APPENDIX

ENERGY TRANSFER

In the past there have been many investigations, which established that electronic excitation energy could, in certain circumstances, be transferred between ions or molecules in the solid phase. The three basic mechanisms for energy transfer are photoconductive, radiative, and nonradiative.[1] The photoconductive mechanism occurs when an absorbed photon creates free electron-hole pairs capable of migration. Many studies have been conducted on the photoconductivity of semiconductors, and these have generally involved measurement of the electrical current that results after optical excitation. The second basic energy transfer mechanism is radiative reabsorption in which a photon is emitted and then reabsorbed by the same system.[1] This process does not shorten the fluorescence lifetimes, and can usually be minimized by adjusting sample size and experimental configuration. The mechanism most extensively studied, and most relevant to this thesis, is nonradiative energy transfer between ions without charge migration. In this case Coulomb interactions of the Van der Waals type allow energy to be transferred directly between the ions.[2]

MICROSCOPIC EQUATIONS

The theory of nonradiative energy transfer was first developed by

Forster[3], who used quantum mechanics to describe energy transfer in terms of a

resonant dipole-dipole interaction. It was assumed that interactions would be

strongest if the two dipole-dipole transitions were symmetry allowed.[2] The

interaction energy is then proportional to the inverse third power of the interionic

distance and transfer probability is given by:

$$P_{SA} = \frac{2p}{\hbar} \left| \left\langle S^e A^o \middle| H_{SA} \middle| S^e A^o \right\rangle \right|^2 r E \tag{1}$$

H_{SA} interaction Hamiltonian

$r E$ density of states provided by the vibrational motion contributing tot

      he line broadening of the transition

which is proportional to the inverse sixth power of that distance. The

wavefunctions to be considered for the matrix element are describing an initial

state of the system with the donor in its excited state and the acceptor in its

ground state, the final state having the sensitizer in its ground state and the

acceptor in its excited state.

Therefore, the transfer probability can be written as

$$P_{SA} = \frac{1}{t_s}\left(\frac{R_0}{R}\right)^6 \tag{2}$$

t_S actual lifetime of the donor excited state

R_0 critical transfer distance for which excitation transfer and

spontaneous deactivation of the donor have equal probability.

R_0 can be written as

$$R_0^{\,6} = \frac{3.10^3 hS^0}{64p^6 n^4 N\bar{n}^{-4}} \int_0^\infty f_S(n)e_A(n)dn \tag{3}$$

where ν is the wavenumber, $\varepsilon_A(\nu)$ the molar extinction coefficient, hS^0 the

quantum efficiency of the donor in the absence of the acceptor, n the refractive

index, N Avogadro's number, $\bar{n}$ the average frequency of the transition, and the

integral represents the energy overlap between the absorption in the donor and

the acceptor emission.[2]

Forster's theories on energy transfer in terms of dipole-dipole interactions

were expanded by Dexter to also include multipole and exchange interactions.[4]

In fact, for an isolated atom, one can consider the transition probability as

decreasing as $(a_0/\lambda)^{2n}$ where a_0 is the Bohr radius, λ the wavelength, and n an

integer. However, in an energy transfer process with a dependence on near-

zone interactions, the transition probabilities drops off as $(a_0/r)^{2n}$ where r is the

separation of the interacting ions. r can be as much as three orders of magnitude

smaller than λ, so that the energy transfer effect tends to be more pronounced in systems with forbidden transitions. This holds true for the rare-earth ions, which we shall discuss later.

The energy transfer probability for electric multipolar interactions can be more generally written as

$$P_{SA}(R) = \frac{1}{t_s}\left(\frac{R_0}{R}\right)^s \tag{4}$$

where s is a positive integer taking the following values:

    s = 6   for dipole-dipole interactions

    s = 8   for dipole-quadrupole interactions

    s = 10 for quadrupole-quadrupole interactions.[2]

Inokuti and Hirayama[5] advanced Dexter's theoretical treatment of exchange interactions by determining relationships to experimentally observable phenomena. They developed a quantitative relationship between yield and decay time of donor luminescence as a function of acceptor concentration.[5]

When the two ions involved in energy transfer have excited states of different energies, the overlap intergral $\int_0^\infty f_S(n)e_A(n)dn$ goes to zero and according to equation (3) the probability for energy transfer should also be zero.[2] Experimentally, however, it is found that energy transfer can still take place between nonresonant ions as long as the energy difference is compensated by

the production or annihilation of a lattice phonon. The incorporation of lattice

vibrational states called phonons allows energy transfer while maintaining the

overall energy conservation of the system. For a one phonon-assisted

nonradiative energy transfer the energy of the phonon created or destroyed

should approach $k\mathrm{q}_d$ or kT, where q_d is the Debye temperature of the host

crystal.[2] If the energy transfer between ions involves an energy mismatch larger

than the Debye cutoff frequency of the host, the transfer is described in terms of

a multiphonon process.

MACROSCOPIC MODELS

Much effort has been made in finding experimental evidence for the

specific terms of the microscopic interaction equations. Of course examining the

energy transfer from individual excited ions is experimentally impossible and

microscopic interactions must be deduced from luminescence measurements

made on a macroscopic scale.   Commonly the nature of the transfer

mechanism is inferred by examining how the luminescence decay of an

ensemble of "equivalent" ions within a host lattice depends on their concentration

and temperature.[6] Figure 21 shows a schematic of the possible luminescence

processes which can occur when ion within a larger ensemble is excited.
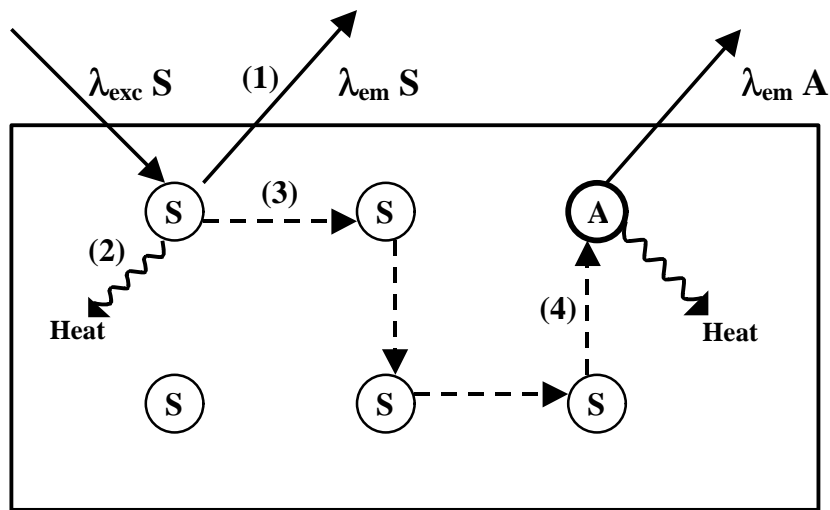
Figure 20. Schematic representation of the possible luminescence processes of a crystal system with donor D and acceptor A ions. Following excitation D may: (1) emit radiatively, (2) decay nonradiatively, (3) transfer energy to another D ion, or (4) transfer energy to an A ion. In the last case, energy transfer to A is followed by either radiative or nonradiative decay.

In the host lattice the ion which absorbs the radiation is referred to as the donor, and the ion which excitation energy is transferred is the acceptor. From the schematic presented in Figure 21, four different processes following excitation of D can be distinguished: (1) D may luminesce, (2) D may decay nonradiatively producing heat, (3) D may transfer energy to another D type ion, or (4) D may transfer energy to an A type ion. If energy transfer to A is followed by nonradiative decay, A is referred to as a killer site, because it acts to quench luminescence.[7]

A great deal of progress in this field of research has been made since the introduction of tunable dye lasers.[7] This instrument has led to the development site selective spectroscopy, in which only specific types of ions are initially excited. The short and intense excitation pulses produced by the lasers also make it possible to perform time-resolved spectroscopy, where the sample luminescence following excitation is measured as a function of time.[7]

For systems where the D ions are isolated, no energy transfer to A ions can take place, and luminescence decay following pulsed excitation is exponential. The intensity of emission is described by the following expression

$$I = I_0 \exp(-A_s t) \tag{5}$$

where I_0 is the emission intensity immediately after excitation, and A_s is the spontaneous transition probability. The exponential term can also be written as $\exp(-t/\tau_R)$, where τ_R is the radiative lifetime of the excited state, with $\tau_R^{-1} = A_s$.[8]

For systems where D ions are not isolated, and energy transfer from D to A is possible, time-resolved spectroscopy provides a method to follow energy migration through the host lattice. Provided the lifetime of the D excited state is known, information about D to D and D to A transfer can be obtained by fitting the decay curve to appropriate theoretical expressions.[9] However, these expressions involve a statistical averaging of the microscopic interactions taking place and are only exact for two limiting cases. The first case assumes no D to

D transfer, no A to A transfer, and a random distribution of D and A ions.[10] The following expression developed by Inokuti and Hirayam[5] describes this decay

$$I = I_0 \exp\left(-\frac{t}{\hat{o}_R} - \tilde{A}\left(1 - \frac{3}{s}\right)\frac{C_a}{C_{a0}}\left(\frac{t}{\hat{o}_R}\right)^{3/s} \right)$$

(6)

where Γ is the gamma function, C_a is the concentration of acceptor ions, C_{a0} is the critical acceptor concentration, and s is the multipolar interaction parameter. Due to the random distribution of acceptors some donors will find acceptors in very close proximity. These donors will decay rapidly by energy transfer causing an initially fast decay. As time passes only the more distantly separated D-A pairs remain excited, the decay rate decreases, and will eventually approach an exponential decay with a slope of τ_R^{-1}.[7, 8]

The second case that can be calculated exactly occurs for concentrated systems in which D to D transfer is much faster than D to A transfer. The fast transfer between D ions allows the D system to reach equilibrium before transfer to an A ion can occur. This is referred to as the fast diffusion limit. The following expression describes the decay

$$I = I_0 \exp\left(-\frac{t}{\hat{o}_R} - C_a \cdot P_{sa} \cdot t \right)$$

(7)

The resulting curve is a single exponential with a decay constant related to the concentration of A ions (C_a), and the D to A transfer probability (P_{sa}).[7]

ENERGY TRANSFER IN Eu$_2$O$_3$

The decay curve of Eu$_2$O$_3$ shows an initial nonexponential decay which becomes exponential at long times, this points to three-dimensional diffusion-limited energy migration (refer to figure 20). The exponential part of the decay can be expressed by

$$\tau^{-1}=\tau_0^{-1}+\tau_D^{-1} \tag{8}$$

where t$_0$ is the intrinsic decay time of an isolated Eu^{3+} ion and t$_D$ is the decay time due to migration.[11] Assuming that energy transfer occurs by a dipolar donor-acceptor interaction the following expression for τ_D^{-1} can be derived:

$$\tau_D^{-1} = 11.404 \, N_a C^{1/4} D^{3/4} \tag{9}$$

where N$_a$ is the amount of acceptor ions (in this case impurity ions) per unit volume, C is the interaction parameter for donor-acceptor interaction and D is the diffusion constant.[11] The following expression approximates luminescence decay in Eu$_2$O$_3$:

$$I(t) = I_0 \exp(-\frac{t}{t_0})\exp\{-\frac{4}{3}p^{3/2}N_a(Ct)^{1/2}(\frac{1+10.87x+15.50x^2}{1+8.743x})^{3/4}\}$$

$$\tag{10}$$

where x = DC$^{-1/3}$t$^{2/3}$. When t $\rightarrow$ ¥ the expression within the brackets transforms to the right hand side of eq. (9). Fitting eq. (10) to the experimental decay curves of Eu$_2$O$_3$ works well at low temperatures. However at higher temperatures a deviation occurs at the beginning of the curves, this likely due to the fact that

donor-acceptor interactions are not only of a dipolar nature.[11] Due to the close

proximity of Eu^{3+} ions in Eu_2O_3 an exchange interaction is also expected.

Nonlinear luminescence quenching may also be a factor at very early times in the

decay, this further complicates any attempts at mathematical modeling.

Appendix References

[1]   R. C. Powell, G. Blasse, in *Luminescence and Energy Transfer, Vol. 42*

(Ed.: J. D. Dunitz), Springer-Verlag, Berlin, **1980**, pp. 43.

[2]   F. E. Auzel, *Proceedings of the IEEE* **1973**, *61*, 758.

[3]   T. Forster, *Annalen der Physik (Leipzig)* **1948**, *2*, 55.

[4]   D. L. Dexter, *Journal of Chemical Physics* **1953**, *21*, 836.

[5]   M. Inokuti, F. Hirayama, *Journal of Chemical Physics* **1965**, *43*, 1978.

[6]   W. J. C. Grant, *Physical Review B-Condensed Matter* **1971**, *4*, 648.

[7]   G. Blasse, *Materials Chemistry and Physics* **1987**, *16*, 201.

[8]   B. Henderson, G. F. Imbush, *Optical Spectroscopy of Inorganic Solids*,

Clarendon Press, Oxford, **1989**.

[9]   D. L. Huber, in *Luminescence of Inorganic Solids, Vol. 49* (Eds.: W. M.

Yen, P. M. Selzer), Springer Verlag, Berlin, **1981**, pp. 83.

[10]   G. Blasse, *Progress in Solid State Chemistry* **1988**, *18*, 79.

[11]   M. Buijs, J. I. Vree, G. Blasse, *Chemical Physics Letters* **1987**.