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**MID-IR TRANSITION METAL LASERS (POSTPRINT)**

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# Mid-IR transition metal lasers

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## ABSTRACT

Transition metal ions have been of great interest from the beginning of laser development because of their broadband emission. The first demonstration of a transition metal laser used  $\text{Ni}^{2+}$  as the active ion in 1963. Other transition metal ions such as  $\text{Co}^{2+}$  have also been developed as lasers but low cross sections and the need for cryogenic cooling to achieve high efficiency hindered their transition from discovery to applications. The 1995 innovation of pairing  $\text{Cr}^{2+}$  with a host that has tetrahedral symmetry substitution sites led to demonstration of broadly tunable, room temperature, mid-IR lasers. Progress in advancing this class of transition metal laser to output power of 18 W, tuning range to several hundred nanometers, and modelocked operation down to 100 fsec will be reviewed. Plans for future development in the areas of femtosecond pulse operation, high speed frequency tuning, fiber format, and direct electronic pumping will be discussed.

**Keywords:** transition metal lasers, infrared, chromium, solid-state, chalcogenide

## 1. INTRODUCTION

Transition metal ions have been of great interest from the beginning of laser development because of their broadband emission. Basically, transition metals are broadly tunable laser active centers because the partially-filled, electronic d orbitals extend far from the nucleus and interact strongly with the surrounding lattice. The lattice interaction provides strong vibrational coupling giving rise to broad absorption and emission features. In contrast, rare earth active ions have partially filled f levels that are screened from lattice interactions by the filled d levels.

Ruby ( $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ ), the first demonstrated laser medium, [1] turned out to be an exception to the rule that transition metal lasers are broadly tunable. So tunable chromium ion lasing was not discovered until  $\text{Cr}^{3+}$ :alexandrite was demonstrated in 1979. [2]  $\text{Cr}^{4+}$  and  $\text{Cr}^{2+}$  infrared laser materials took even longer to be discovered. However, transition metal laser development actually had an early start with flashlamp-pumped demonstration of  $\text{Ni}^{2+}$  [3] and  $\text{Co}^{2+}$  [4] doped fluoride hosts as discussed in more detail below.

This paper will review the development of infrared lasers based upon stimulated emission from transition metal ions. A historical review will be followed by an emphasis on recent development of room temperature  $\text{Cr}^{2+}$  lasers. Current performance records will be discussed next and finally, current issues will be addressed.

## 2. EARLY TRANSITION METAL INFRARED LASERS

The first demonstration of an infrared transition metal laser was in 1963 and used  $\text{Ni}^{2+}$  in  $\text{MgF}_2$  operating at 1.63  $\mu\text{m}$  with flashlamp pumping and cryogenic cooling. [3] A cryogenically cooled  $\text{Co}^{2+}$  laser was demonstrated the next year with operation at various wavelengths in the 1.75-2.15  $\mu\text{m}$  region. [4]  $\text{Co}^{2+}$  ( $3d^7$  configuration) and  $\text{Ni}^{2+}$  ( $3d^8$  configuration) have two and three unpaired electrons respectively. The free-ion levels split in an octahedral symmetry crystal field when these ions substitute for  $\text{Mg}^{2+}$  in crystals like  $\text{MgF}_2$ . The crystal field splitting gives rise to the observed broadband absorption and emission features. But spectral laser tuning is often less than the observed fluorescence of these active ions. This restriction in tuning range was found to be caused by excited state absorption. [5] Efficient laser operation requires cryogenic cooling due to a rapid decrease in fluorescence lifetime [6, 7] with increasing temperature. This decrease in lifetime is caused by the rapid increase of nonradiative multi-phonon relaxation with increasing temperature.

Greater than 30% efficient cw operation of cryogenically cooled  $\text{Co}^{2+}:\text{MgF}_2$  lasers has been demonstrated. [8, 9] But all cw operation has required cryogenic cooling. Pulsed operation of  $\text{Co}^{2+}:\text{MgF}_2$  lasers at room temperature has been

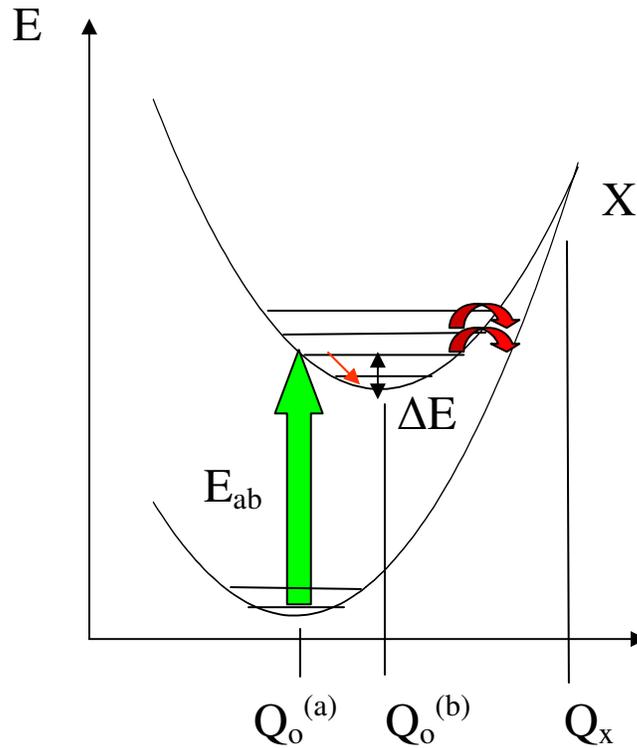
demonstrated at the expense of higher threshold and lower efficiency. [10] However, if the pump pulse is maintained shorter than the lifetime of the upper laser level the efficiency and threshold can approach the cryogenic levels. Pulse energy is limited by the surface damage threshold of the host material.

Use of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  lasers in infrared applications has been meager. While  $\text{Co}^{2+}:\text{MgF}_2$  lasers were at one time commercially available, the need for cryogenic cooling has limited their potential to one-of-a-kind laboratory uses.

### 3. $\text{Cr}^{2+}$ TRANSITION METAL LASERS

The large phonon energies in oxide and fluoride host crystals lead to nonradiative relaxation rates that exceed radiative relaxation rates for many active ions at room temperature. This results in poor laser performance for infrared transition metal ions when operated at or near room temperature. The nonradiative rate depends upon the number of phonons  $p$  required to equal the energy gap  $\Delta E$  as shown in Equation 1 and Figure 1.

$$p = \Delta E / h\nu \quad (2)$$



**Figure 1. Configuration coordinate model of nonradiative transitions between electronic levels in transition metal ions.  $Q_0$  is the equilibrium position of the configuration coordinate with “a” referring to the ground electronic manifold and “b” referring to the first excited electronic manifold. The horizontal lines are harmonic oscillator vibrational sublevels. The crossover point at  $Q_x$  is too high for significant nonradiative transfer but tunneling from “b” to “a” can occur (the curved arrows) leading to nonradiative transfer that increases with temperature.**

In general, compounds have phonon energies that decrease as the mass of the anion increases. Thus the phonon energy decreases in the following order: oxide, fluoride, selenide, chloride, iodide, and bromide compounds. [11] If we consider cation-anion pairs as harmonic oscillators with spring constant  $k$  and mass  $m$ , the frequency  $\nu$  is

$$\nu \propto \sqrt{k/m} \quad (3)$$

so the higher mass anions would lead to a lower frequency phonon. To achieve efficient room-temperature operation of an infrared transition metal laser, we should therefore look for hosts with small phonon energies for low nonradiative relaxation rates and small crystal fields for appropriate infrared energy level splittings.

### 3.1 The II-VI breakthrough

In 1995, a group of researchers at Lawrence Livermore National Laboratory reported a new class of room-temperature, widely tunable, mid-IR laser materials. The active ion was  $\text{Cr}^{2+}$  and the host materials consisted of II-VI semiconductor compounds. [12, 13] This breakthrough discovery initiated a flurry of activity in the development of  $\text{Cr}^{2+}$  lasers. The initial Livermore report used ZnS and ZnSe as the II-VI host materials. Other researchers, including my group at the Air Force Research Laboratory, showed that other II-VI host materials such as CdSe [14, 15] and even ternary mixtures of  $\text{Cd}_x\text{Mn}_{1-x}\text{Te}$  [16] could be used as  $\text{Cr}^{2+}$  laser host materials. These room temperature laser demonstrations were possible because of the low maximum phonon frequencies observed in II-VI compounds, e.g.  $250 \text{ cm}^{-1}$  in ZnSe. The  $\text{Cr}^{2+}$  nonradiative relaxation rate remains small relative to the radiative rate below 300K for many of the II-VI host materials.

### 3.2 $\text{Cr}^{2+}$ spectroscopy

The  $\text{Cr}^{2+}$  ion has the  $3d^4$  electronic configuration. So there are 4 unpaired electrons in the d orbitals or equivalently one hole. The single hole aspect of the  $\text{Cr}^{2+}$  ion makes its energy level splitting in a crystal field analogous to the splitting observed for the  $\text{Ti}^{3+}$  ion, a  $3d^1$  configuration. One difference lies in the fact that  $\text{Cr}^{2+}$  ions substitute for II-Group elements in II-VI compounds and thus experience tetrahedral crystal field symmetry while in  $\text{Ti}^{3+}$ -doped oxides, the  $\text{Ti}^{3+}$  ion experiences an octahedral crystal field symmetry. The tetrahedral field for identical ion-to-ligand distances changes the sign of the  $Dq$  splitting parameter and reduces it in value compared to an octahedral field according to the following formula: [17]

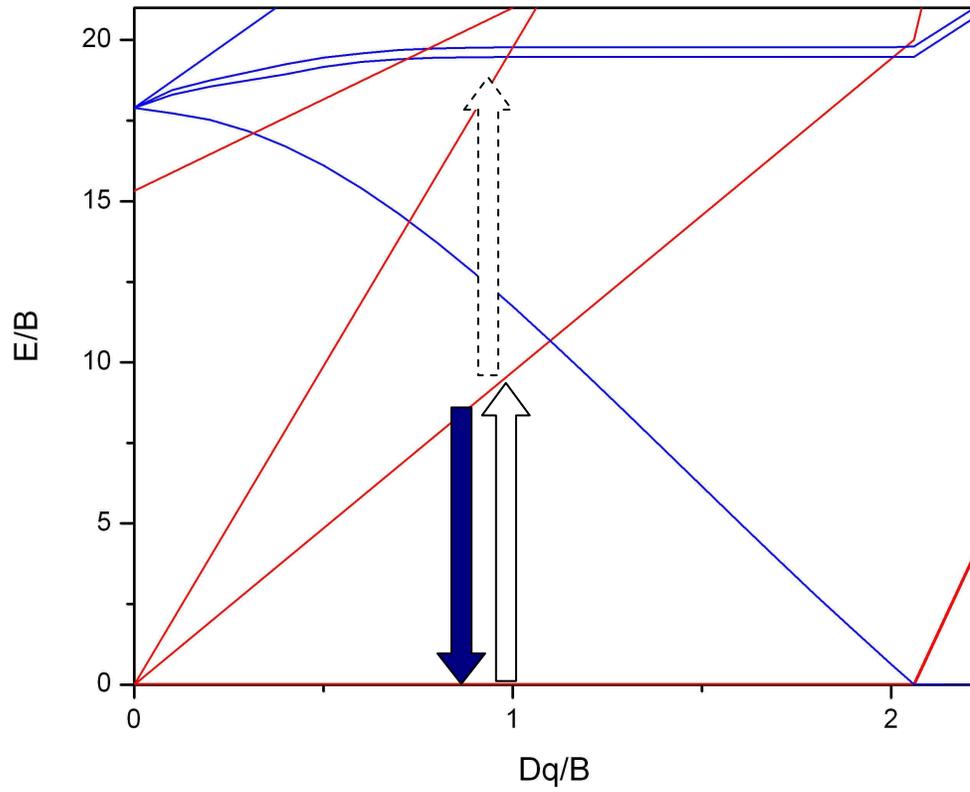
$$Dq(\text{tetrahedral}) = -4/9 Dq(\text{octahedral}) \quad (4)$$

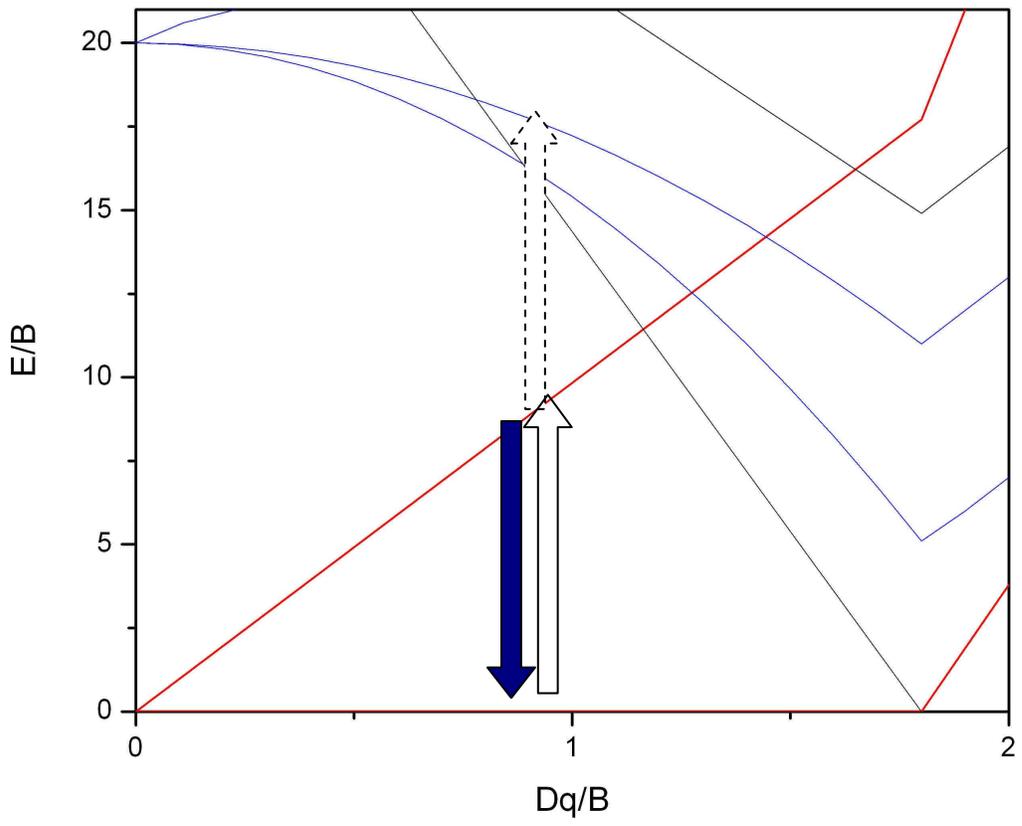
However, consideration of the  $3d^4$  configuration of the  $\text{Cr}^{2+}$  ion as a single hole rather than a single electron negates the sign change. Thus  $\text{Cr}^{2+}$  has the same level labels as  $\text{Ti}^{3+}$  (except for total electron spin of 5 vs. 2) and a smaller crystal field splitting. For this reason  $\text{Cr}^{2+}$  is sometimes known as the infrared titanium sapphire laser.

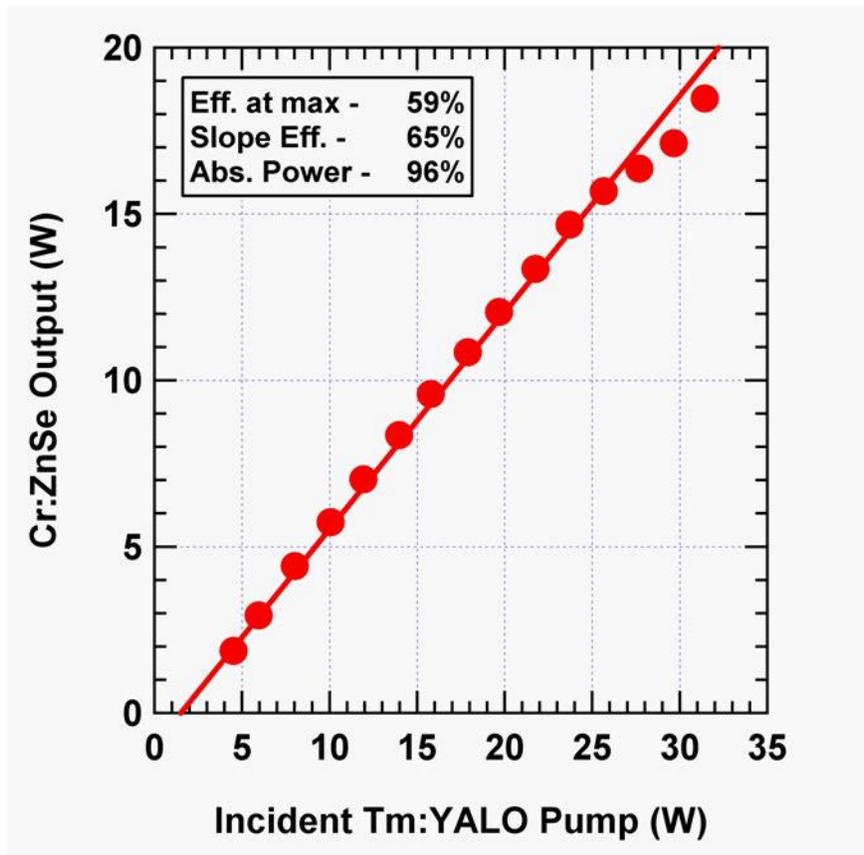
The crystal field splitting and Jahn-Teller splitting of upper and lower degenerate d levels result in broadband absorption in the 1.5-2.1  $\mu\text{m}$  region and broadband emission in the 1.8-3.1  $\mu\text{m}$  region for  $\text{Cr}^{2+}:\text{ZnSe}$ . Other II-VI hosts show small shifts in these bands due to differences in the crystal field  $Dq$  splitting. CdSe has a smaller crystal field with a shift of absorption and emission peaks to longer wavelengths; a  $\text{Cr}^{2+}:\text{CdSe}$  laser has been tuned out to 3.4  $\mu\text{m}$ . [18]  $\text{Cr}^{2+}:\text{ZnS}$  has a higher crystal field splitting with a  $\sim 100 \text{ nm}$  shift of absorption and emission peaks to shorter wavelengths.

### 3.3 Why no $\text{Cr}^{2+}$ Excited State Absorption?

The tuning limitations of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  caused by excited state absorption have already been mentioned. Other transition metal laser ions such as  $\text{Cr}^{3+}$  in alexandrite [19] and  $\text{Ti}^{3+}$  in  $\text{YAlO}_3$  [20] have excited state absorption (ESA) which limits tuning or prevents lasing altogether. Tanabe-Sugano diagrams [21] show the crystal field splitting of  $d^1$ - $d^9$  electronic configurations. A look at these diagrams is helpful for understanding optical transitions in transition metal ions.  $\text{Co}^{2+}$  in a site with octahedral symmetry has a  $^4F$  free ion state split by the crystal field into a  $^4T_1$  ground state, a  $^4T_2$  first excited state, and a  $^4A_2$  second excited state. Absorption and emission transitions between the  $^4T_1$  ground state and the  $^4T_2$  first excited state are spin allowed. However, as Figure 2 shows, ESA from the  $^4T_2$  first excited state to the  $^4A_2$  second excited state is also spin allowed. Transitions from the  $^4T_2$  first excited state to the  $^4T_1$  state that comes from the  $^4P$  free ion level may also contribute to ESA. All other relatively low states are spin multiplicity  $2S + 1 = 2$  levels and are spin forbidden.







## 5. Fe<sup>2+</sup> TRANSITION METAL LASERS

The Fe<sup>2+</sup> ion has a 3d<sup>6</sup> electronic configuration. Five of the electrons compose a half-filled d shell so the d<sup>6</sup> configuration has similarities to the d<sup>1</sup> configuration. In II-VI hosts it is expected to have spectroscopy similar to Cr<sup>2+</sup> ions but with opposite sign due to the presence of a single electron rather than a single hole. The <sup>5</sup>D free ion level is split by a tetrahedral crystal field into a <sup>5</sup>E ground state level and a <sup>5</sup>T<sub>2</sub> first excited state. Higher levels come from free ion levels with lower spin multiplicity and thus are expected to not have significant ESA.

However, Fe<sup>2+</sup> ions in hosts studied to this time have multiphonon nonradiative transition rates that increase rapidly with temperature, quenching the <sup>5</sup>T<sub>2</sub> first excited state lifetime strongly at room temperature. Thus the first demonstration of Fe<sup>2+</sup> lasing [32] was done at a temperature of 2K in 1983. Laser oscillation was observed at 3.53 μm in n-InP. The longer absorption and emission wavelengths of Fe<sup>2+</sup> imply that the crystal field splitting parameter  $Dq$  is smaller for Fe<sup>2+</sup> compared to Cr<sup>2+</sup>. For the same phonon coupling strength, this is likely to lead to the higher nonradiative relaxation rate observed for Fe<sup>2+</sup>.

More recently (1999), use of ZnSe for the Fe<sup>2+</sup> host enabled laser operation at temperatures up to 180K. [33] The authors achieved temperature tuning of the wavelength between 3.98 μm and 4.54 μm. Room temperature operation was achieved in 2005 [34] by keeping the pump pulse and lasing pulse shorter than the relaxation lifetime, i.e. using gain switched pumping. Unfortunately, the limitation of Fe<sup>2+</sup> lasers to gain-switched pulses or cryogenic cooling is likely to limit Fe<sup>2+</sup> to being an interesting but somewhat impractical laser ion for most commercial applications similar to Co<sup>2+</sup>.

## 6. CR<sup>2+</sup> TRANSITION METAL LASER ISSUES

### 6.1 Cr<sup>2+</sup>:ZnSe thermal lensing

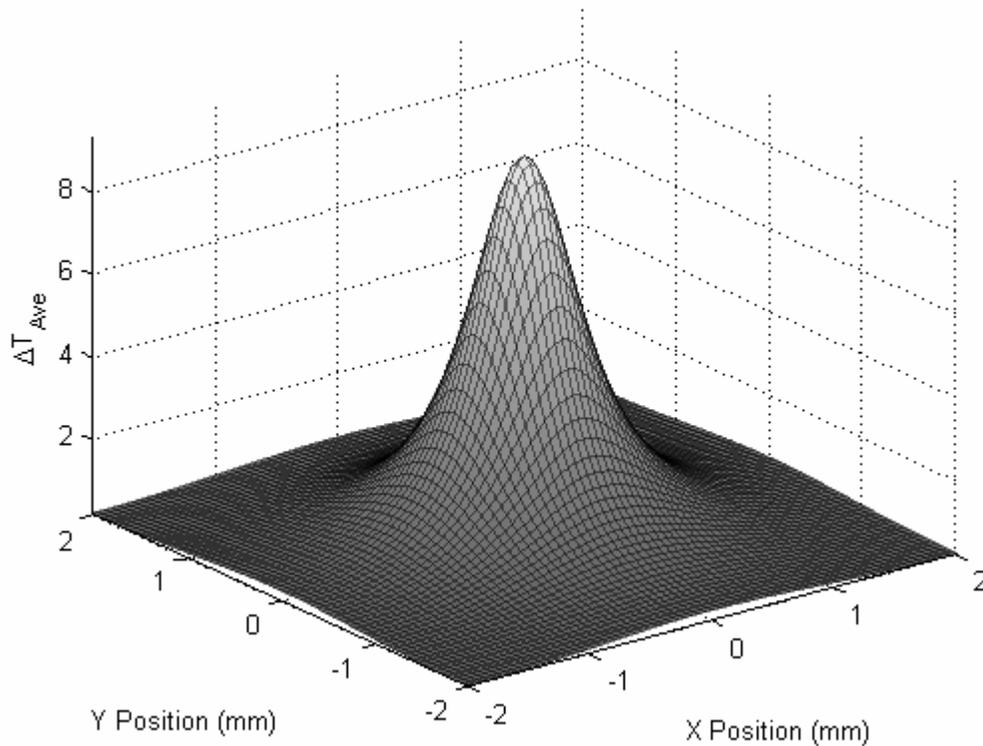
Assuming a uniformly pumped, side-cooled cylinder, and neglecting the impact of strains in the laser rod, thermal lens power  $TLP$  (diopters) can be estimated as [12]:

$$TLP = 1/f \approx \frac{P_a}{2\kappa A} \frac{dn}{dT} \quad (5)$$

where  $f$  is thermal lens focal length,  $\kappa$  is thermal conductivity,  $A$  is laser beam cross sectional area,  $P_a$  is the absorbed power in the rod, and  $dn/dT$  is the change in refractive index with temperature. Note that the thermal lens power is proportional to the product of absorbed power per unit area (absorbed intensity) and the ratio of  $dn/dT$  to  $\kappa$ . The lower the ratio of  $dn/dT$  to  $\kappa$ , the more power per unit area can be absorbed for the same thermal lens power. While ZnSe has good thermal conductivity, it has a very large  $dn/dT = 70 \times 10^{-6} \text{ K}^{-1}$ . This makes power scaling difficult due to the generation of thermal lensing in the material by absorbed pump power not reconverted to optical radiation. Thermal lensing power for a given heat load will be 9x stronger in ZnSe than in sapphire, and 4.3x stronger than in YAG. Thermal lensing in CdSe will be 19x stronger even than in ZnSe. Thermal management is therefore expected to be a significant issue in designing lasers based upon II-VI materials.

Power scaling Cr<sup>2+</sup> laser output to multi-watt levels requires a geometry designed for maximum suppression of thermal effects. An attractive approach is the face-cooled disk design, [23] essentially a gain medium which is both pumped and cooled longitudinally through its large polished faces. Use of a pump spot larger in diameter than the disk thickness ensures that the pump-induced heat is primarily extracted longitudinally, reducing the radial thermal gradients responsible for thermal lensing in the active medium. Such a strategy has contributed to outputs in the hundreds of watts from Nd:YAG systems. [35] Although the thermal lensing effect is stronger in ZnSe, the technique has promise for Cr<sup>2+</sup> lasers as well.

Both severe thermal lensing and strong disk heating were observed in an interferometric characterization of Cr<sup>2+</sup>:ZnSe disks pumped by a 0.4-mm radius, multi-mode, 2.05-μm laser beam. [36] Thermal lensing as strong as 2.3 diopters per watt of pump power was measured in a 1-mm disk, and longitudinally averaged temperature increases of up to 10 °C per watt of pump power were calculated from a finite element model (see Figure 5). Disk heating to the point of increased Cr<sup>2+</sup> nonradiative relaxation is possible with only a few watts of pump power indicating that absolute material temperature and thermal gradients must be controlled to achieve high efficiency and high power.



**Figure 5. Longitudinally [along the disk thickness] averaged temperature distribution in a 1-mm thick Cr<sup>2+</sup>:ZnSe disk predicted for 1-W heat load with a 0.4-mm radius Gaussian beam.**

Various geometries designed to reduce absolute temperature and thermal gradients have been considered. Using ZnSe windows as heat sinks on both sides of a Cr<sup>2+</sup>:ZnSe thin disk to achieve cooling from both sides appeared promising. However, laser performance was disappointing primarily due to the difficulty in achieving good optical contact between the window and laser disk. Improved polishing techniques are needed to produce highly flat surfaces.

## 6.2 Cr<sup>2+</sup>:ZnSe concentration quenching

The quenching of radiative lifetime with increasing concentration above ~100 ppm substitution for the Zn<sup>2+</sup> ion is well known. But the reason for this is not well understood. In other solid-state laser materials, like Nd:YAG, concentration quenching does not take effect until concentrations reach several percent. At this concentration, nearest neighbor pairs of Nd<sup>3+</sup> are likely to occur assuming random substitution at the Y<sup>3+</sup> sites. The Nd<sup>3+</sup> neighbor pairs act as sinks for the excitation energy which can hop from ion to ion until fluorescence occurs or a Nd<sup>3+</sup>-Nd<sup>3+</sup> pair is found. But Cr<sup>2+</sup> ions exhibit quenching at concentration levels at least two orders of magnitude smaller. This may indicate that Cr<sup>2+</sup> ions are not randomly distributed but are concentrated at certain locations in the laser material. One possibility is that the Cr<sup>2+</sup> ions preferentially diffuse into polycrystalline material along grain boundaries. Typical grain sizes of polycrystalline ZnSe are 70 μm. A boundary layer 1 μm thick would compose 0.9% of the sample volume thus explaining the two order of magnitude discrepancy. A volume scan for emission intensity with 1-μm<sup>3</sup> resolution could confirm or refute this hypothesis. Polycrystalline material with smaller grain size should also be investigated; a 10-μm grain would have 60% of its volume in a 1-μm thick boundary allowing a potential 60x increase in Cr<sup>2+</sup> concentration based on this hypothesis.

### 6.3 Direct electrical pumping of Cr<sup>2+</sup>:ZnSe

It has been known for decades that wide-band-gap II-VI semiconductors (pure and doped with acceptors and donors) are electroluminescent. It was also noticed that the presence of transition metal ions as inadvertent dopants effectively quenched the visible light emission from donor-acceptor pairs. In 1974 Grebe and Schultz reported the details of Cr<sup>2+</sup> absorption and emission in ZnS and interpreted quenching as Cr<sup>2+</sup> capture of conduction band free carriers. [37] Indirect optical excitation of Fe<sup>2+</sup> lasing via free carriers in InP was demonstrated in 1984 [32] indicating that Cr<sup>2+</sup> lasing via indirect optical pumping of the bandgap and perhaps even electrical pumping of Cr<sup>2+</sup> lasing may be possible. Recently, Mirov's group demonstrated room temperature direct electroluminescence of Cr<sup>2+</sup> in n-ZnSe at 2-3 μm, 8 μm and visible 0.600 μm wavelengths. [38] They expect use of p-n junction structures should lead to increased efficiency of energy transfer and a possible lasing demonstration.

### 6.4 A fiber Cr<sup>2+</sup>:II-VI laser?

The strong thermal lensing of Cr<sup>2+</sup>-doped II-VI materials is a major issue when designing Cr<sup>2+</sup> lasers and especially when scaling power. The thin disk design exchanges the benefit of reduced thermal lensing for the added complexity of multi-pass pumping to assure that the pump power is efficiently absorbed. It does not solve the problem of overall temperature rise that gets worse as the disk thickness gets smaller and leads to higher nonradiative relaxation rates.

An interesting possibility would be a fiber format. A fiber with the proper core radius and core/cladding refractive indices can confine beam propagation in a way that is insensitive to radial temperature gradients. In addition, doping can be low as required to prevent concentration quenching. But pump power can be efficiently absorbed by making the fiber long enough to efficiently absorb the pump power. The only limit to concentration would be the requirement that gain per unit length would need to be greater than passive loss per unit length.

Unfortunately, expertise in silica fiber pulling does not translate easily to making fiber cores from polycrystalline II-VI materials. Chalcogenide glass has been fabricated and shown to incorporate rare earth ions. [39] However, incorporation of chromium in the proper oxidation state (Cr<sup>2+</sup>) with the proper tetrahedral site symmetry has not been achieved in any infrared glass to my knowledge. Promising ideas to fabricate Cr<sup>2+</sup>-doped II-VI fibers have not yet been found.

## 7. CONCLUSIONS

The history of transition metal lasers is as long as the history of lasers themselves but great progress has been made in their development for practical applications since the advent of the Cr<sup>2+</sup> laser. The 1995 innovation of pairing Cr<sup>2+</sup> with a II-VI semiconductor host that has tetrahedral symmetry substitution sites has led to demonstration of broadly tunable, room temperature, mid-IR lasers. Cr<sup>2+</sup> lasers have achieved output power of 18 W, tuning range of 1100 nm, and modelocked operation down to 100 fsec.

Thermal lensing, thermally induced emission quenching, and concentration quenching are issues that challenge further power scaling. Concepts to address these issues are under development. New ideas such as direct electrical pumping and fabrication of a Cr<sup>2+</sup> fiber laser are currently being tested. Use of Cr<sup>2+</sup> lasers in future applications looks promising.

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