms up to 6th degree

\[ V(x, y, z) = \frac{-Ze}{4\pi \varepsilon_o} \left\{ \frac{6}{a} - \frac{35}{4a^3} \left[ x^4 + y^4 + z^4 - \frac{3}{5} r^4 \right] - \frac{21}{2a^2} \left[ x^6 + y^6 + z^6 + \frac{15}{4} \left( x^2 y^4 + x^2 z^4 + y^2 z^4 + y^2 z^4 + z^2 x^4 + z^2 y^4 \right) - \frac{15}{14} r^6 \right] \right\} \]

Or in terms of spherical harmonics

\[ H_c^{O_h}(r) = \frac{Ze^2}{4\pi \varepsilon_o} \left\{ \frac{6}{a} + \frac{7r^4}{2a^5} \left[ C_0^4(\theta, \phi) + C_0^4(\theta, \phi) \right] \right\} \]

\( r \) is the position of the 3d electron and we have neglected terms greater than \( r^4 \)
We can calculate the matrix elements of the 3d states \( |3dm_i\rangle \) or look them up where \( m_i \) is the angular momentum quantum number.

Let

\[
D \equiv \frac{1}{4\pi\varepsilon_o} \frac{35Ze^2}{4a^5} \quad q \equiv \frac{2}{105} \langle r^4 \rangle
\]

Non-zero matrix elements are

\[
\langle 3d0 | H_c | 3d0 \rangle = 6Dq \\
\langle 3d1 | H_c | 3d1 \rangle = \langle 3d -1 | H_c | 3d -1 \rangle = -4Dq \\
\langle 3d2 | H_c | 3d2 \rangle = \langle 3d -2 | H_c | 3d -2 \rangle = Dq \\
\langle 3d2 | H_c | 3d -2 \rangle = \langle 3d -2 | H_c | 3d2 \rangle = 5Dq
\]

Obviously, \( |3d0\rangle, |3d1\rangle \) and \( |3d-1\rangle \) are eigenstates since only diagonal matrix elements are non-zero. The \( m_i = \pm 2 \) states are mixed.

Diagonalizing \( m_i = \pm 2 \) states we get 3 eigenstates [labeled \( t_2 \)] with energy \(-4Dq\) and 2 eigenstates [labeled \( e \)] with energy \( 6Dq \)

\[
\begin{array}{cccccc}
-2 & -1 & 0 & 1 & 2 \\
\end{array}
\]

\[
\begin{bmatrix}
Dq & 5Dq \\
-4Dq & \quad & 6Dq \\
\quad & -4Dq & \quad & Dq
\end{bmatrix}
\]

\[
\Delta
\]

\[
+6Dq \quad g=2 \\
-4Dq \quad g=3
\]

\( g = \text{degeneracy} \)
3d orbitals

t₂ orbitals have lower energy because they avoid the negative ions.
e orbitals have higher energy because they overlap negative ion neighbors.

http://www.slideshare.net/surya287/crystal-field-theory
High Spin Vs. Low Spin (d¹ to d¹⁰)

Electron Configuration for Octahedral complexes of metal ion having d¹ to d¹⁰ configuration [M(H₂O)₆]⁺ⁿ.

Only the d⁴ through d⁷ cases have both high-spin and low spin configuration.

http://www.slideshare.net/surya287/crystal-field-theory
**Tanabe-Sugano Diagram for Cr$^{3+}$**

Cr$^{3+}$ has three 3d electrons. They mix to form the free ion energy levels shown on the left. Addition of an octahedral crystal field results in the splitting shown. D$\text{q}/B$ is a measure of the crystal field strength.

The terminology for the crystal field energy levels has its basis in group theory. The leading superscript in either the free ion or the crystal field cases is $2S + 1$ where $S$ is the total spin of the three electrons.

For 3 electrons $S = 1/2$ or $3/2$ and $2S + 1 = 2$ or 4

---

**Fig. 3.20.** Energy levels of a 3d$^3$ system in an octahedral crystal field. The values have been calculated for $\gamma = 4.8$, a value appropriate for Cr$^{3+}$ in aluminium oxide. For this material $D\text{q}/B = 2.8$. The theoretical free-ion levels, obtained by putting $D\text{q} = 0$, are shown on the left.
Cr$^{3+}$ Crystal Fields

Ruby
Alexandrite
GSGG
Cr\textsuperscript{3+} SCCM Diagram

high crystal field

Narrow bandwidth emission

Ruby
Cr$^{3+}$ SCCM Diagram
low field

$^2E$  
$^4A_2$  
$^4T_1$  
$^4T_2$  
Brodband emission

GSGG
Nonradiative Transitions

\[ \Delta E = \frac{hE_p}{\# \text{ phonons}}, \]

- as \( p \) increases the nonradiative relaxation rate rapidly decreases

- phonon energy decreases in the following order:
  - oxide
  - fluoride
  - selenide
  - chloride
  - iodide
  - bromide

\[ p = \frac{\Delta E}{h\Omega} \]
Crossover Transitions

Crossover lower than absorption level

Crossover higher than absorption level
As temperature increases the population of the higher vibrational levels in state b will increase. At high enough temperatures, there will be some population at the crossover point resulting in nonradiative transitions to the ground state.

The thermal relaxation path can be described by a rate constant N and an activation energy $E_{\text{act}}$.

$$W_{nr}(T) = N \exp[-E_{\text{act}} / kT]$$

Usually, the calculated activation energy is too high compared to the measured effect. The reason is that we have not allowed for tunneling.
Nonradiative Tunneling

Because the wavefunctions extend beyond the edge of the parabola there is a finite probability that tunneling from one parabola to another can take place. This makes the Mott activation energy too high. A more correct way is to calculate the transition probability, the overlap integral for the vibrational wavefunctions and add the results for all overlapping pairs.

Struck and Fonger* have done the calculation and found the tunneling rate to be:

$$W_{tunnel} = N \exp[-S(2m+1)\sum_{j=0}^{\infty} \frac{(S\langle m \rangle)^j(S\langle m+1 \rangle)^{p+j}}{j!(p+j)!}]$$

$N$ depends on the electronic part of the wavefunction overlap and is typically $\sim 10^{13} \text{ s}^{-1}$

$p$ is the number of phonons it takes to equal the zero phonon energy gap between the electronic energy levels involved.

$<m>$ is the mean thermal occupancy

Ti$^{3+}$ Lifetime Fits

Figure 33. Model fit of Ti$^{3+}$:GSAG fluorescence lifetime.

Figure 31. Model fit of Ti$^{3+}$:sapphire fluorescence lifetime.
Why are there only Ti:sapphire Lasers?

Ti³⁺ doped into many crystals other than Al₂O₃
• YAG
• GSAG
• YAlO₃

None of them work as lasers:
• Ti³⁺:YAG and Ti³⁺:GSAG have low crystal fields resulting in high nonradiative relaxation rates
• Ti³⁺:YAlO₃ has a high crystal field with strong beautiful yellow fluorescence but excited state absorption
In 1996 LLNL researchers demonstrated Cr\(^{2+}\) lasing in a II-VI semiconductor host:
- Small phonon energy $\rightarrow$ small nonradiative relaxation rate $\rightarrow$ RT operation
- Widely tunable mid-IR wavelength tuning
- No ESA

Flurry of activity in many labs demonstrating new Cr\(^{2+}\) lasers (ZnS, CdSe, CdMnTe)
Cr\textsuperscript{2+}:ZnSe Chalcogenide Laser Sources

- Broad absorption at 1500-2000 nm
- Room Temperature Operation
- CW or Pulsed Output from 2000-3100 nm

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Absorption Cross Section $\sigma_{abs}$ (cm\textsuperscript{-2})</th>
<th>Emission Cross Section $\sigma_{em}$ (cm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>$1\times10^{-18}$</td>
<td>$5\times10^{-19}$</td>
</tr>
<tr>
<td>1500</td>
<td>$5\times10^{-19}$</td>
<td>$1\times10^{-18}$</td>
</tr>
<tr>
<td>2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Configuration coordinate

- $^5T_2$ absorption
- $^5E$ emission
Early TM IR lasers

Ni$^{2+}$, Co$^{2+}$ lasers [1980]
Broadband tuning in the mid-IR but ESA present
Flashlamp pumped and cryogenically cooled
High nonradiative relaxation at 300K
Pulsed pumping makes RT operation possible

Co:MgF$_2$ Laser
Was a commercial product (Cobra 2000)
developed and sold by Q-Peak (1.7-2.6 µm)
Tanabe-Sugano diagram for octahedrally coordinated $3d^7$ electronic configuration of Co$^{2+}$ ions. ESA is possible because upper levels with the same $S = 3/2$ ($2S + 1 = 4$) spin state are present.
Why no Cr$^{2+}$ ESA?

Tanabe-Sugano diagram for tetrahedrally coordinated Cr$^{2+}$ 3d$^4$ configuration. ESA should be small because overlapping levels have different spins, S = 2 vs. S = 1.
## Cr$^{2+}$:II-VI Host Comparison

<table>
<thead>
<tr>
<th>Property</th>
<th>Cr:ZnS</th>
<th>Cr:ZnSe</th>
<th>Cr:CdSe</th>
<th>Cr:CdMnTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Cross Section (10$^{-18}$ cm$^2$)</td>
<td>1.0</td>
<td>1.1</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Absorption Peak (nm)</td>
<td>1700</td>
<td>1770</td>
<td>1900</td>
<td>1900</td>
</tr>
<tr>
<td>Stim. Emission Cross Section (10$^{-18}$ cm$^2$)</td>
<td>1.4</td>
<td>1.3</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Emission Peak (nm)</td>
<td>2350</td>
<td>2450</td>
<td>2500</td>
<td>2550</td>
</tr>
<tr>
<td>Lifetime at 293 K (μs)</td>
<td>6.2</td>
<td>5.5</td>
<td>5</td>
<td>4.5</td>
</tr>
<tr>
<td>dn/dT (10$^{-6}$ K$^{-1}$)</td>
<td>46</td>
<td>70</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>
Temperature Dependence of Cr\textsuperscript{2+} Fluorescence in II-VI hosts

![Graph showing temperature dependence of Cr\textsuperscript{2+} excited state lifetime in CdSe, CdMnTe, and ZnSe hosts.](image)

- **Cr:CdSe**
- **Cr:CdMnTe**
- **Cr:ZnSe**

Sensitivity Limit due to slow pump pulse decay
# Thermo-mechanical properties of laser hosts

<table>
<thead>
<tr>
<th>Material</th>
<th>( \kappa ) (W/mK)</th>
<th>( R_T ) (W/m(^{1/2}))</th>
<th>( \frac{dn}{dT} ) ((10^{-6}/K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>17</td>
<td>7.1</td>
<td>+46</td>
</tr>
<tr>
<td>ZnSe</td>
<td>18</td>
<td>5.3</td>
<td>+70</td>
</tr>
<tr>
<td>CdSe/CdMnTe</td>
<td>4</td>
<td>No data</td>
<td>No data, but likely to be similar to ZnSe</td>
</tr>
<tr>
<td>YAG</td>
<td>10</td>
<td>4.6</td>
<td>+8.9</td>
</tr>
<tr>
<td>YLF</td>
<td>5.8</td>
<td>1.1</td>
<td>-2.0,-4.3</td>
</tr>
<tr>
<td>Phosphate glass</td>
<td>0.6</td>
<td>0.35</td>
<td>-5.1</td>
</tr>
<tr>
<td>Al(_2)O(_3) (sapphire)</td>
<td>28</td>
<td>22</td>
<td>+12</td>
</tr>
<tr>
<td>Milestone</td>
<td>Authors</td>
<td>Year</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>--------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>1st Cr²⁺:ZnSe laser</td>
<td>DeLoach et al.</td>
<td>1996</td>
<td></td>
</tr>
<tr>
<td>1st CW Cr²⁺:ZnSe laser</td>
<td>Wagner et al.</td>
<td>1999</td>
<td></td>
</tr>
<tr>
<td>1st modelocked Cr²⁺:ZnSe laser</td>
<td>Carrig et al.</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>400 mW, 4 ps pulses</td>
<td>Sorokina et al.</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>2.2-2.8 µm tuning</td>
<td>Sorokina et al.</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>1.4 W CW, 73% slope η</td>
<td>Mond et al.</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>14% efficient diode pumping</td>
<td>Mond et al.</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>4.2 W gain-switched</td>
<td>McKay et al.</td>
<td>2002</td>
<td></td>
</tr>
<tr>
<td>18.5 W gain-switched, 65% slope η</td>
<td>Carrig et al.</td>
<td>2004</td>
<td></td>
</tr>
<tr>
<td>Single frequency, &lt; 20 MHz bandwidth</td>
<td>Wagner et al.</td>
<td>2004</td>
<td></td>
</tr>
<tr>
<td>&lt; 100 fs passive modelocking</td>
<td>Sorokina et al.</td>
<td>2006</td>
<td></td>
</tr>
<tr>
<td>14 W CW MOPA, 2-9 W over 400 nm tuning</td>
<td>Berry et al.</td>
<td>2010</td>
<td></td>
</tr>
<tr>
<td>1.4 MW peak power, gain switched</td>
<td>Fedorov et al.</td>
<td>2010</td>
<td></td>
</tr>
</tbody>
</table>
Cr$^{2+}$:ZnSe Laser Power Scaling

- Broadband tunability (2.3-3 µm)
- Room temperature operation
- Simple pumping scheme
- But severe thermal issues
  - High dn/dT
  - Thermal lensing
  - Thermal quenching

Beam quality changing with output power
14-W CW MOPA Cr\textsuperscript{2+} IR Laser

\[
\frac{\partial n^*(t,z,r)}{\partial t} = \frac{I_p(t,z,r)}{h \nu_p} \left( \sigma_{pa} n_g(t,z,r) - \sigma_{pe} n^*(t,z,r) \right) - \frac{I_s(t,z,r) \sigma_{se} n^*(t,z,r) - n^*(t,z,r)}{\tau} \frac{\partial}{\partial z}
\]

\[
\frac{\partial I_p(z,r)}{\partial z} = I_p(z,r) \left[ -\sigma_{pe} (n_0 - n^*(z,r)) + \sigma_{pe} n^*(z,r) - \gamma_p \right]
\]

\[
\frac{\partial I_s(z,r)}{\partial z} = I_s(z,r) \left( \sigma_{se} n^*(z,r) - \gamma_s \right)
\]

\[ L_\text{cavity} \quad \frac{\partial n^*(t,z,r)}{\partial t} = \frac{I_p(t,z,r)}{h \nu_p} \left( \sigma_{pa} n_g(t,z,r) - \sigma_{pe} n^*(t,z,r) \right) - \frac{I_s(t,z,r) \sigma_{se} n^*(t,z,r) - n^*(t,z,r)}{\tau} \frac{\partial}{\partial z}
\]

\[ Z\text{-cavity} \quad \frac{\partial I_p(z,r)}{\partial z} = I_p(z,r) \left[ -\sigma_{pe} (n_0 - n^*(z,r)) + \sigma_{pe} n^*(z,r) - \gamma_p \right]
\]

\[ \frac{\partial I_s(z,r)}{\partial z} = I_s(z,r) \left( \sigma_{se} n^*(z,r) - \gamma_s \right)
\]
Actual Hardware of Power Amplifier Stage

Pump  L_{PA}  L_{MO}

Cr^{2+}:ZnSe

Output

Signal
Cr\textsuperscript{2+} Broadband High Power Tuning

- Z-cavity MOPA = 8.9 W @ 2450 nm
- 300 gr/mm, 2.5 μm blaze grating, ~ 2 nm linewidth
- Multi-watt over 400 nm tuning–grating/coating limited
High-speed octagon mirror scanner is installed into the mode path between the intracavity lens and a Littrow-mounted diffraction grating.

Kerr Lens Modelocking

Thermal lensing

\[ f \approx \frac{k_T A}{P_a} \left( \frac{1}{2} \frac{dn}{dT} \right)^{-1} \]

- Lensing leads to damage or resonator instability
- Thin disk reduces radial index grating
- Thin disk results in higher material temperature – more nonradiative loss

- Thermal lens focal length
- Cross sectional rod area
- Absorbed power
- Thermal conductivity
- Thermal Shock Parameter
- Variation of refractive index
- with temperature
Cr$^{2+}$ Laser Issues

Thermal Lifetime Quenching

few watts of absorbed power $\rightarrow$ higher $T_{mat}$ and increased nonradiative relaxation

![Graph showing excited state lifetime vs. temperature for different materials: Cr:CdSe, Cr:CdMnTe, Cr:ZnSe. The graph indicates sensitivity limit due to slow pump pulse decay.]
Cr\textsuperscript{2+} Laser Issues

**Cr\textsuperscript{2+} Concentration Quenching**

- ZnSe quenching at 1000 ppm (half value)
- CdSe quenching at 50 ppm (half value)

Nd\textsuperscript{3+}:YAG doesn’t concentration quench until Nd is at the ~5% (50,000 ppm) doping level.
Concentration Quenching Mechanism

CdSe quenching value is for single crystal material
ZnSe quenching is for polycrystalline ceramic material

- Hypotheses:
  - Cr^{2+} concentration quenching is due to Cr-Cr pairs
  - Cr^{2+} ions are not randomly distributed but concentrated at grain boundaries or defect sites

- Commonly fabricated ZnSe grain size of 70 μm is consistent with a 50x magnitude difference in active ion, nearest neighbor pair density

\[ V \propto r^3 \text{ and } A \propto r^2 \text{ so } A/V \propto 1/r \]

So the ratio of area to volume will decrease as the radius of the grain increases. As the grain size decreases, the effective density of surface dopants decreases for a given average volume density

- If Cr preferred to substitute at grain boundaries, we could increase Cr^{2+} ion doping by using ZnSe with smaller grain sizes
- But we do not see any evidence of higher Cr density near grain boundaries so preference for Cr-Cr clustering seems to be the more probable mechanism
Way Ahead?

• Direct electrical pumping of Cr$^{2+}$:ZnSe

• Fiber/waveguide TM:II-VI laser
Fiber Cr\textsuperscript{2+}:II-VI laser

- Fiber form eliminates thermal lensing issue (e.g. silica fibers with > kW power)
- Low Cr\textsuperscript{2+} doping not an issue
  - make the fiber long enough to efficiently absorb the pump power
  - need gain per unit length > loss per unit length
- Chalcogenide glass shown to incorporate rare earth ions (Aggarwal et al. 2005)
- But no known TM glass lasers exist?
  - TM energy levels coupled to lattice vibrations → rapid relaxation to nonradiative energy sinks
  - Cr\textsuperscript{2+} doped host requires tetrahedral site symmetry and proper oxidation state

(assumption: fibers must be made from glass)
Waveguides were inscribed in Cr$^{2+}$ doped ZnSe.

**Laser output of 1.7 W @ 2.5 µm.**

Tunable Cr Waveguide Laser

Broad tunability in the 2077–2777 nm region

Narrow linewidth output as low as 53 pm (3 GHz)

Fiber beam confinement of $\text{Cr}^{2+}:\text{ZnSe}$ provides:

- Robust and compact direct mid-IR source
- Low thermal lensing effects
- Extended frequency and waveform modulation
- Excellent tunable pump source for nonlinear waveguide
- **Laser host material, nonlinear material and transport material all in one!**
ZnSe Fibers

ZnSe: laser host material, QPM nonlinear material and transport material all in one!

Progress:
• ZnS$_x$Se$_{(1-x)}$/ZnSe layers deposited in silica capillary
• Loss < 1 dB/cm @ 1.55 µm for ZnSe core

Cr\textsuperscript{2+} IR Fiber Lasers

- Er or Tm-doped silica fiber laser
- Cr\textsuperscript{2+}:ZnSe gain medium
- Diode Pump
- Cr\textsuperscript{2+}:ZnSe fiber core fabricated
- Cr\textsuperscript{2+} emission confirmed
- Cr lasing – not confirmed
Direct electrical pumping of \( \text{Cr}^{2+}:\text{ZnSe} \)

- 1941: Electroluminescence in II-VI semiconductors
- 1974: \( \text{Cr}^{2+} \) identified as the luminescence sink and IR emission source
- 2006: Room temperature electroluminescence was achieved in n-type Cr:Al:ZnSe (Mirov’s Group at UAB)
- Can the energy transfer be made efficient?

Figure 1. Energy levels of chromium in the forbidden band of ZnSe

Fe$^{2+}$ Transition Metal Lasers

- **3d$^6$ configuration for Fe$^{2+}$**
  - $\sim 3d^1$ (half-filled d shell) with single electron
  - Cr$^{2+}$ is $3d^4 \sim 3d^1$ with single hole
  - Spectroscopy of Fe$^{2+}$ similar to Cr$^{2+}$ but with ground and first excited levels switched

- **Fe$^{2+}$ lasing in n-InP and ZnSe (LLNL group)**
  - Smaller crystal field $\rightarrow$ longer wavelength ($\sim$ 3.5-5 $\mu$m in ZnSe)
  - Higher nonradiative relaxation
  - No RT lasing except with sub-lifetime pulsed pumping
Fe$^{2+}$ Lifetime Quenching

This work: unpublished measurements at AFRL
SC = single crystal, PC = polycrystalline
Fe:ZnSe Tunable Mid-IR Laser

Laser Setup

Fe Laser Performance

- 0.840 W @ 4.140 µm (increased to 1.6 W by IPG)
- 3.8-4.3 µm tunability
- Passively Q-switched, 850 kHz, 4.045 µm, 515 mW
- Scaling is currently limited only by 2.9 µm pump power
- Fe:ZnSe requires cryocooling – seek RT Fe hosts

Gain-switched 2-J Fe:ZnSe Laser

- Pump laser: 2.94 µm Er:YAG flashlamp-pumped
- Free-running 750-µs series of spikes
- Gain-switched 4.1 µm output follows pump train dynamics

Conclusions / Future work

• Transition metal ions doped into crystals offer broadly tunable, efficient lasing [e.g. Ti$^{3+}$:sapphire

• Tremendous advances in Mid-IR transition metal lasers in recent years

• Cr$^{2+}$:ZnSe is the champion in this class of lasers

• Fe$^{2+}$:ZnSe should be capable of laser performance analogous to Cr$^{2+}$:ZnSe but shifted to the 3.5-6 µm region

• Future work to further scale up power and improve overall utility include
  – Direct electrical pumping
  – Development of techniques to mitigate thermal lensing, e.g. fiber version of TM:II-VI ceramic material
  – Are there other TM laser ion-host combinations waiting to be discovered?
**SOA as of 2014**


### TABLE IV
STATE-OF-THE-ART IN Cr:ZnSe/S AND Fe:ZnSe/S LASERS

<table>
<thead>
<tr>
<th>Gain element</th>
<th>WAVELENGTH, µM</th>
<th>LINE WIDTH</th>
<th>W, AV.</th>
<th>W, Peak</th>
<th>Rep Rate</th>
<th>Pulse Energy</th>
<th>τp</th>
<th>Eff.,%</th>
<th>Type</th>
<th>T</th>
<th>Pump</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr:ZnS</td>
<td>2.3</td>
<td>1 nm</td>
<td>0.5 W</td>
<td></td>
<td></td>
<td></td>
<td>40%</td>
<td>CW</td>
<td>RT</td>
<td>Diode</td>
<td>[50]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnSe</td>
<td>2.4</td>
<td>0.5 nm</td>
<td>3.7 W</td>
<td></td>
<td></td>
<td></td>
<td>12%</td>
<td>CW</td>
<td>RT</td>
<td>Diode@1.7 µm</td>
<td>[74]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnSe</td>
<td>2.4</td>
<td>1 nm</td>
<td>30 W</td>
<td></td>
<td></td>
<td></td>
<td>50%</td>
<td>CW</td>
<td>RT</td>
<td>Tm-fiber@1.9 µm</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnSe</td>
<td>2.3</td>
<td>&lt;0.7 kHz</td>
<td>5.5 W</td>
<td></td>
<td></td>
<td></td>
<td>12%</td>
<td>CW</td>
<td>RT</td>
<td>Tm-fiber@1.9 µm</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnSe</td>
<td>2.3</td>
<td>100 kHz</td>
<td>160 mW</td>
<td></td>
<td></td>
<td></td>
<td>12%</td>
<td>CW</td>
<td>RT</td>
<td>Diode/Er-fiber@1.56 µm</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnSe</td>
<td>2.94</td>
<td>1 nm</td>
<td>10 W</td>
<td></td>
<td></td>
<td></td>
<td>25%</td>
<td>CW</td>
<td>RT</td>
<td>Tm-fiber@1.9 µm</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.3</td>
<td>82 nm</td>
<td>2 W</td>
<td>275 kW</td>
<td>94.5 MHz</td>
<td>21 nJ</td>
<td>20%</td>
<td>ML</td>
<td>RT</td>
<td>Er-fiber@1.56 µm</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.3</td>
<td>120 nm</td>
<td>0.6 W</td>
<td>140 kW</td>
<td>94.5 MHz</td>
<td>7 nJ</td>
<td>&lt;46 fs</td>
<td>12%</td>
<td>ML</td>
<td>RT</td>
<td>Er-fiber@1.56 µm</td>
<td>[1]</td>
</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.475</td>
<td>37 nm</td>
<td>0.35 W</td>
<td>1 GW</td>
<td>1 kHz</td>
<td>0.35 mJ</td>
<td>346 fs</td>
<td>MLm</td>
<td>RT</td>
<td>Tm-fiber@1.9 µm</td>
<td>[26]</td>
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</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.45</td>
<td>18.5 W</td>
<td>26 kW</td>
<td>7 kHz</td>
<td>2.64 mJ</td>
<td>125 ns</td>
<td>56%</td>
<td>GS</td>
<td>RT</td>
<td>Tm:YAP@1.94 µm</td>
<td>[75]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.35</td>
<td>2 GHz</td>
<td>8.8 kW</td>
<td>5 kHz</td>
<td>1.1 mJ</td>
<td>125 ns</td>
<td>30%</td>
<td>GS</td>
<td>RT</td>
<td>Tm:YAP@1.94 µm</td>
<td>[75]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.94</td>
<td>150 nm</td>
<td>200 mW</td>
<td>2 MW</td>
<td>10 Hz</td>
<td>20 mJ</td>
<td>50 ns</td>
<td>4.5%</td>
<td>GSm</td>
<td>RT</td>
<td>Tm-fiber@1.9 µm</td>
<td>[59]</td>
</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.43</td>
<td>500 W</td>
<td>0.33 MW</td>
<td>10 Hz</td>
<td>50 mJ</td>
<td>150 ns</td>
<td>15%</td>
<td>FR</td>
<td>RT</td>
<td>Er:Glass@1.54 µm</td>
<td>[60]</td>
<td></td>
</tr>
<tr>
<td>Cr:ZnS</td>
<td>2.65</td>
<td>50 nm</td>
<td>110 mW</td>
<td>160 W</td>
<td>0.1 Hz</td>
<td>1.1 J</td>
<td>7 ms</td>
<td>30%</td>
<td>CW</td>
<td>77 K</td>
<td>Cr:ZnS@2.7 µm</td>
<td>[1]</td>
</tr>
<tr>
<td>Fe:ZnSe</td>
<td>4.1</td>
<td>50 nm</td>
<td>1.6 W</td>
<td>8.3 W</td>
<td>850 kHz</td>
<td>0.6 µJ</td>
<td>64 ns</td>
<td>30%</td>
<td>CW</td>
<td>77 K</td>
<td>Cr:ZnS@2.7 µm</td>
<td>[1]</td>
</tr>
<tr>
<td>Fe:ZnSe</td>
<td>4.065</td>
<td>40 nm</td>
<td>515 mW</td>
<td></td>
<td></td>
<td></td>
<td>22%</td>
<td>QS</td>
<td>77 K</td>
<td>Er:YAG@2.9 µm</td>
<td>[76]</td>
<td></td>
</tr>
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<td>20 nm</td>
<td>1 W</td>
<td>0.2 MW</td>
<td>1 kHz</td>
<td>1 mJ</td>
<td>5 ns</td>
<td>30%</td>
<td>GS</td>
<td>RT</td>
<td>Cr:ZnS@2.7 µm</td>
<td>[1]</td>
</tr>
<tr>
<td>Fe:ZnS</td>
<td>3.95</td>
<td>300 nm</td>
<td>0.5 W</td>
<td>0.15 MW</td>
<td>0.7 kHz</td>
<td>0.7 mJ</td>
<td>5 ns</td>
<td>25%</td>
<td>GS</td>
<td>RT</td>
<td>Cr:ZnS@2.7 µm</td>
<td>[1]</td>
</tr>
<tr>
<td>Fe:ZnS</td>
<td>3.85</td>
<td>200 nm</td>
<td>0.5 W</td>
<td>68 kW</td>
<td>5 Hz</td>
<td>3.4 mJ</td>
<td>50 ns</td>
<td>32%</td>
<td>GS</td>
<td>RT</td>
<td>Er:YAG@2.9 µm</td>
<td>[77]</td>
</tr>
<tr>
<td>Fe:ZnS</td>
<td>4.1</td>
<td>30 nm</td>
<td>0.25 MW</td>
<td>5 Hz</td>
<td>5 mJ</td>
<td>20 ns</td>
<td>19%</td>
<td>GS</td>
<td>RT</td>
<td>Er:YSGG@2.8 µm</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>Fe:ZnS</td>
<td>4.1</td>
<td>20 nm</td>
<td>2.5 W</td>
<td>1.6 kW</td>
<td>5 Hz</td>
<td>0.4 J</td>
<td>250 µs</td>
<td>32%</td>
<td>FR</td>
<td>77 K</td>
<td>Er:YAG@2.9 µm</td>
<td>[43]</td>
</tr>
<tr>
<td>Fe:ZnS</td>
<td>4.1</td>
<td>10 nm</td>
<td>2.8 kW</td>
<td>2.1 J</td>
<td>750 µs</td>
<td>25%</td>
<td>FR</td>
<td>77 K</td>
<td>Er:YAG@2.9 µm</td>
<td>[43]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe:ZnS</td>
<td>4.1</td>
<td>60 nm</td>
<td>4.2 mW</td>
<td>2.8 kHz</td>
<td>5 Hz</td>
<td>0.4 J</td>
<td>250 µs</td>
<td>1%</td>
<td>FR</td>
<td>77 K</td>
<td>Er:YAG@2.9 µm</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Wavelength is central oscillation wavelength for tunable lasers; Lasers regimes of oscillation: CW-continues wave; ML- mode-locked; QS- Q-switched; GS-gain-switched; FR- long pulse (free running); superscript “m”- MOPA configuration; [*] -current paper.
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