ENHANCED LASER COOLING OF ION-DOPED NANOPOWDERS

Xiulin Ruan and Massoud Kaviany
Department of Mechanical Engineering
University of Michigan
Ann Arbor, Michigan 48109-2125
xruan@umich.edu, kaviany@umich.edu

ABSTRACT
Laser cooling of rare-earth ion doped nanocrystalline powders is analyzed, using \( \text{Yb}^{3+}:\text{Y}_2\text{O}_3 \) as the model material. The dopant concentration is optimized based on the energy transfer theory, and is found to be larger than the currently used value, suggesting noticeable enhancement effects for laser cooling. Multiple scattering of photons in random nanoparticles results in a larger photon absorption of the pumping beam, which also contributes significantly to laser cooling enhancement. Using molecular dynamics simulations, the phonon density of states (DOS) of nanoparticles is calculated, and found to have the extended, small tails at low and high frequencies. The second-order, electronic transition rate for the anti-Stokes luminescence, which includes the influence of phonon DOS, is used along with this DOS and also shows enhancement of laser cooling efficiency using nanopowders.

NOMENCLATURE

- \( a_{i-p} \): ion-phonon coupling constant
- \( c_o \): speed of light in vacuum (m/s)
- \( D_p \): phonon density of states (1/m\(^3\))
- \( d_s \): diameter of the solid particle (m)
- \( E \): complex electric field (V/m)
- \( E \): energy flow rate (W)
- \( E_{\text{pump}} \): pumping energy (J)
- \( e_e \): electron charge (C)
- \( e_{\text{ph},i} \): energy density of the pumping field (J/m\(^3\))
- \( e_a \): photon polarization (V/m)
- \( f_p, f_{\text{ph}} \): phonon, photon distribution function
- \( H \): Hamiltonian (J)
- \( I \): intensity (W/m\(^2\))
- \( k \): wave vector (1/m), thermal conductivity (W/m-K)
- \( L \): optical pathlength, (m)
- \( l \): index of the layers
- \( M \): interaction matrix
- \( m_f, m_s \): complex refractive index of fluid, solid
- \( N \): number of layers, number of phonons
- \( N_p \): number of phonons
- \( n_{a, b} \): electronic population at the ground and excited states, cm\(^{-3}\)
- \( n_d \): dopant concentration, (cm\(^{-3}\))
- \( n_f, n_s \): refractive index of fluid, solid
- \( Q \): power, (W)
- \( q \): charge, (C)
- \( r \): interatomic distance (m)
- \( S \): Energy conversion (W)
- \( t \): time (s)
- \( u_{\beta} \): velocity of particle \( i_\beta \) (m/s)
- \( u_p \): average phonon speed (m/s)
- \( V \): volume (m\(^3\))

Greek symbols

- \( \alpha_{\text{ph},i} \): absorptance
- \( \Gamma \): velocity autocorrelation function
- \( \dot{\gamma} \): transition rate (1/s)
- \( \gamma_{e,a} \): transition probability per unit time per unit energy density [1/(s/J/m\(^3\))]
INTRODUCTION

The concept of laser cooling (optical refrigeration) by the anti-Stokes luminescence in solids dates back to 1929, when Pringsheim recognized that thermal vibrational energy can be removed by the anti-Stokes fluorescence, if a material is excited with photons having an energy below the mean fluorescence energy [1]. Initially, it was believed that optical cooling by the anti-Stokes fluorescence contradicted the second law of thermodynamics, suggesting that the cycle of excitation and fluorescence is reversible, and hence an energy yield greater than one would be equivalent to the complete transformation of heat to work [2, 3]. This was cleared by Landau when he assigned entropy to radiation [4], by showing that the entropy of a radiation field is proportional to its frequency bandwidth and also to the solid angle through which it propagates. Since the incident laser light has a small bandwidth and propagates in a well-defined direction, it has almost zero entropy. On the other hand, the fluorescence is broadband and is emitted in all directions, so, if the power of the emission is equal to or greater than the incident beam, the emission has a comparatively larger entropy.

Since then, many attempts to realize radiative refrigeration experimentally have been made, and the associated theoretical interpretations have been discussed. Fig. 1(a) shows the fundamental energy carriers of the laser cooling system. There is a host crystal which is idealized as transparent to the pumping laser, and some of the host atoms are replaced by optically active, doped ions, such as Yb$^{3+}$. The ion is represented with an effective transition dipole moment $\mu_r$, which is defined as a quantum mechanical spatial integral of the product of $e_{\alpha r}$ and the initial and final state wave functions ($\psi_f$ and $\psi_i$) connected by the transition, i.e.,

$$\mu_r = \int \psi_f^* e_{\alpha r} \psi_i d^3 r. \tag{1}$$

The electromagnetic field, with a polarization vector $e_{\alpha r}$, may interact with the electron if the coupling factor $e_{\alpha r} \cdot \mu_r$ is nonzero. Fig. 1(b) shows the principles of the photon-electron-phonon energy interactions which result in cooling of the solid. When the medium is irradiated by laser light with a frequency $\omega_{ph,i}$ that is below the resonance frequency $\omega_0$ (10,250 cm$^{-1}$ for Yb$^{3+}$: Y$_2$O$_3$), the electron may be excited by absorbing a photon from the laser pumping and one phonon of frequency $\omega_p$ from the host. The electron then decays by emitting another photon of frequency $\omega_{ph,e}$ and, possibly, phonons. If the average emitted photon frequency $\omega_{ph,e}$ is larger than $\omega_{ph,i}$, the medium loses internal energy and is cooled. The earliest experiment was performed by Kushida and Geusic [5] on Nd: YAG. Reduced heating was observed, but not net cooling. This was conjectured to be due to the impurities in the crystals and multiphonon decay across the optical transition. In 1981, Djeu and Whitney [6] laser cooled low-pressure CO$_2$ by 1 K from 600 K by using a CO$_2$ laser for pumping. In 1995, Epstein et al. [7] reported the first successful experiment of laser cooling in solids. A local temperature decrease was detected by a photothermal deflection technique, and the cooling efficiencies up to 2% achieved in a Yb-doped glass were more than $10^4$ times those observed in Doppler cooling of...
We report on enhanced laser cooling of Yb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} nanopowder as a model material. The dopant concentration is optimized based on the energy transfer theory. Multiple scattering of photons in random nanopowders results in a larger photon absorption. Using molecular dynamics simulations and the velocity autocorrelation, the phonon density of states (DOS) of nanoparticles is calculated, and used in the second-order, electronic transition rate for the anti-Stokes luminescence. These effects result in a significant enhancement of laser cooling performance.

**Improving Laser Cooling Performance**

Figure 3 shows an energy diagram for laser cooling of nanopowder, in which the unabsorbed irradiation power includes the reflected, transmitted, and scattered power out of the nanopowder medium.

Based on the Einstein theory of absorption and emission of radiation [18], the rate equation for the two level system shown in Fig. 1(b) is

\[
\frac{dn_b}{dt} = -\gamma_{e,d} n_b + \gamma_{e,a} n_a e_{ph,i},
\]

where \(n_b\) and \(n_a\) are the populations at the excited and ground states, respectively. Here \(\gamma_{e,d}\) is the transition rate for the decay processes, which include radiative decay (spontaneous and stimulated emission) and nonradiative decay. Also, \(\gamma_{e,a}\) is the transition rate for absorption, and \(e_{ph,i}\) is the energy density of the pumping filed in the nanopowder. In steady state, we have

\[
\frac{dn_b}{dt} = -\gamma_{e,d} n_b + \gamma_{e,a} n_a e_{ph,i} = 0.
\]

Since one excitation transition leads to the absorption of one
An energy diagram for laser cooling of a nanopowder. The unabsorbed irradiation power includes the reflected, transmitted, and scattered power.

The net cooling power $\dot{S}_{ph-e-p}$ is given as the difference between the absorbed and emitted radiation, i.e.,

$$\dot{S}_{ph-e-p} = Q_{ph,a} - Q_{ph,e} = (1 - \frac{\bar{\omega}_{ph,e}}{\omega_{ph,i}})Q_{ph,a},$$

Assume that the system is far from saturation, namely, the electronic population in the ground state is much larger than that in the excited state, we may approximate the ground state population as the dopant concentration, i.e.,

$$n_a = n_d.$$  

Treating the pumping source as monochromatic, the total pumping energy inside the medium becomes

$$E_{pump} = \int_{V} e_{ph,i} dV = \int_{V} \frac{1}{2} |E_{e,r}|^2 dV,$$

where $E_{e,r}$ is the local electric field.

By definition, in Eq. (9) a negative value of $\dot{S}_{ph-e-p}$ indicates cooling. As a result, only those $\omega_{ph,i}$ larger than $\bar{\omega}_{ph,e}$ may result in cooling, and this range is defined as the cooling range. Also the quantum efficiency $\eta_{e-ph}$ must be higher than $\bar{\omega}_{ph,i}/\bar{\omega}_{ph,e}$, which is satisfied in cooling experiments on bulk crystals. Note that here we assume the quantum efficiency of nanopowders is the same as the bulk material, although there are reports of decreased quantum efficiency in nanocrystals, due to surface defects, adsorbed gas molecules, and other quenching centers [19]. It then can be seen that to enhance the cooling power using the same incident energy, an increase in the dopant concentration $n_d$, the total pumping energy inside the nanopowder medium $E_{pump}$, and the excitation rate $\dot{\gamma}_{e,a}$ are needed. These will be discussed in following sections for ion-doped nanopowders.

**Optimum Dopant Concentration**

As $n_d$ is increased, ions come closer to each other, and the excitation energy may hop around neighboring ions until it finds a quenching center to decay nonradiatively. This energy transfer phenomenon leads to a drop of the quantum efficiency $\eta_{e-ph}$, and this is called the concentration quenching. An optimum dopant concentration is found as the balance reached between the increase in $n_d$ and the decrease in $\eta_{e-ph}$. Due to prior lack of a theory to determine this optimum concentration, arbitrary concentrations of 1 wt.% and 2 wt.% have been used in most of the
where $\tau(n_d)$ is the lifetime at extremely low concentration, $n_{d,c}$ is defined as a critical concentration which is intrinsically dependent on the ion-host coupling, and $N_p$ is the number of phonons needed to fulfill the energy gap $\Delta E_c$. Since the lifetime is the reciprocal of the transition rate, then Eq. (12) becomes

$$\dot{\gamma}_{e,d}(n_d) = \dot{\gamma}_{e,d}(n_d = 0)[1 + 1.45(n_d/n_{d,c})\exp(-N_p/3)],$$

where based on the process shown in Fig. 4, we have

$$\dot{\gamma}_{e,d}(n_d = 0) = \dot{\gamma}_r + \dot{\gamma}_{nr},$$

and

$$\dot{\gamma}_{e,d}(n_d) = \dot{\gamma}_r + \dot{\gamma}_{nr} + \dot{\gamma}_{12}.$$  

Equation (13) shows that an increase in $n_d$ results in the increase in the total decay rate $\dot{\gamma}_{e,d}$, compared to that for an isolated ion, due to the presence of the self-generated, non-radiative decay rate $\dot{\gamma}_{12}$.

For an isolated ion, the relationship for the radiative and non-radiative decay rates is [22]

$$\frac{\dot{\gamma}_r}{\dot{\gamma}_r + \dot{\gamma}_{nr}} = (1 + f_p^o)^{-N_p},$$

where $f_p^o$ is the equilibrium phonon distribution function (Bose-Einstein distribution)

$$f_p^o = \frac{1}{\exp(h\omega_p/k_BT) - 1}. $$

In Eq. (16) $\dot{\gamma}_{nr}$ increases with temperature, since more phonons are excited and participate in the nonradiative decay processes.

Using Eqs. (13-16), the quantum efficiency $\eta_{e-ph}$ can be written as a function of the concentration, as

$$\eta_{e-ph} = \frac{\dot{\gamma}_r}{\dot{\gamma}_r + \dot{\gamma}_{nr}} = \frac{\dot{\gamma}_r}{\dot{\gamma}_r + \dot{\gamma}_{nr}} \frac{\dot{\gamma}_r + \dot{\gamma}_{nr}}{\dot{\gamma}_{e,d}(n_d)} = (1 + f_p^o)^{-N_p}[1 + 1.45(n_d/n_{d,c})\exp(-N_p/3)]^{-1},$$

The total cooling power given by Eq. (9) is now written as a function of the concentration, i.e.,

$$\dot{S}_{ph-e-p} = \left\{1 - \frac{\dot{\omega}_{ph,c}}{\dot{\omega}_{ph,i}}(1 + f_p^o)^{-N_p}[1 + 1.4\frac{n_d}{n_{d,c}}\exp(-N_p/3)]^{-1}\right\}$$

The maximum cooling power is reached when

$$\frac{\partial\dot{S}_{ph-e-p}}{\partial n_d} = 0,$$

which yields the optimum concentration

$$n_{d,o} = \frac{n_{d,o}}{n_{d,c}} = a \cdot \frac{(1 - b)^{1/2}}{1 - (1 - b)^{1/2}},$$

where $a$ and $b$ are

$$a = \frac{1}{1.45} \exp(N_p/3), \quad b = \frac{\dot{\omega}_{ph,c}}{\dot{\omega}_{ph,i}}(1 + f_p^o)^{N_p}.$$
Equation (21) indicates that the critical concentration \( n_{d,c} \) is the one and the only one unknown that needs to be specified before the optimum concentration can be determined. Note that, \( n_{d,c} \) is an intrinsic property depending on the ion-dopant pair and the temperature, and may be calculated using quantum mechanics. Here we use a more practical approach, namely, fitting Eq. (12) or Eq. (18) to experiments, as reported in [20].

In an experiment [11], a Yb\(^{3+}\) doped ZBLANP fibre was cooled by 65 K from the room temperature, with a concentration \( n_d = 2.42 \times 10^{20} \text{ cm}^{-3} \), and a measured quantum efficiency \( \eta_{e-ph} = 0.996 \). Using Eq. (18) the critical concentration is readily calculated to be \( n_{d,c} = 1.18 \times 10^{21} \text{ cm}^{-3} \). Then using Eqs. (18) and (19), the variations of quantum efficiency and the cooling power are plotted as a function of the concentration, shown in Fig. 5. The results show that the quantum efficiency \( \eta_{e-ph} \) decreases monotonically with the dopant concentration, i.e., the closely placed neighboring ions result in a larger nonradiative decay rate. However, the cooling power first increases and then decreases, when \( n_d \) is increased. At an optimum concentration \( n_{d,o} = 1.02 \times 10^{21} \text{ cm}^{-3} \), which is three times higher than that used by Gosnell [11], the maximum cooling power is achieved and is 2.5 times that obtained by Gosnell [11].

In Fig. 5(b), note that if the concentration becomes higher than a transition value \( n_{d,t} \), which is \( 2.05 \times 10^{21} \text{ cm}^{-3} \), the cooling effect is eliminated. This is as expected, due to the low quantum efficiency.

**Enhanced Total Pumping Energy by Photon Localization**

Nanopowder medium is an ideal structure to increase \( E_{pump} \), the total pumping energy inside the medium. Fig. 6 shows different regimes of photon scattering in nanopowders [23]. When the mean free path \( l_m \) is much larger than the laser wavelength, photons may experience single scattering and the transport is diffusive [24]. As \( l_m \) decreases, photons begin to undergo multiple scattering. When \( l_m \) is comparable or smaller than the laser wavelength, recurrent scattering takes place. As a result, photons are confined in a finite, small spatial region, forming a random resonator. This phenomenon, termed photon localization, is the counterpart of the electron localization suggested by Anderson [25]. The field of localized light, as shown in Figure 6(d), can be orders of magnitude higher than the incident field [26]. As a result, photon absorption can be enhanced considerably, due to this enhanced local photon density, or alternatively, electromagnetic field energy density \( e_{ph,i} \).

Here we consider the simplest nanostructure model of Yb\(^{3+}\)-doped \( \text{Y}_2\text{O}_3 \) particles, i.e., parallel solid layers with random thicknesses, as shown in Fig. 7(a). The dielectric solid material has a complex refractive index \( n_f = (n_i + ik) \), while the fluid is assumed to be air and has a refractive index \( n_f = n_f = 1 \). To solve the internal field subject to a normal laser irradiation, we start with the Helmholtz equation

\[
\frac{d^2E(x)}{dx^2} + k_0^2n_f^2E(x) = 0, \quad (23)
\]

where \( k_0 \) is the vacuum wave vector, and \( m_f \) is the local complex index of refraction at the incident frequency. This is the electromagnetic wave equation in a source-free medium, and is equivalent to the Maxwell equations in the multilayer system. For the medium shown in Fig. 7(a), the solution of Eq. (23) at a
A particular location $x_l$ in the $l$-th layer is given by

$$E(x) = E_l^+ e^{ik_l(x-x_l)} + E_l^- e^{-ik_l(x-x_l)},$$

$$l = 1, 2, ..., N + 1,$$  \hspace{1cm} (24)

where $k_l = m_l \omega_0/c_o$ is the wave vector, where $c_o$ is the speed of light in vacuum. The field in the medium is divided into two components, the forward (transmitted) component $E_l^+$ and the backward (reflected) component $E_l^-$. The boundary conditions require that the tangential electric and magnetic fields be continuous across each interface. Thus the relationship between the amplitudes of the $l$-th and $(l+1)$-th interfaces are related by a transfer matrix $M$ \cite{22, 26}. Then the full fields $E$ are solved using this transfer matrix approach, subject to a uniform, normal incident field $E_i$. A detailed solution procedure can be found in \cite{22, 26}. A typical field distribution is shown in Figure 7(b), where the dimensionless electric field $|E|^+$ is normalized against the incident field. As evident, there is a field enhancement, i.e., the peaks in the field distribution inside the medium that can be much larger than the incident field, for this realization \cite{27}. Thus, the energy density of the electric field can be two or even more orders of magnitude larger than the incident value. The physical basis of field enhancement is electromagnetic wave interference.

In this random multilayer system, the waves will multiply transmit and reflect at all the interfaces, and interfere with each other. At some locations (for some realizations), the interference is so ideally constructive that it results in an extremely large fields.

The pumping energy $E_{pump}$ inside the nanopowder is then calculated for nanopowder medium using Eq. (8), and compared to that for the bulk crystal with the same apparent volume (note however that the volume of the solid phase for nanopowder is smaller than that for the bulk crystal), as shown in Fig. 8. Note that for a model composite given the porosity $\varepsilon$ and the particle size distribution, there are an infinite number of realizations, and hence, the ensemble average of a sufficient number of realizations is used for nanopowders. The ratio of the total pumping energy is shown in Fig. 8, with respect to porosity $\varepsilon$ for different particle mean diameter ($d_i$). For high porosities, the ratio may be as large as 1.5 to 1.7, indicating an enhancement of the total pumping energy $E_{pump}$ by 50% to 70%. Fig. 8 also indicates that there are optimum porosity and mean particle size to be used.
Enhanced Transition Probability for Nanopowders

1 Phonon density of states of the nanopowder

To analyze photon-electron-phonon interactions, the phonon density of states (DOS) needs to be known. Debye density of states is often assumed for bulk material [28], showing a parabolic distribution of \( D_p(\omega_p) \). Nanostructure phonon DOS may, however, deviate from that for the bulk crystals [29], due to quantum size effects.

In molecular dynamics, phonon DOS may be calculated using three different methods [30]. The first calculates the velocity autocorrelation function for each species and the partial phonon DOS is obtained by the Fourier transforms of this autocorrelation function. The second uses the displacement autocorrelation functions calculated by the equation-of-motion method. The third is a direct diagonalization of the dynamical matrix. The results of the three approaches have been found to agree with one another [30]. Since phonon DOS is not available for \( \text{Y}_2\text{O}_3 \), it is calculated here using the first method.

Molecular dynamics simulation determines a trajectory of the ensemble in phase space by solving the Newton equations for an \( N \)-particle system. Generally, the inputs required are an atomic structure and suitable interatomic potential models, which can be obtained from experiments and/or \textit{ab initio} calculations [31]. For ionic materials interatomic potentials in the form of a Buckingham potential [32] has been shown to perform sufficiently well, and therefore, widely used for modeling of various oxides. The interatomic potential can be assumed to be in the form

\[
\varphi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp \left( \frac{r_{ij}}{r_{0,ij}} \right) + C_{ij} r_{ij}^{-6},
\]

where \( r_{ij} \) is the interatomic distance between atoms \( i \) and \( j \), \( q_i \) is an effective charge of the \( i \)th atom, \( A_{ij} \) and \( (r_{0,ij}, C_{ij}) \) are parameters for the repulsive interactions, and \( C_{ij} \). These parameters are obtained from [33] and are listed in Table 1.

<table>
<thead>
<tr>
<th>Atom-Atom</th>
<th>( A_{ij} ), eV</th>
<th>( r_{0,ij}, \AA )</th>
<th>( C_{ij} ), eV-Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-Y</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Y-O</td>
<td>1345.6</td>
<td>0.3491</td>
<td>0</td>
</tr>
<tr>
<td>O-O</td>
<td>22799</td>
<td>0.149</td>
<td>27.93</td>
</tr>
</tbody>
</table>

These parameters were confirmed using a computer code GULP [34] to reproduce the crystal structure. The X-ray diffraction [35] and neutron diffraction [36] showed that \( \text{Y}_2\text{O}_3 \).
has a face-centered cubic structure, which is retained down to nanocrystals [37]. Eight metal ions are in the positions 1/4, 1/4, 1/4; the remaining twenty four occupy the sites $u,0,1/4$. The forty eight oxygen ions are in general positions $x,y,z$, arranged in distorted octahedra around the metal ions, the metal-oxygen bonding distances being unequal. The values of $u,x,y,z$ are listed in [35, 36].

For the bulk crystal, molecular dynamics simulations are carried out in a cubic computational domain which contains $2 \times 2 \times 2 = 8$ unit cells and $N = 640$ atoms (256 Y and 384 O). Periodic boundary conditions are used in all directions. For nanopowder, the computational domain is a sphere of diameter $d_s$ which is cut from a much larger bulk crystal, with the center of the sphere randomly chosen, as shown in Figure 10. Hence, there are many possible configurations given the diameter. We have considered a range of spherical particles with different configurations. The free boundary condition is used.

For both bulk and nano crystals, an initialization period of $5 \times 10^4$ time steps is used. The system is run in the NVT (constant mass, volume and temperature) ensemble. To set the temperature for the NVT ensemble, the potential energy of the system is monitored every time step. When it reaches a value within $10^{-4}\%$, the ensemble is switched to NVE, and the system is run until the total number of time steps is $1.5 \times 10^5$.

The normalized velocity-velocity autocorrelation function for the $\beta$th species ($\beta = Y, O$) is

$$\Gamma_\beta(t) = \left\langle \sum_{i=1}^{N_\beta} u_{i\beta}(t) u_{i\beta}(0) \right\rangle / \left\langle \sum_{i=1}^{N_\beta} u_{i\beta}(0) u_{i\beta}(0) \right\rangle,$$

where $u_{i\beta}$ is the velocity of particle $i\beta$ and $\langle \rangle$ is an ensemble average. At low temperatures, the frequency spectrum of the normalized velocity autocorrelation function gives the partial phonon density of states $D_{\rho,\beta}(\omega)$, as

$$D_{\rho,\beta}(\omega) = \int_0^\infty \Gamma_\beta(t) \cos(\omega t) dt. \quad (27)$$

The total phonon DOS is obtained by summing over the partial DOS weighted with the population, i.e.,

$$D_{\rho}(\omega) = \sum_\beta c_\beta D_{\rho,\beta}(\omega), \quad (28)$$

where $c_\beta$ is the population of the $\beta$th species in the MD system. Here for $Y_2O_3$, we use $c_Y = 2/5$, and $c_O = 3/5$.

The partial phonon density of states of Y and O atoms are calculated for the bulk and nanoparticle $Y_2O_3$ crystals. The partial-phonon DOS, $D_{\rho,\beta}(\omega)$, is normalized to 1 such that $\int_0^\infty D_{\rho,\beta}(\omega) d\omega = 1$. The total DOS, calculated using Eq. (28), is shown in Fig. 11. This normalization makes it possible to compare the partial and total DOS of MD systems with different number of atoms.

It can be seen that the phonon DOS of nanocrystals is distinct from that of the bulk crystal in its extended, small tails at low and high frequencies. In the median frequency range, the two DOSs are nearly the same.
2 Anti-Stokes transition rate: a Fermi golden rule calculation

Since a much longer pumping wavelength than the resonance is used in laser cooling, the probability of a purely electronic transition (the first order process) between electronic sublevels becomes very small. While the phonon-assisted transition, a second-order process, begin to contribute significantly to absorption. As a result, the absorption turns out to be a combination of the first-order and second-order transitions. Since the first-order process does not involve phonons, only the second-order process is analyzed here for the purpose of understanding the role of phonons in laser cooling.

In the second order process, the ion in its ground state absorbs an incident photon and a phonon, and goes up to the excited state. The probability per unit time of such a process can be evaluated using the perturbation theory. The Hamiltonian for the physical system considered is given by [12]

\[ H = H_{\text{ion}} + H_p + H_{\text{ph}} + \varphi_{\text{ion-\text{ph}}} + \varphi_{\text{ion-p}}, \]  

where

\[ H_{\text{ion}} = \hbar \omega_{e,g} a^+ a \]  

is the Hamiltonian of the ion electronic levels being \( \hbar \omega_{e,g} \) the energy difference between the optically active energy levels of the dopant ion (considered as a two level ion) and \( a^+ (a) \) the creation (annihilation) operator of an electronic excitation;

\[ H_p = \sum_p \hbar \omega_p b^+_p b_p \]  

is the phonon field Hamiltonian with \( \omega_p \) the phonon frequency and \( b^+_p (b_p) \) the creation (annihilation) operator of a phonon in mode \( p \);

\[ H_{\text{ph}} = \hbar \omega_{ph,i} c^+ c \]  

is the electromagnetic laser field with \( \omega_{ph,i} \) the pumping frequency and \( b^+_p (b_p) \) the creation (annihilation) operator of a photon;

\[ \varphi_{\text{ion-\text{ph}}} = -e_\alpha \cdot \mu_e \left( \frac{\hbar \omega_{ph,i}}{2 \varepsilon_0 V_s} \right)^{1/2} (a^+ + a) (c^+ + c) \]  

is the ion-photon interaction Hamiltonian, \( e_\alpha \) being the polarization factor of the photon, \( \mu_e \) the dipole moment of the electronic transition, \( \varepsilon_0 \) the vacuum permittivity, and \( V_s \) the interacting volume;

\[ \varphi_{\text{ion-\text{ph}}} = \varphi_{\text{ion-\text{ph}}}, \]  

\[ \varphi_{\text{ion-p}} = \varphi_{\text{ion-p}}, \]  

\[ \hbar \omega_p \]  

is the ion-phonon interaction Hamiltonian, where \( a_{i-p} \) is the ion-phonon coupling constant, \( u_p \) is the speed of sound, and \( \rho \) the mass density.

This process appears in the second-order term of the perturbation expansion, and the transition rate \( \gamma_f \) is given by the Fermi golden rule

\[ \gamma_f = \sum_f |\varphi_{\text{ion-\text{ph}}} + \varphi_{\text{ion-p}}|^2 \]  

(35)

where \( E_i \) and \( E_f \) are, respectively, the initial and final energies of the system. The \( M_{fi} \) matrix admits a perturbative expansion given by [12]

\[ M_{fi} = \langle f | \varphi_{\text{ion}} | i \rangle + \sum_{m,n} \frac{\langle f | \varphi_{\text{ion}} | m \rangle \langle m | \varphi_{\text{ion}} | i \rangle}{E_{f,i} - E_{e,m}} + \sum_{m,n} \frac{\langle f | \varphi_{\text{ion}} | m \rangle \langle m | \varphi_{\text{ion}} | n \rangle \langle n | \varphi_{\text{ion}} | i \rangle}{E_{f,i} - E_{e,m}} + \cdots, \]  

(36)

with \( \varphi_{\text{ion}} = \varphi_{\text{ion-\text{ph}}} + \varphi_{\text{ion-p}} \). The summations on \( m \) and \( n \) include all the intermediate phonon and photon states.

We calculate the transition probability \( \gamma_f \) between initial \( |i\rangle = |\psi_i, f_{ph,i}, f_p + 1 \rangle \) and final \( |f\rangle = |\psi_f, f_{ph,f}, f_p \rangle \) states of the system, where the first ket element, \( \psi_i \), refers to the ion state, the second one, \( f_{ph,i} \), to the photon distribution function, and the third one, \( f_p \), to the phonon distribution function. This type of processes only appears in the second order perturbation expansion of the \( M_{fi} \) matrix, which is

\[ M_{fi, 2nd} = \sum_m \frac{\langle f | \varphi_{\text{ion}} | m \rangle \langle m | \varphi_{\text{ion}} | i \rangle}{E_{f,i} - E_{e,m}} \]

\[ = \sum_m \left[ \frac{\langle \psi_f, f_{ph,f}, f_p | \varphi_{\text{ion}} | \psi_{m, f_{ph,m}, f_p + 1} \rangle \times}{E_i - (E_m - \hbar \omega_{ph})} \right] \]

\[ \times \frac{\langle \psi_{m, f_{ph,m}, f_p + 1} | \varphi_{\text{ion}} | \psi_{m, f_{ph,m}, f_p + 1} \rangle}{E_i - (E_m - \hbar \omega_{ph})} \]

\[ \times \frac{\langle \psi_m, f_{ph,m}, f_p + 1 \rangle \varphi_{\text{ion}} | \psi_{m, f_{ph,m}, f_p + 1} \rangle \times}{E_i - (E_m - \hbar \omega_{ph})} \]

\[ \times \sum_m \langle \psi_f, f_{ph,f}, f_p | \varphi_{\text{ion}} | \psi_{m, f_{ph,m}, f_p + 1} \rangle \times \]

\[ \times \frac{\langle \psi_{m, f_{ph,m}, f_p + 1} | \varphi_{\text{ion}} | \psi_{m, f_{ph,m}, f_p + 1} \rangle}{E_i - (E_m - \hbar \omega_{ph})} \times \]
In order to perform the summation on the phonon modes in Eq. (38), we must introduce the phonon density of states. Substituting Eq. (37) into Eq. (35), we have [12]

$$\gamma_c = \sum_f \gamma_{c,i-f} = \frac{2\pi}{\hbar} \frac{\omega_{p,i} \omega_{e,g}}{\omega_{ph,i}} \sum_p \left( \frac{\hbar \omega_p}{\hbar \omega_p - \hbar \omega_{ph,i}} \right)^2 f_{ph,p} f_{p} \delta (\hbar \omega_{ph,i} - \hbar \omega_{p,i} + \hbar \omega_{p} - \hbar \omega_{e,g}), \quad (38)$$

where

$$g^2 = \left( \frac{\omega_{ph,i} \omega_p}{2 \epsilon V_s} \right)^2 \frac{h \omega_{ph,i}}{2 \epsilon V_s} - \frac{\hbar \omega_{p,i}}{2 \mu_p}, \quad (39)$$

In order to perform the summation on the phonon modes in Eq. (38), we must introduce the phonon density of states. In terms of this distribution function, the transition rate, Eq. (38), becomes

$$\gamma_c = \frac{2\pi}{\hbar} \frac{\omega_{p,i} \omega_{e,g}}{\omega_{ph,i}} \sum_p \left( \frac{\hbar \omega_p}{\hbar \omega_p - \hbar \omega_{ph,i}} \right)^2 f_{ph,p} f_{p} \delta (\hbar \omega_{ph,i} - \hbar \omega_{p,i} + \hbar \omega_{p} - \hbar \omega_{e,g})$$

$$= \frac{2\pi}{\hbar} \frac{\omega_{p,i} \omega_{e,g}}{\omega_{ph,i}} \sum_p \left( \frac{\hbar \omega_p}{\hbar \omega_p - \hbar \omega_{ph,i}} \right)^2 f_{ph,p} f_{p} \delta (\hbar \omega_{ph,i} - \hbar \omega_{p,i} + \hbar \omega_{p} - \hbar \omega_{e,g})$$

$$= \frac{2\pi}{\hbar} \frac{\omega_{p,i} \omega_{e,g}}{\omega_{ph,i}} \sum_p \left( \frac{\hbar \omega_p}{\hbar \omega_p - \hbar \omega_{ph,i}} \right)^2 f_{ph,p} f_{p} \delta (\hbar \omega_{ph,i} - \hbar \omega_{p,i} + \hbar \omega_{p} - \hbar \omega_{e,g})$$

$$= \frac{2\pi}{\hbar} \frac{\omega_{p,i} \omega_{e,g}}{\omega_{ph,i}} \sum_p \left( \frac{\hbar \omega_p}{\hbar \omega_p - \hbar \omega_{ph,i}} \right)^2 f_{ph,p} f_{p} \delta (\hbar \omega_{ph,i} - \hbar \omega_{p,i} + \hbar \omega_{p} - \hbar \omega_{e,g})$$

$$= \frac{2\pi}{\hbar} \frac{\omega_{p,i} \omega_{e,g}}{\omega_{ph,i}} \sum_p \left( \frac{\hbar \omega_p}{\hbar \omega_p - \hbar \omega_{ph,i}} \right)^2 f_{ph,p} f_{p} \delta (\hbar \omega_{ph,i} - \hbar \omega_{p,i} + \hbar \omega_{p} - \hbar \omega_{e,g})$$

$$= \frac{2\pi}{\hbar} \frac{\omega_{p,i} \omega_{e,g}}{\omega_{ph,i}} \sum_p \left( \frac{\hbar \omega_p}{\hbar \omega_p - \hbar \omega_{ph,i}} \right)^2 f_{ph,p} f_{p} \delta (\hbar \omega_{ph,i} - \hbar \omega_{p,i} + \hbar \omega_{p} - \hbar \omega_{e,g})$$

where $E_p$ is the phonon energy given by $E_p = \hbar \omega_{p,i} - \hbar \omega_{ph,i}$. It implies that the excitation spectra can be well associated with the phonon spectra, as observed in [38]. Here we have used the equilibrium distribution functions for phonons.
The phonon DOS size effect is also considered. The phonon DOS of nanoparticle crystal is determined using molecular dynamics simulations and the Fourier transform of the velocity autocorrelation function. The DOS of nanocrystals possesses the extended, small tails at low and high frequencies. Treating the cooling process as a phonon-assisted transition, a second order quantum mechanical calculation is performed to predict the transition rates. As shown in Fig. 13, this mechanism may enhance or reduce the cooling performance, depending on the pumping wavelength used. In the practical cooling range ($\lambda_i = 1,020$ to $1,030$ nm), more enhancement is shown than reduction. If the broadening of the absorption spectra is taken into account, we can conclude that the phonon size effect would generally enhance the cooling performance.

Considering all these three mechanisms, the cooling power is predicted to be enhanced by about 275%.

ACKNOWLEDGEMENT

The support of Rackham School of Graduate Studies/Vice President for Research, University of Michigan, through a research grant, is greatly appreciated. We are also thankful to Professor Stephen Rand, Professor Carl Mungan, and Dr. Angel Garcia for many discussions/suggestions.

REFERENCES


Appendix: Thermodynamics Limit of Laser Cooling of Solids

The theoretical limit of laser cooling is governed by the second law of thermodynamics. An excellent analysis has been given by Mungan [39], in which the ideal cooling efficiency is calculated to be 20%. Here we briefly review the basic concepts and derivation.
That is, the entropy carried by monochromatic or unidirectional radiation is zero, so that one can characterize an ideal laser beam as pure work or high-grade energy.

It is useful to define the flux temperature \( T_f \) of the radiation, which is given by

\[
T_f \equiv \frac{I_E(\omega)}{I_S} = \frac{h \nu \omega}{k_B} \frac{f_{ph}}{(1 + f_{ph}) \ln(1 + f_{ph}) - f_{ph} \ln f_{ph}}.
\]

(44)

Again, for an ideal laser, we have

\[
T_f \approx \frac{h \nu \omega}{k_B} \frac{f_{ph}}{\ln f_{ph}} \to \infty, \quad \text{as } f_{ph} \to \infty.
\]

which is consistent with the zero entropy at a finite irradiance. It can be further deduced by Eq. (45) that the flux temperature of narrowband radiation propagating in a well-defined direction is higher than that of broadband radiation propagating in all directions.

In laser cooling of solids, according to the first law, we have

\[
\dot{E}_{\text{out}} = \dot{E}_{\text{in}} + Q,
\]

(46)

The cooling coefficient of performance is defined in the usual way for a refrigerator as

\[
\eta = \frac{Q}{\dot{E}_{\text{in}}}
\]

(47)

The maximum value of \( \eta \) is the Carnot limit, \( \eta_C \), and is determined by the second law of thermodynamics. The entropy carried by the fluorescence cannot be less than the sum of the entropy withdrawn from the cooling sample and the entropy transported in by the pump laser, i.e.,

\[
\frac{\dot{E}_{\text{out}}}{T_f} = \frac{\dot{E}_{\text{in}}}{T_0} + \frac{Q}{T},
\]

(48)

where \( T \) is the steady-state operating temperature of the refrigerator, and \( T_f \) and \( T_0 \) are the flux temperatures of the fluorescence and pump radiation, respectively. The reversible Carnot limit is obtained by choosing the equality sign in Eq. (48). By substituting Eqs. (46) and (47) into Eq. (48), we have

\[
\eta_C = \frac{T - \Delta T}{T_f - T},
\]

(49)

where \( \Delta T = T/T_f - T_0 \).

Consider an example using actual values relevant to laser cooling of Yb\(^{3+}\)-ZBLANP [39]. The temperatures of the pump laser and the fluorescence are calculated using Eq. (44) to be \( T_0 = 7 \times 10^{11} \text{ K} \) and \( T_f = 1,760 \text{ K} \), respectively. Thus the Carnot efficiency of this optical cooler is about 20% at room temperature, and it diminishes approximately linearly to zero as \( T \to 0 \). However, the actual cooling efficiency achieved to date is only around 3%, which indicates that much irreversibility has been introduced into the process. One might use a longer pumping
wavelength to obtain higher cooling efficiency, but the absorption coefficient of Yb$^{3+}$ would become too small, as a result, the trace impurity absorption will dominate over the Yb$^{3+}$ absorption, and the cooling efficiency $\eta$ decreases. To reduce these irreversibilities introduced into this process, the sample should be purified to suppress the trace absorption, and also the Yb$^{3+}$ absorption coefficient should be enhanced.