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POSSIBLE WAYS OF RELAXATIONS FOR EXCITED STATES OF RARE EARTH IONS IN AMORPHOUS MEDIA

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Abstract - The various mechanisms of relaxation of rare earths in glasses are outlined. Examples are given for radiative transfer as a means of increasing pumping efficiencies. Nonradiative relaxation of rare earths in oxide and fluoride glasses follow an exponential law when two glass former phonons are subtracted. Cross-relaxations are calculated for Pr(III), Ho(III) and Nd(III).

The excited state of a rare earth ion in an amorphous matrix can relax by four main channels: 1. Radiative transfer; 2. Multiphonon relaxation; 3. Cross-relaxation to another ion of the same nature; 4. Energy transfer to an ion of different nature.

1. The radiative transfer consists of absorption of the emitted light from a donor molecule or ion by the acceptor species. In order that such transfer takes place the emission of the donor has to coincide with the absorption of the acceptor. The radiative transfer can be increased considerably by designing a proper geometry. Such transfer may be important in increasing pumping efficiencies of glass lasers /1/ and luminescent solar concentrators whereby energy emitted from organic molecules can be absorbed by ions such as Cr(III), Mn(II) or Nd(III) followed by characteristic emission from these ions.

2. Multiphonon relaxation in lanthanide ions is today a well understood process contrary to transition metal ions which still requires additional understanding. Excited electronic levels of rare earths (RE) in solids decay nonradiatively by exciting lattice vibrations (phonons). When the energy gap between the excited level and the next electronic level is larger than the phonon energy several lattice phonons are emitted in order to bridge the energy gap. It was recognized that the most energetic vibrations are responsible for the non-radiative decay since such a process can conserve energy in the lowest order. In glasses the most energetic vibrations are the stretching vibrations of the glass network polyhedra and it was shown that these distinct vibrations are active in the multiphonon process rather than the less energetic vibrations of the bond between the RE and its surrounding ligands. It was demonstrated that these less energetic vibrations may...
participate in cases when the energy gap is not bridged totally by the high energy vibrations. The experimental results reveal that the logarithm of the multiphonon decay rate decreases linearly with the energy gap, or the number of phonons bridging the gap when the number of phonons is larger than two. Figure 1 presents the logarithm of the non-radiative relaxation rate versus the number of phonons of the glass-forming material. Figure 2 presents the same dependence however two phonons are taken as the origin of the abscissa.

![Graph 1](image1)

**Fig. 1.** Dependence of multiphonon relaxation of the number of phonons in the glass former.

![Graph 2](image2)

**Fig. 2.** Dependence of multiphonon relaxation of the number of phonons in the glass former (note that abscissa starts at 2 phonons).
Application of the multiphonon theory to glasses requires the knowledge of the structural units forming the glass. Similar to the electronic spectra in glasses, the vibrational frequencies show in homogeneous broadening due to the variation of sites. Table I shows the average frequencies of the network formers. The vibrations involving the network modifiers are lower by a factor of 2 to 4. Considering the dependence of the multiphonon relaxation rate, \( W_p \), on the phonon occupation number for a \( p \)-order multiphonon decay at temperature \( T > 0 \)

\[
W_p = B[n(T)+1]^P \exp(-\alpha \Delta E)
\]  

where \( \Delta E \) is the energy gap between the emitting and next lower level

\[
\alpha = -\ln(\varepsilon)/\hbar \omega
\]  

and \( \alpha \) and \( B \) are dependent on the host but independent of the specific electronic level of RE from which the decay occurs.

In calculating theoretically the multiphonon relaxation Siebrand /2/ has used the Condon approximation in which the electronic matrix elements are separated from the vibrational ones and assuming that the transition is dominated by a small number of promoting modes which consume the energy \( \hbar \omega \). The accepting modes provide only for the remaining energy difference \( \Delta E_0 = \hbar \omega_{\text{max}} \).

The theoretical results arising from this theory are

\[
W_{\text{NR}} = B e_l \exp[-\Delta E - 2\hbar \omega \alpha]
\]  

The multiphonon decay rate from a given level to the next lower level decreases with the lowering of energy of the stretching frequencies of the glass former. Since a large number of phonons is needed in fluoride glasses and more so in chalcogenide glasses in order to reach the same energy gap the nonradiative relaxations are smallest in these hosts.

A tabulation of the parameters \( B \) and \( \alpha \) of eq. (1) together with the highest phonon energy for a variety of glasses and crystals is presented in Table I. For oxide glasses \( \alpha \) is fairly constant while \( B \) differs by several orders of magnitude between various glasses. Recently this phenomenon was elaborated by Schuurmans and Van Dijk /3/ who propose formula (3) rather than eq. (1). Hence one can define a revised \( B_{e_l} \)

\[
\log_{10} B_{e_l} = \log_{10} B - 0.86 \alpha \hbar \omega
\]  

(0.86 = \log_{10} e^2)

The \( \log_{10} \) of electronic factor \( B_{e_l} \) is also presented in Table I where it can be seen that it is of the same order of magnitude for all glasses contrary to \( B \) which varies by several orders of magnitude for various glasses. See Fig. 2.

The multiphonon transition rates for rare earths in a variety of glasses can be obtained from formula (4) by use of the tabulated values of \( B_{e_l} \), \( \alpha \) and \( \hbar \omega \) in Table I and energy differences to the next electronic level \( \Delta E \). The correspondence of theory with experiment has been shown for Pr(III) /4/, Nd(III) /5/, Ho(III) /6/, and Er(III) /7/.

The multiphonon processes compete with luminescence as excitation energy is lost to the local vibrations of the glass formers. The other nonradiative losses arise from energy transfer to the electronic states of atoms in the vicinity of the excited ion. The energy transfer process may be either resonant or phonon-assisted where the excess of energy is dissipated as heat. The energy deficiency in nonresonant processes may be supplied by the thermal reservoir of the low energy phonons \( (kT = 210 \text{ cm}^{-1} \text{ at } 300 \text{K}) \) to match the missing energy. Because of the thermodynamical
consideration the last process is much less efficient.

TABLE I. Parameters for Nonradiative Relaxations in Glasses

<table>
<thead>
<tr>
<th>Matrix</th>
<th>( B \text{ s}^{-1} )</th>
<th>( \alpha \text{ cm} )</th>
<th>( \hbar \omega \text{ cm}^{-1} )</th>
<th>( \log_{10} B_{\text{el}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tellurite</td>
<td>6.3 \times 10^{10}</td>
<td>4.7 \times 10^{-3}</td>
<td>700</td>
<td>7.97</td>
</tr>
<tr>
<td>Phosphate</td>
<td>5.4 \times 10^{12}</td>
<td>4.7 \times 10^{-3}</td>
<td>1200</td>
<td>7.88</td>
</tr>
<tr>
<td>Borate</td>
<td>2.9 \times 10^{12}</td>
<td>3.8 \times 10^{-3}</td>
<td>1400</td>
<td>7.89</td>
</tr>
<tr>
<td>Silicate</td>
<td>1.4 \times 10^{12}</td>
<td>4.7 \times 10^{-3}</td>
<td>1100</td>
<td>7.89</td>
</tr>
<tr>
<td>Germanate</td>
<td>3.4 \times 10^{10}</td>
<td>4.9 \times 10^{-3}</td>
<td>900</td>
<td>6.74</td>
</tr>
<tr>
<td>ALS, GLS</td>
<td>1 \times 10^{6}</td>
<td>2.9 \times 10^{-3}</td>
<td>350</td>
<td>5.13</td>
</tr>
<tr>
<td>ZBLA</td>
<td>1.59 \times 10^{10}</td>
<td>5.19 \times 10^{-3}</td>
<td>500</td>
<td>7.97</td>
</tr>
<tr>
<td></td>
<td>1.88 \times 10^{10}</td>
<td>5.77 \times 10^{-3}</td>
<td>460-500</td>
<td>7.89</td>
</tr>
</tbody>
</table>

ALS \( = 3\text{Al}_2\text{S}_3, 0.872\text{La}_2\text{S}_3, 0.128\text{Nd}_2\text{S}_3 \)
GLS \( = 3\text{Ga}_2\text{S}_3, 0.85\text{La}_2\text{S}_3, 0.15\text{Nd}_2\text{S}_3 \)
ZBLA \( = 57\text{ZrF}_4, 34\text{BaF}_2, 3\text{LaF}_3, 4\text{AlF}_3, 2\text{REF}_3, \text{mole \%} (\text{RE} = \text{rare earth}) \)

3. Cross-relaxations. Special cases of energy transfer are cross-relaxation where the original system loses the energy \( (E_1 - E_2) \) by obtaining the lower state \( E_1 \) (which may also be the groundstate \( E_1 \)) and another system acquires the energy by going to a higher state \( E_2 \). Cross-relaxation may take place between the same lanthanide (being a major mechanism for quenching at higher concentration in a given material) or between two differing elements, which happen to have two pairs of energy levels separated by the same amount.

The cross-relaxation between a pair of RE ions is graphically presented in Fig. 3.

The two energy gaps may be equal or can be matched by one or two phonons. Cross-relaxation has been measured in a variety of ions and it is a dominating factor in nonradiative relaxations at high concentration. The non-radiative relaxation rates can be obtained by analysis of the decay curves of RE fluorescence using the formula of the general form where the population number of state \( i \), \( N_i \) is proportional to the intensity of emitted light \( I_i \).

\[
\frac{\mathrm{d}N_i(t)}{\mathrm{d}t} = -\left( \gamma_R^i + \sum_{i \neq j} W_{ij} \right) N_i(t) + \sum_{i \neq j} W_{ij} N_j(t)
\]  

(5)

\( \frac{\mathrm{d}N_i(t)}{\mathrm{d}t} \) is the decrease of intensity after pulse excitation, \( \gamma_R \) is the reciprocal lifetime of the excited state in the absence of cross-relaxation process. \( \sum_{i \neq j} W_{ij} \) is the probability for cross-relaxation, \( W_{ij} \) is the probability of inverted process, and \( W_{ij} \) is the rate of cross-relaxation.

Theoretically the cross-relaxation rate for a dipole-dipole transfer can be obtained from formula (6) /8/:

\[
P_{\alpha}^{\text{DD}} = \frac{1}{(2J_A^S+1)(2J_{\alpha}^S+1)} \left( \frac{2}{3} \right) \left( \frac{\pi}{\hbar} \right) \left( \frac{e^2}{R_S} \right)^2 \left[ \sum_{\lambda} \sum_{\lambda}^{\alpha} \langle J_{\lambda}^A \rangle \langle J_{\lambda}^S \rangle \langle U^{(\lambda)} \rangle \langle J_{\lambda}^{S*} \rangle \right] x \langle \sum_{\lambda} \sum_{\lambda}^{\alpha} J_{\lambda}^A \rangle \langle U^{(\lambda)} \rangle \langle J_{\lambda}^{S*} \rangle
\]  

(6)
Fig. 3. Scheme for cross-relaxation between two ions of the same or different nature.

Here $\Omega$ are the Judd-Ofelt intensity parameters, $\langle J || U^{(\lambda)} || J' \rangle$ is the matrix element of the transition between the ground and excited state of the sensitizer and activator respectively (the calculation of these matrix elements in the intermediate-coupling scheme is now a well known procedure and may be found in references /8/ and /9/: $S$ is the overlap integral and $R$ is the interionic distance.

The measured lifetime of luminescence is related to the total relaxation rate by

$$\frac{1}{\tau} = \Sigma W_{nr} + \Sigma A + P_{CR} = \frac{1}{\tau_0} + P_{CR}$$

where $\Sigma A$ is the total radiative rate, $\Sigma W_{nr}$ is the nonradiative rate and $P_{CR}$ is the rate of cross-relaxation between adjacent ions.

The possible cross-relaxation channels for Pr(III), Ho(III) and Nd(III) are outlined in Table II. /10/

In order to obtain the critical radii which are the distances at which the probability for cross-relaxation is equal to the sum of the radiative and multiphonon probabilities the decay curves are analyzed with respect to the Inokuti-Hirayama model /11/.

The energy transfer between Cr(III) and Nd(III) /12/ and Cu(III) and Yb(III) /13/ has been studied extensively by static and dynamic methods. The transfers occur by dipole-dipole mechanisms and are important in increasing the pumping range of Nd(III) and Yb(III) ions.
<table>
<thead>
<tr>
<th>Ion</th>
<th>Matrix</th>
<th>Concentration [10^17/cm³]</th>
<th>Lifetime µs</th>
<th>Possible cross relaxation path</th>
<th>Critical radius [Å]</th>
<th>R₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr³⁺</td>
<td>ZFG</td>
<td>13</td>
<td>3.25</td>
<td>(F₆⁺F₄⁻) + 3F₆⁻ + (3H₄ + 1G₄⁻)</td>
<td>3.29 ± 0.18</td>
<td>10.0 ± 0.82</td>
</tr>
<tr>
<td>Ho³⁺</td>
<td>ZFG</td>
<td>60</td>
<td>3.25</td>
<td>(F₅⁺F₄⁻) + 3H₆</td>
<td>3.32 ± 0.56</td>
<td>5.54 ± 0.28</td>
</tr>
<tr>
<td>Ho³⁺</td>
<td>ZFG</td>
<td>105</td>
<td>3.20</td>
<td>(S₃⁺S₂⁻) + 5I₈</td>
<td>3.32 ± 1.62</td>
<td>3.32 ± 1.32</td>
</tr>
<tr>
<td>Ho³⁺</td>
<td>ZFG</td>
<td>12.3</td>
<td>1.90</td>
<td>(S₃⁺S₂⁻) + 5I₈</td>
<td>3.44 ± 0.56</td>
<td>4.21 ± 0.44</td>
</tr>
<tr>
<td>Ho³⁺</td>
<td>ZFG</td>
<td>10.2</td>
<td>1.90</td>
<td>(S₃⁺S₂⁻) + 5I₈</td>
<td>3.44 ± 0.56</td>
<td>4.21 ± 0.44</td>
</tr>
<tr>
<td>Ho³⁺</td>
<td>LLP</td>
<td>9.3</td>
<td>5.80</td>
<td>(S₃⁺S₂⁻) + 5I₈</td>
<td>3.44 ± 0.56</td>
<td>4.21 ± 0.44</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>ZFG</td>
<td>216</td>
<td>2.70</td>
<td>(F₄⁺I₂⁻) + 4I⁻/2</td>
<td>6.58 ± 0.29</td>
<td>6.50 ± 0.36</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>LLP</td>
<td>167</td>
<td>5.49</td>
<td>(F₄⁺I₂⁻) + 4I⁻/2</td>
<td>6.58 ± 0.29</td>
<td>6.50 ± 0.36</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>LLP</td>
<td>96</td>
<td>8.40</td>
<td>(F₄⁺I₂⁻) + 4I⁻/2</td>
<td>6.58 ± 0.29</td>
<td>6.50 ± 0.36</td>
</tr>
</tbody>
</table>

ZFG - Zirconium fluoride glass  
ZTG - Zinc tellurite glass  
LPP - Lithium lanthanum phosphate glass
REFERENCES