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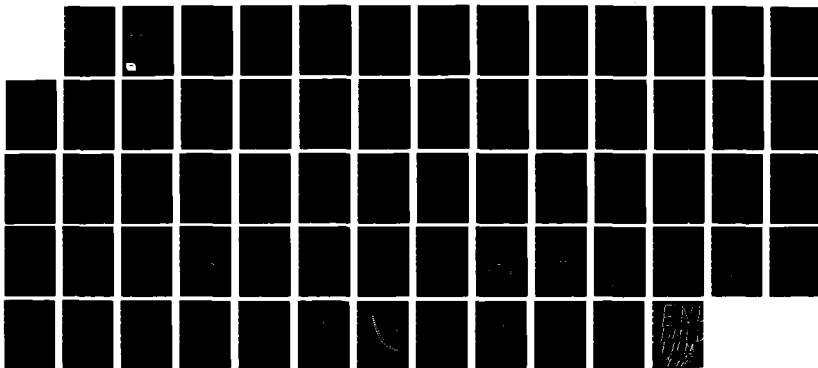
SOLID-STATE LASER RESEARCH REPORT: ENERGY TRANSFER IN
NON-UNIFORM CODOPED (U) INSTITUTE FOR DEFENSE ANALYSIS
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IDA/HQ-87-32921 MDA903-84-C-0031

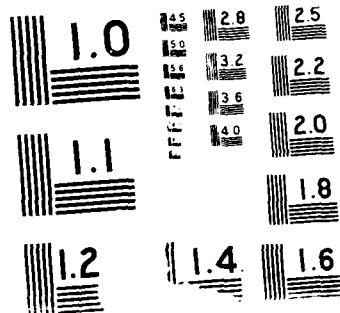
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IDA MEMORANDUM REPORT M-405

SOLID-STATE LASER RESEARCH REPORT:
ENERGY TRANSFER IN NON-UNIFORM CODOPED CRYSTALS

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Stanley R. Rotman
Francis X. Hartmann

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March 1988

Prepared for
Defense Advanced Research Projects Agency



INSTITUTE FOR DEFENSE ANALYSES
1801 N. Beauregard Street, Alexandria, Virginia 22311

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IDA MEMORANDUM REPORT M-405

SOLID-STATE LASER RESEARCH REPORT:
ENERGY TRANSFER IN NON-UNIFORM CODOPED CRYSTALS

Stanley R. Rotman
Francis X. Hartmann

March 1988

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Contract MDA 903 84 C 0031
DARPA Assignment A-107

FOREWORD

This paper serves to document work performed partially under task assignment A-107, sponsored by the Defense Advanced Research Projects Agency, Office of Directed Energy. This paper does not constitute a majority portion of the total work performed and reported in that task assignment. It describes three open literature works concerned with non-radiative energy transfer between codoped donors and acceptors in solid-state laser materials, an area of interest to controlling thermal gradients, achieving new laser frequencies and improving laser efficiency.

ACKNOWLEDGEMENTS

We are most thankful to Professors Ward and Tuller of the MIT Crystal Physics Laboratory for continuing helpful discussions on non-radiative energy transfer in co-doped solid state laser materials. We also wish to acknowledge helpful visits to Dr. Leon Esterowitz of the Naval Research Laboratory and Dr. Yuc Chen of Oak Ridge National Laboratory. The review and comments by Dr. William Hong at IDA are warmly appreciated.

PREFACE

Non-radiative energy transfer between donors and acceptors in codoped solid state laser materials is of interest in the development of medium to high average power solid state lasers and is also of fundamental interest in understanding the lifetimes of fluorescent emissions. We have previously reported (IDA P-1970 mid-task report) a detailed treatment of non-radiative energy transfer in extending the uniform Foerster-Dexter model. This is a key step towards the simulation of energy transfer in a realistic model -- both for applications in multiple codoped systems of interest in new laser frequencies and of interest in designing crystals to counter thermal gradients. In addition we have applied these ideas in a number of presentations and open literature documents presented to the scientific community. This report provides for a collection of those presentations.

In particular, this collection addresses the extension of the Foerster-Dexter model for correlated donor-acceptor placement in solid state materials, non-radiative transfer between correlated donor-acceptor pairs in solid state laser materials and finally, energy transfer between defects and rare-earth ions in garnet crystals.

Prior to the completion of the task assignment my colleague, Dr. Stan Rotman, has moved to Ben-Gurion University in Israel, where he is pursuing these ideas in the experimental growth of certain crystals. This work should serve as good tests of some of the work described in this paper. In addition, plans are underway to develop a crystal model incorporating non-uniform donor-acceptor placements as the next step towards understanding the engineering implications in crystal design.

Technical review of this report has been accomplished by Dr. William Hong of the IDA staff.

F.X. Hartmann

ABSTRACT

We develop an analytical model describing energy transfer between microscopically correlated donor-acceptor pairs in solid state laser materials. We re-examine experimental data for several laser systems; host properties promoting enhanced non-radiative energy transfer are discussed. The results of this more general model are compared to the standard Foerster-Dexter approach of randomly placed donors and acceptors. This work is of interest to controlling thermal gradients, achieving new laser frequencies and improving laser efficiency.

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I. AN EXTENDED FOERSTER-DEXTER MODEL FOR CORRELATED DONOR-ACCEPTOR PLACEMENT IN SOLID- STATE MATERIALS

A. INTRODUCTION

This paper was presented by Rotman and Hartmann at the Joint 1986 Optical Society of America Annual Meeting (19-24 October 1986) and 1986 American Physical Society and Optical Society of America International Laser Science Conference (20-24 October 1986) held in Seattle, Washington. The abstract appears in the September 1986 issue of Optics News. The summary appears in the Bulletin of the American Physical Society. The final paper was reviewed and published in the book *Advances in Laser Science: Proceedings of the International Laser Science Conference ILS-II*. The presentation was given orally in the session on Novel Solid-State Lasers, W. Krupke, Presiding.

Note: Further details on the mathematical steps reported in this document are contained in the reviewed classified mid-task report P-1970 which is not available to the open literature. Explicit derivations are thus currently being prepared for open publication. Fits to data reported here are best fits to the data and we have not yet obtained the correlation parameters discussed herein from a microscopic theory. We do, however, explain qualitative insights from these parameters.

B. ABSTRACT

A model of non-radiative energy transfer including locally correlated donor-acceptor placement is compared to the standard Foerster-Dexter approach of randomly placed donors and acceptors.

C. SUMMARY

In models of non-radiative energy transfer applied to doped solid-state laser materials, the distance between excited donors and neighboring acceptors critically affects

the calculated energy transfer rates. In the generally successful formulation of non-radiative transfer theory,¹ the donors and acceptors are taken to be distributed evenly throughout the crystal and are independent (uncorrelated) in position. We derive a general expression to treat donor-acceptor transfer rates for locally correlated donor-acceptor placement. Several specific cases appropriate to actual laser materials are: (1) an "excluded" volume around a donor diminished in acceptor concentration and (2) an "enhanced" volume around a donor in which acceptors preferentially locate. Physical effects which can lead to such microscopic distributions are discussed.

D. PAPER

¹D.L. Dexter, J. Chem. Phys. 21 (5), 836 (1953) and M. Inokuti and F. Hirayama, J. Chem. Phys. 43 (6), 1978 (1965).

AN EXTENDED FOERSTER-DEXTER MODEL FOR CORRELATED DONOR-ACCEPTOR PLACEMENT IN SOLID STATE MATERIALS

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ABSTRACT

The current theory of donor-acceptor interactions in solid-state materials is based on a random distribution of donors and acceptors through the crystal. In this paper, we present a model to calculate the observable transfer rates for the correlated positioning of donors and acceptors in laser materials. Chemical effects leading to such correlations are discussed.

INTRODUCTION

A good phosphor or laser candidate ion, in a particular lattice, must be able to absorb the pumping light efficiently as well as emit at the desired wavelengths. Recently, based on a theory originated by Foerster¹ and Dexter,² and further developed by Inokuti, et al.,³ there has been an increasing desire to separate the absorption and emission processes to different ions, rather than attempt to identify one single dopant which can both absorb and emit. The advantage of such an approach is that a good donor (which absorbs the external radiation flux) can be paired with a good acceptor (the emitting lasing ion). An efficient transfer of energy between the two ions (donor to acceptor) is necessary in this scheme.

In models of non-radiative transfer applied to doped solid-state laser materials, the distance between excited donors and neighboring acceptors critically affects the calculated energy transfer rates. In the generally successful formulation of non-radiative transfer theory, the donors and acceptors are taken to be randomly distributed and are independent (uncorrelated) in position.^{4,5} For real crystals this is not necessarily the case, and actual non-radiative transfer rates may deviate from the simple Foerster-Dexter description.

In this paper we present a more general expression to treat donor-acceptor transfer rates. In comparing our results to the Foerster-Dexter theory, we consider two specific cases appropriate to actual laser materials: (1) an "excluded" volume around a donor diminished in acceptor concentration and (2) an "enhanced" volume around a donor in which acceptors preferentially locate. These are simpler cases of our general result and the details are to published elsewhere.

ENERGY TRANSFER THEORY

For radiationless electromagnetic interactions, the strength of the non-radiative transfer rate is proportional to r^{-s} where r is the radial distance between the donor and the acceptor and s takes on specific integer values. In particular, $s = 6$ for a dipole-dipole interaction, $s = 8$ for a dipole-quadrupole interaction, $s = 10$ for a quadrupole-quadrupole interaction, etc. Energy transfer between uniformly distributed ions was examined by Inokuti et.al.³ They show that the time-dependent excited donor concentration $N_D(t)$ is

$$N_D(t) = N_D(0) \exp \left[-t/\tau_0 - \Gamma(1-3/s) c/c_0 (t/\tau_0)^{3/s} \right] \quad (1)$$

where c is the acceptor doping concentration, Γ is the gamma function, c_0 is the critical concentration of acceptors, and τ_0 is the natural decay rate of the donor. The critical concentration c_0 is that concentration at which the energy transfer rate and the natural donor decay rate are equal for the average donor-acceptor distance r_0 . For the dipole-dipole interaction ($s = 6$) the decay rate contains an exponential $t^{1/2}$ factor.

Locally correlated donor decay rates are found by starting with eq. (2):

$$N_D(T) = N_D(0) \exp(-t/\tau_0) \lim_{\substack{N_A \rightarrow \infty \\ V \rightarrow \infty}} \left\{ \int_V \exp[-t n(r) u(r) dV]^{N_A} \right\} \quad (2)$$

where the number of acceptors N_A and the volume V extend to infinity such that the concentration N_A/V remains finite. Here $n(r)$ is the radially dependent transfer rate. For the "excluded volume" case where there are no acceptors within a volume V_i (of radius r_i), the distribution function $u(r)$ is depicted in Fig. 1a. Solving for $N_D(t)$ we obtain

$$N_D(t) = N_D(0) \exp \{ -t/\tau_o - CV_i [1 - \Phi(Z_i)/\exp(Z_i)] \} \quad (3)$$

where

$$Z_i = (r_o/r_i)^6 (t/\tau_o) \quad (4)$$

and $\Phi(1, 1 - 3/s; Z)$ is the degenerate hypergeometric function (written as $\Phi(Z_i)$ for the case $s = 6$).

For the case of dipole-dipole interactions, as r_i goes to zero Z_i goes to infinity. For large Z_i , the ratio $\Phi(Z_i) \exp(-Z_i)$ approaches $\sqrt{\pi Z_i}$. In this case, eq. (3) reduces to eq. (1) for $s = 6$ (since $\Gamma(1/2) = \sqrt{\pi}$). As physically required, the Foerster-Dexter solution is obtained in the small r_i limit. Specifically, the correlation effects appear as a deviation from Gaussian behavior of the term-by-term ratio of the series expansion of $\Phi(Z_i)$ to $\exp(Z_i)$.

One possible distribution for an enhanced placement of acceptors near donors is shown in Fig. 1b. The solution for $N_D(t)$ is now:

$$\begin{aligned} N_D(t) = N_D(0) \exp [& -t/\tau_o - A\sqrt{\pi} \frac{C}{C_o} \left(\frac{t}{\tau_o}\right)^{1/2} \\ & - (B - A) \Phi(Z_i)/\exp(Z_i) \\ & - (1 - B) \Phi(Z_D)/\exp(Z_D)] \end{aligned} \quad (5)$$

From the results it can be shown that for a generalized distribution $u(r)$ in eq. (2), the donor decay is:

$$N_D(t) = N_D(0) \exp \left[-t/\tau_0 - \int \frac{du(r)}{dr} CV(r) \frac{\Phi(Z_r)}{\exp(Z_r)} dr \right] \quad (6)$$

In Fig. 2 we show the corresponding donor and acceptor decays obtained by both the excluded-volume and enhanced volume models.

CHEMISTRY OF CORRELATED PLACEMENT

The natural correlation of donors and acceptors may occur due to the chemistry of the codoped ions--both electronic structure and ionic size play a role. Such correlation would be especially useful in crystals in which deliberate macroscopic or microscopic non-uniform doping would help control thermal gradients or facilitate the usage of larger crystals.

Size mismatch between dopants and sites leads to local correlations. A dramatic example of this effect has been noted in Eu:Mn:RbMgF₃. Shinn, et al.⁶ find 95 percent of the Eu⁺² paired with Mn²⁺ ions.

Aliovalent doping also provides a promising approach to new laser materials. If one codopes both with ions which are effectively negative and ions which are effectively positive relative to the sites they enter, charge neutrality is maintained; moreover, the coulombic attraction will cause the ions to attract each other. For example, codoping Ni⁺² and Zr⁺⁴ into trivalent - cation sites leads to Zr-Ni pairs which tend to be correlated and can affect the type of lattice site occupied, i.e. Ni⁺² goes partially into tetrahedral sites in YAG only when codoped with zirconium.⁷

CONCLUSIONS

A model for analyzing Foerster-Dexter non-radiative transfer under the conditions of correlated donor acceptor placement has been analyzed. Chemical effects leading to such correlation has been discussed.

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2. D.L. Dexter, *J. Chem. Phys.* **21** (5), 836 (1953).
3. M. Inokuti and F. Hirayama, *J. Chem. Phys.* **43** (6), 1978 (1965).
4. L.A. Riseberg and M.J. Weber, "Relaxation Phenomena in Rare-Earth Luminescence" in *Progress in Optics XIV*, ed. E. Wolf, publ. by North-Holland, pp. 91-158 (1976).
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6. M.D. Shinn and W.A. Sibley, *Phys. Rev. B* **29** (7), 3834 (1984).
7. S.R. Rotman, "Defect Structure of Luminescent Garnets", Ph.D. thesis in the Department of Electrical Engineering, M.I.T., September 1985.

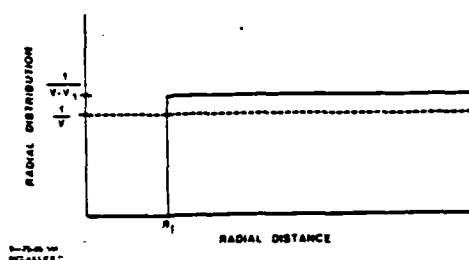


Fig. 1a) Excluded-volume, donor-acceptor radial-distance probability distribution

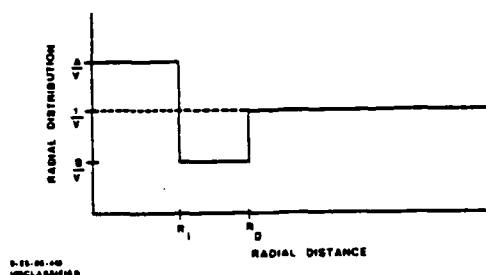


Fig. 1b) Enhanced-volume, donor-acceptor radial-distance probability distribution

Effect of Correlation on Donor Decay

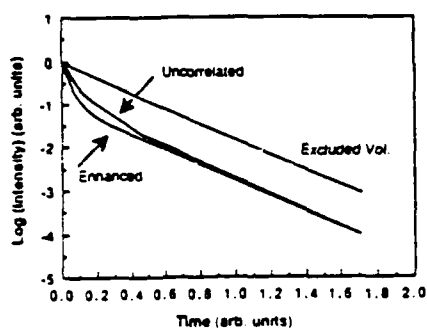


Fig. 2a) Time-resolved excited-donor concentration

Effect of Correlation on Excited Acceptor Concentration

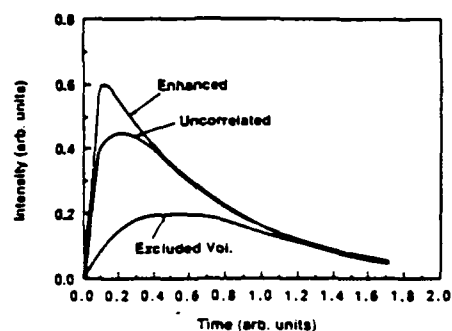


Fig. 2b) Time-resolved excited-acceptor concentration

E. PRESENTATION

The presentation associated with the preceding written work is reproduced here for convenience.

**EXTENDED FOERSTER-DEXTER MODEL FOR CORRELATED
DONOR-ACCEPTOR PLACEMENT IN SOLID STATE MATERIALS**

S.R. ROTMAN and F.X. HARTMANN

INSTITUTE FOR DEFENSE ANALYSES

October 23, 1986

(SPONSORED BY THE DIRECTED ENERGY OFFICE, DARPA)

**SRP:ad-1
10/14/86**

**OVERALL
GOAL:**

TO UNDERSTAND THE FACTORS WHICH AFFECT THE EFFICIENCY
OF PRESENT-DAY SOLID-STATE LASERS

**SPECIFIC
GOAL:**

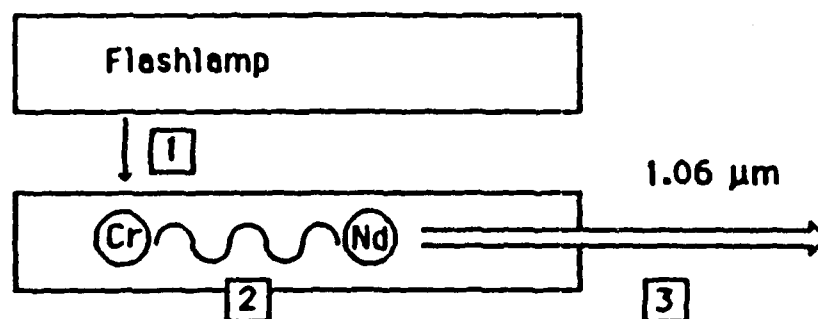
TO ANALYZE FOERSTER-DEXTER NON-RADIATIVE TRANSFER
UNDER CONDITIONS OF DONOR-ACCEPTOR COORDINATION

METHOD:

THEORETICAL CALCULATIONS OF SEVERAL DONOR-ACCEPTOR
PLACEMENT MODELS; EXPERIMENTAL EXAMPLES ANALYZED

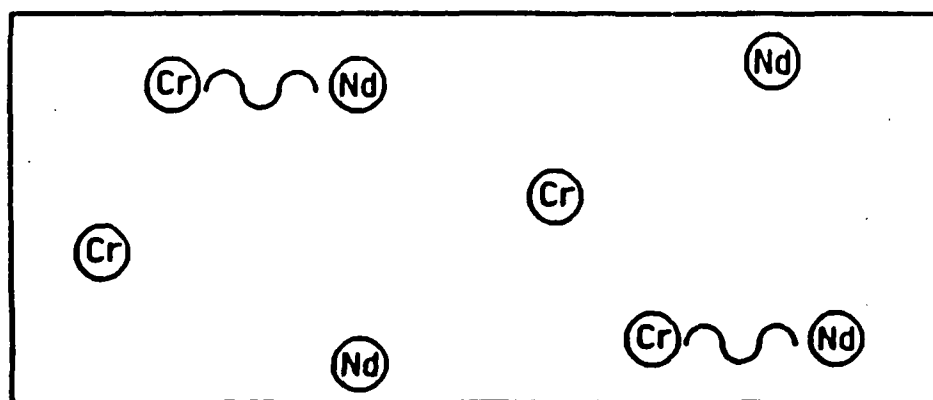
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ENERGY TRANSFER



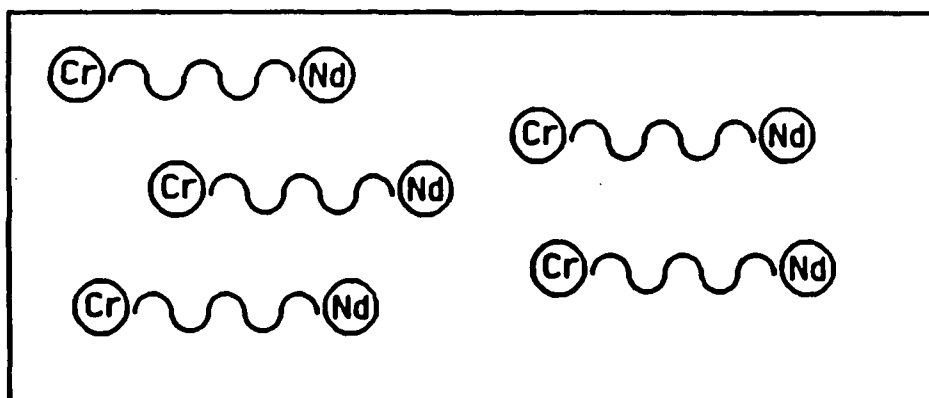
Energy Flow in Optically Pumped Laser Materials

UNCORRELATED DOPANT PLACEMENT



**Donor (Cr) - Acceptor (Nd) Random Placement
in a Laser Material**

CORRELATED DOPANT PLACEMENT



**Donor (Cr) - Acceptor (Nd) Correlated Placement
in a Laser Material**

PLAN OF RESEARCH

- 1. CONSIDERATION OF PHYSICAL EFFECTS TO PROMOTE CORRELATION**
- 2. CONSIDERATION OF SEVERAL THEORETICAL MODELS FOR CORRELATION**
- 3. THEORETICAL CALCULATION OF AN EXPRESSION FOR FOERSTER-DEXTER TRANSFER**
- 4. COMPARISON OF DATA TO EXPERIMENTAL RESULTS ON SELECTED CRYSTALS
(e.g., GARNETS)**

FOERSTER-DEXTER ENERGY TRANSFER VIA MULTIPOLE INTERACTION

- MULTIPOLE INTERACTION RESULTS IN THE TRANSFER OF ENERGY VIA A VIRTUAL PHOTON BETWEEN TWO IONS
- STRENGTH OF TRANSFER IS PROPORTIONAL TO $(1/R)^S$, WHERE $S = 6$ FOR DIPOLE-DIPOLE INTERACTION, $S = 8$ FOR DIPOLE-QUADRUPOLE INTERACTION, ETC.

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METHODS TO ACHIEVE CORRELATION

DOPANT SIZE vs. SITE SIZE

EXAMPLE: 95% CORRELATION BETWEEN Eu^{+2} AND Mn^{+2} IN $\text{Eu} : \text{Mn} : \text{RbMgF}_3$

[M.D. Shinn and W.A. Sibley, *Phys. Rev. B* 29 (7), 3834 (1984)]

<u>ION</u>	<u>SIZE</u>
Eu^{+2}	1.12 Å
Rb^{+1}	1.48 Å
Mn^{+2}	.80 Å
Mg^{+2}	.65 Å

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METHODS TO ACHIEVE CORRELATION

CHARGE MISMATCH BETWEEN DOPANT AND SITE

EXAMPLE: Ni^{+2} AND Zr^{+4} IN $\text{Ni} : \text{Zr} : \text{YAG}$

<u>ION</u>	<u>CHARGE</u>
Ni	+2
Zr	+4
Y	+3
Al	+3

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FOERSTER-DEXTER ENERGY TRANSFER EQUATION

$$N_D(t) = N_O \exp(-t/\tau_O) N_A \lim_{V \rightarrow \infty} \left[\int_V \exp[n(r,t)] w(r) dr \right]^{N_A}$$

$n(r,t)$ $\equiv$ rate of energy transfer

$w(r)$ $\equiv$ probability distribution for the distance of an acceptor
from a particular donor

FOERSTER-DEXTER ENERGY TRANSFER EQUATION-- STANDARD

$$\lim_{\substack{N_A \rightarrow \infty \\ V \rightarrow \infty}} \left[\int \exp[n(r,t)] w(r) dr \right]$$

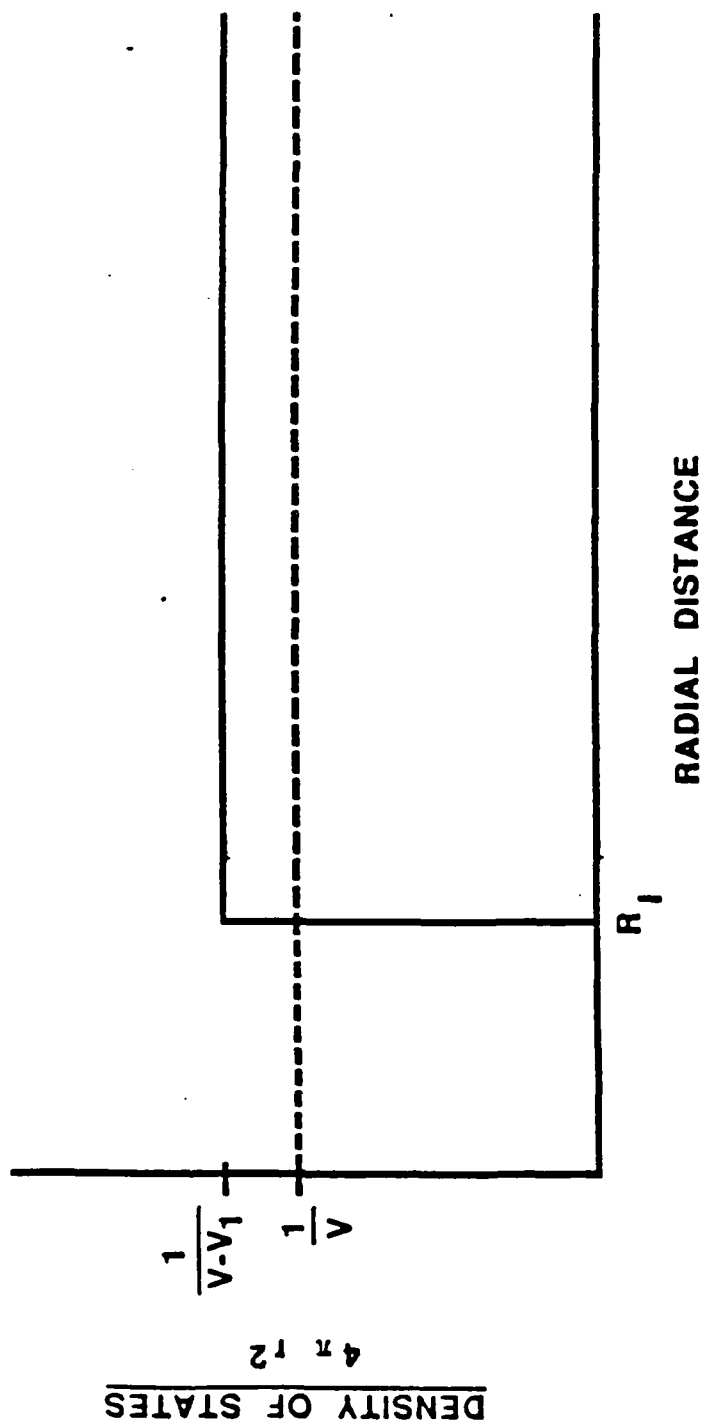
$$\lim_{\substack{N_A \rightarrow \infty \\ V \rightarrow \infty}} \left\{ \int_0^{R_V} \frac{4\pi R^2}{V} \exp \left[- \left(\frac{R_0}{R} \right)^S \left(\frac{1}{\tau_0} \right) \right] dR \right\}^N_A$$

$$\left(\frac{R_0}{R} \right)^S \left(\frac{1}{\tau_0} \right) \equiv \text{rate of transfer from a donor to a site a distance } R \text{ away}$$

$$\frac{4\pi R^2}{V} dR \quad \text{-- probability distribution of acceptor-donor distance for a single acceptor}$$

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EXCLUDED-VOLUME ACCEPTOR-DONOR DISTANCE DISTRIBUTION



9-25-86-5M

MODIFIED FOERSTER-DEXTER ENERGY TRANSFER EQUATION--EXCLUDED VOLUME

$$\lim_{\substack{N_A \rightarrow \infty \\ V \rightarrow \infty}} \left[\int \exp [n(r,t)] w(r) dr \right]$$

$$\lim_{\substack{N_A \rightarrow \infty \\ V \rightarrow \infty}} \left\{ \int_{R_1}^{R_v} \frac{4\pi R^2}{V-V_1} \exp \left[- \left(\frac{R_0}{R} \right)^S \left(\frac{t}{\tau_0} \right) \right] dR \right\}^{N_A}$$

$$\left(\frac{R_0}{R} \right)^S \left(\frac{1}{\tau_0} \right) \quad \text{-- rate of transfer}$$

$$\frac{4\pi R^2}{V-V_1} dR \quad \text{-- probability distribution for the acceptor-donor distance for a single acceptor in the excluded volume case}$$

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10/14/86

SOLUTION FOR DIPOLE-DIPOLE INTERACTION

STANDARD SOLUTION:

$$N_D(t) = N_o \exp \left[-t/\tau_o - \frac{c}{c_o} \sqrt{\pi} \left(\frac{t}{\tau_o} \right)^{1/2} \right]$$

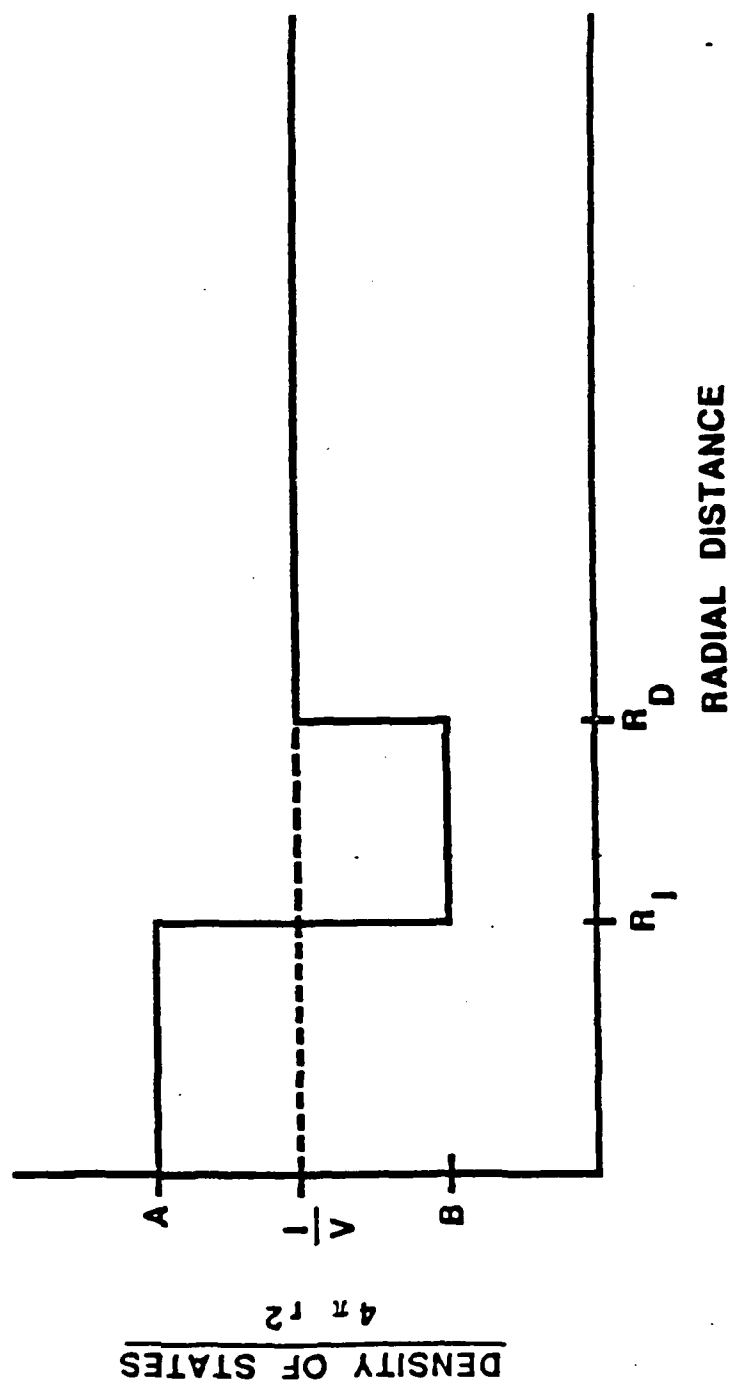
SOLUTION WITH EXCLUDED VOLUME:

$$N_D(t) = N_o \exp \left[-t/\tau_o - cV_1 (\Phi(Z_1) / \exp(Z_1)) \right]$$

$$Z \equiv \left(\frac{R_o}{R} \right)^6 \left(\frac{t}{\tau_o} \right)$$

$$\Phi(Z) = \sum_{i=0}^{\infty} \frac{(2z)^i}{(2i-1)!!}$$

ENHANCED-VOLUME DONOR-ACCEPTOR DISTANCE DISTRIBUTION



9-25-86-4M

SOLUTION FOR ENHANCED CORRELATION DIPOLE-DIPOLE INTERACTION

ENHANCED VOLUME:

$$N_D(t) = N_o \exp \left\{ -t / \tau_o - A \frac{c}{c_o} \sqrt{\pi} \left(\frac{t}{\tau_o} \right)^{1/2} \right.$$

$$- (B - A) c V_1 \left[\Phi(Z_1) / \exp(Z_1) \right]$$

$$\left. - (1 - B) c V_D \left[\Phi(Z_D) / \exp(Z_D) \right] \right\}$$

$$Z \equiv \left(\frac{R_o}{R} \right)^6 \left(\frac{t}{\tau_o} \right)$$

SRR:ad-11
10/14/86

GENERAL SOLUTION FOR FOERSTER-DEXTER

$$N_D(t) = N_0 \exp \left[-t/\tau_0 - \int \frac{dA(R)}{dR} c V_1(R) \Phi(Z_R) / \exp(Z_R) dR \right]$$

$$Z_R \equiv \left(\frac{R_0}{R} \right)^6 \left(\frac{t}{\tau_0} \right)$$

SRR:ad-12
10/14/86

Nd:Cr:GSGG DATA

**"IN THE GALLIUM GARNET CRYSTALS THE LUMINESCENCE
AT SHORT TIMES INCREASES MORE QUICKLY THAN THE
THEORY PREDICTS."**

V.G. Ostroumov, et al.,

***J. Opt. Soc. Am. B* 3 (1), 1986, pp. 81-93.**

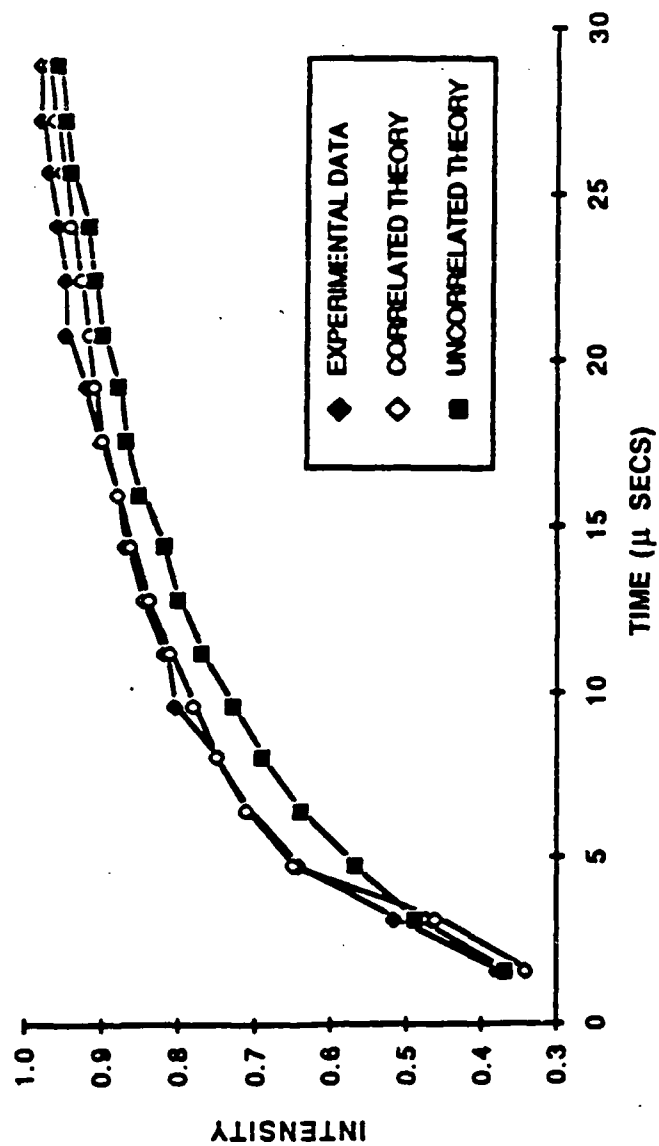
**SRR:ad-13
10/14/86**

ION AND SITE SIZES

<u>ION</u>	<u>SIZE (Å)</u>	<u>SITE</u>
Y ⁺³	1.01	Dod
Nd ⁺³	1.10	Dod
Cr ⁺³	.61	Oct
Sc ⁺³	.81	Oct
Ga ⁺³	.62	Oct
Gd ⁺³	1.05	Dod
Al ⁺³	.53	Oct

SRR:pae-1
10/17/86

COMPARISON OF THEORETICAL AND EXPERIMENTAL EXCITED ACCEPTOR POPULATIONS FOR Nd:Cr:GSGG



9-25-86-3M

CONCLUSIONS

- A SOLUTION TO THE FOERSTER-DEXTER EQUATION FOR CORRELATED DONOR-ACCEPTOR PLACEMENT HAS BEEN OBTAINED
- METHODS TO ACHIEVED CORRELATED DONOR-ACCEPTOR PLACEMENTS HAVE BEEN SUGGESTED
- RESULTS FROM Nd:Cr:GSGG ARE CONSISTENT WITH THIS MODEL

II. NON-RADIATIVE TRANSFER BETWEEN CORRELATED DONOR-ACCEPTOR PAIRS IN SOLID STATE LASER MATERIALS

A. INTRODUCTION

This chapter summarizes the work by Rotman and Hartmann on correlated donor-acceptor materials as applied to the experimental data for real garnets. The work was presented at the Conference on Lasers' 86, November 1986 in Orlando, Florida in the Session on Solid State Lasers. The complete paper was reviewed and the proceedings published in the book *Lasers '86* which is associated with the conference.

Note: The ordinate in Fig. 2 on page 35 is the "intensity" and not the "log (intensity)" as depicted there.

B. SUMMARY

One prominent approach to increasing the efficiency of solid-state laser materials is to codope with two types of ions: donors which absorb the pump energy and acceptors which emit at the lasing wavelength. In the standard approach to non-radiative transfer, both donors and acceptors are assumed to be uniformly distributed throughout the crystal. From analyses of recent experimental data, we suggest this is not necessarily the case in all luminescent materials--due to effects, such as size mismatch between the dopant ions and the lattice sites, donors and acceptors attract or repel each other, producing short range order. We develop an analytical model to study experimental transfer-rate data for several potential laser systems. In particular, the failure of codoped chromium-neodymium YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) to have significantly improved lasing efficiency relative to neodymium YAG can be partially due to such an effect. Methods which result in the correlated placement of donors and acceptors through coulombic attraction or size effects in hosts are discussed.

C. ABSTRACT

We develop an analytical model describing energy transfer between microscopically correlated donor-acceptor pairs in solid-state laser materials. We re-examine experimental data for several laser systems; host lattice properties promoting enhanced non-radiative transfer are discussed.

D. PAPER

NON-RADIATIVE TRANSFER BETWEEN CORRELATED DONOR-ACCEPTOR
PAIRS IN SOLID-STATE LASER MATERIALS

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Abstract

An analytical model describing energy transfer between microscopically correlated donor-acceptor pairs in solid-state laser materials is developed. Host lattice and dopant properties which promote enhanced non-radiative transfer rates are discussed. We compare fluorescent data for several garnet laser crystals to theoretical fits obtained from our model. Methods to achieve favorable correlation are discussed.

I. Introduction

A good phosphor or laser candidate ion, in a particular lattice, must be able to effectively absorb the pump light, as well as emit at the desired wavelengths. Recently, based on a theory originated by Foerster¹ and Dexter,² crystals have been grown in which the absorbing ion (called the donor) is different from the emitting ion (called the acceptor). The advantage of this approach is that a good donor can be paired with a good acceptor to improve the efficiency of the energy transfer process. The mechanism is not by radiative energy transfer in which the first ion absorbs a photon, reemits it, and then the second ion absorbs it. Rather, it is a non-radiative process, accomplished by the exchange of a virtual photon. One of the most popular candidates for this type of transfer is the chromium-neodymium combination in garnet crystals; the chromium absorbs in the visible region of the spectrum, transfers energy to the neodymium, and then the neodymium emits at 1.06 microns. In order for this process to be efficient, the transfer of energy from Cr^{+3} to Nd^{+3} must be fast compared to the natural decay rate of Nd^{+3} .

In this paper, we consider non-radiative energy transfer between donor-acceptor ion pairs which are positionally correlated in the crystal. A model is developed which can be used to calculate the excited donor and acceptor populations as a function of time for various radial distributions of the donor-acceptor distance. This new result is more general than the Foerster-Dexter equations. A comparison with data of fluorescent emission from the study of several garnet systems is made. Finally, methods to achieve position correlation in solid-state laser materials are discussed.

II. Generalized Non-Radiative Energy Transfer Theory

One assumption in the generally successful Foerster-Dexter theory, as developed by Inokuti et al.,³ is that the distribution of donors and acceptors in a crystal is uniform and independent of each others' location. In this specific case, the time-dependent excited donor concentration $N_D(t)$ is

$$N_D(t) = N_D(0) \exp \left[-\nu \tau_0 \cdot \Gamma(1 - 3/s) c/c_0 (\nu \tau_0)^{3/s} \right] \quad (1)$$

where c is the acceptor doping concentration, Γ is the gamma function, c_0 is the critical concentration of acceptors, and τ_0 is the natural decay rate of the donor. The critical concentration c_0 is that concentration at which the energy transfer rate and the natural donor decay rate are equal for the average donor-acceptor distance r_0 . For dipole-dipole interactions ($s=6$), the decay rates contain an exponential $t^{1/2}$ factor.

In a recent paper,⁴ we have extended the model to include the case in which the donors and acceptors are correlated with each other, i.e., the location of a donor in a particular site is influenced by the presence of nearby acceptors.

The radial distribution for an ideal excluded-volume correlated placement is shown in Fig. 1a. The solution for the excited-state donor concentration is:

$$N_D(t) = N_D(0) \exp \left\{ -\nu \tau_0 - CV \left[1 - \Phi(Z_i) / \exp(Z_i) \right] \right\} \quad (2)$$

$$Z_i = (r_0/r_i)^6 (\nu \tau_0) \quad (3)$$

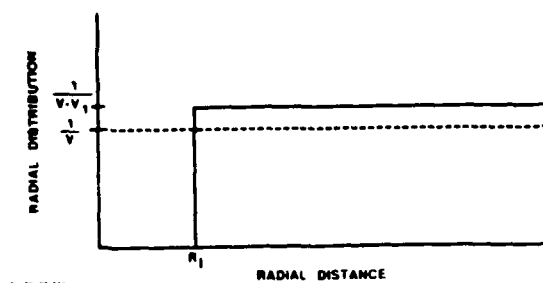


FIGURE 1a. Excluded-volume, donor-acceptor radial-distance probability distribution.

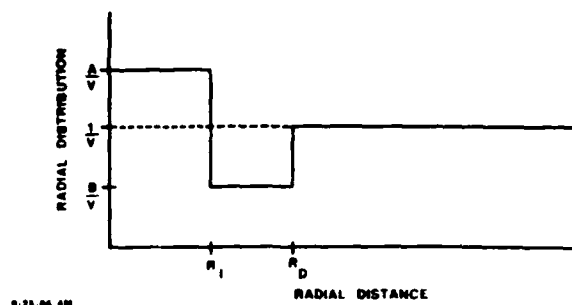


FIGURE 1b. Enhanced-volume, donor-acceptor radial-distance probability distribution.

Here $\Phi(1, 1-3/s; 2)$ is the degenerate hypergeometric function (written as $\Phi(Z_i)$ for the case $s=6$).

Figure 1b shows the distribution for the case of enhanced correlation; $2r_D$ is the average distance between donors while r_i , A and B are free parameters. The resulting excited-state donor concentration is

$$N_D(t) = N_D(0) \exp[-t/\tau_0 - A\sqrt{\pi} \frac{C}{C_0} \left(\frac{t}{\tau_0}\right)^{1/2} - (B-A)\Phi(Z_i)/\exp(Z_i) - (1-B)\Phi(Z_D)/\exp(Z_D)] \quad (4)$$

It can be shown that for a generalized radial distribution $u(r)$, the donor decay can be modelled by:

$$N_D(t) = N_D(0) \exp[-t/\tau_0 - \int \frac{du(r)}{dr} CV(r) \frac{\Phi(Z_r)}{\exp(Z_r)} dr] \quad (5)$$

III. Energy Transfer Rates in Garnets

The overriding factor affecting the chromium-neodymium transfer rates in garnets is the varying crystal field strength and the effect it has on the spacings of the chromium excited-state levels. A strong field splits the d levels of the chromium ion such that the 4T_2 level is considerably higher in energy than the 2E level. Since the ground-state is 4A_2 , the ${}^2E \rightarrow {}^4A_2$ transition is spin-prohibited, while the ${}^4T_2 \rightarrow {}^4A_2$ transition is spin-permitted.

The correlation between the spacing of the 2E and 4T_2 levels (ΔE), the crystal field strength (Dq/B) and the Nd-Cr transfer rate term (r_0^6/τ_0) is seen in Tables 1 and 2. Two explanations have been given for the differences in transfer rates seen in the tables. Zharikov⁷ argues that the ${}^4T_2 \rightarrow {}^4A_2$ transition is spin-permitted; the transfer strength for electronic transitions from this excited state will be much stronger than that for the electronic transitions involving the 2E state. For garnets with relatively high crystal fields, such as YAG, electronic transitions involving the lower 2E level predominate, and a slow rate of transfer ensues. For garnets with lower crystal fields, excitations in the upper 4T_2 level increase (assuming a Boltzmann distribution) because the states are now closer in energy. Consequently, there is an increase in the magnitude of the rate of transfer of energy between the chromium and the neodymium ions.

See next page for Tables 1 and 2

	Neodymium Natural Decay (sec)	Chromium Natural Decay (sec)	Nd-Cr Transfer Rate* (10^{-40} cm ⁶ /sec)	Ref.
YAG	250×10^{-6}	1.53×10^{-3}	9	5
GGG (300°K)	250×10^{-6}	160×10^{-6}	110	6
GGG ($<100^\circ$ K)	250×10^{-6}	1.33×10^{-3}	20	7
GSGG	278×10^{-6}	120×10^{-6}	220	7,8

*(r_0^6/τ_0) from Eq. 3.

TABLE 1. Radiative and non-radiative transfer rates for several garnets

Crystal	GSGG	GGG	YAG
ΔE (cm ⁻¹)	50	380	1000
Dq/B	2.45	2.55	2.6

TABLE 2. Values of ΔE and Dq/B for several garnets

A second effect of the crystal field has been investigated by Struve et al.⁹ They have shown that spin-orbit coupling can mix the 4T_2 and 2E levels. This implies that the nominal 2E level would contain portions of the 4T_2 wavefunction. The dipole moment for the $^2E \rightarrow ^4A_2$ transition would then be influenced by the degree of mixing of the 4T_2 into the 2E state.

It should be noted that this explanation is different from that proposed by Zharikov. Zharikov suggests that the rate of energy transfer from the chromium to the neodymium ions from a particular level is fixed; differences in transfer rates between garnets are due to changes in the relative population of the excited levels. Struve's explanation proposes that the actual strength of the transfer rate from the levels can change because of the mixing of the states.

IV. Correlation Effects in Crystals

Although differences in the Nd-Cr transfer rates in garnets can be mostly explained by changes caused by the different crystal field splittings, several experimental discrepancies from theory have been noted in these materials. Zharikov et al.⁶ have analyzed the neodymium-chromium energy transfer rates in GSGG. They note a small discrepancy between the experimental observation and the theoretical calculations of the Cr emission (Fig. 2); the transfer rate observed in the initial rising region is faster than theory predicts. They suggested that a fit to the data can be made if one assumes that any chromium with a neodymium as a nearest neighbor or next-nearest neighbor will instantaneously transfer its energy through the exchange interaction due to the overlap of wavefunctions on the chromium and neodymium.⁶

Since there is no evidence of a role for the exchange interaction in YAG, and to improve upon the assumption of an instantaneous exchange of energy between next-nearest neighbors, we suggest an alternative explanation. Assuming that the strength of the interaction is constant, but that the chromium ions are positionally correlated with respect to the neodymium ions, we can analyze the results. Figure 2 shows the fit to the excited donor ion concentration using the new model described in Section II, Fig. 1b. The parameters used for this fit are shown in Table 3.

Parameters	Correlated Values	Uncorrelated Values
c/c_0	1.23	1.23
r_0/r_1	1.25	-
A/V	1.26	1
B/V	.88	1

TABLE 3. Parameters for GSGG simulations based on the distribution in Fig. 1b

It should be emphasized that there is a physically reasonable understanding as to why neodymium and chromium would be correlated in GSGG. The replacement of the native constituents of a garnet by neodymium or chromium ions may affect the neighboring ionic sites in the crystal. The data in Table 4 show that the neodymium ion is considerably larger than

the other species it replaces in the dodecahedral sites in garnets (typically yttrium or gadolinium ions). On the other hand, no such blanket statement can be made for the chromium ion; chromium ions are larger than aluminum ions, roughly the same size as gallium ions, and considerably smaller than scandium ions. Since it is known that chromium ions enter the octahedral sites in these garnets, the strain in a GSGG crystal will be relieved by their locating near each other.

<u>Ion</u>	<u>Size (Å)</u>	<u>Site</u>	<u>Ref.</u>
Y ³⁺	1.01	Dod.	13
Nd ³⁺	1.12	Dod.	13
Cr ³⁺	.61	Oct.	14
Sc ³⁺	.81	Oct.	15
Ga ³⁺	.62	Oct.	15
Gd ³⁺	1.05	Dod.	13
Al ³⁺	.53	Oct.	13

TABLE 4. Sizes of trivalent ions in garnets (Oct: Octahedral site; Dod: Dodecahedral site)

The opposite effect in YAG may help explain a second experimental discrepancy. The transfer rate from Cr to Nd in YAG at 300° K is approximately half of that in GGG at temperatures lower than 100° K, even though the natural decay rate of the chromium and neodymium in both cases is roughly the same. Both YAG (due to the crystal field splitting) and GGG (due to the low temperatures) are preferentially in the ²E electronic state. The emission spectrum of chromium and the absorption spectrum of neodymium are at approximately the same wavelengths in both crystals. The higher temperatures would have tended to make the YAG a better medium for energy transfer than GGG due to the presence of more phonons to assist the indirect energy transfer.

The inefficiency of YAG may be due to a decrease in nearest-neighbor proximity for chromium and neodymium. Our calculations show that a model such as that given in Section II, Fig. 1a, can explain this data. A fit to the YAG data for a transfer rate equal to that of GGG (twice as strong as previously assumed) fits the data well if one used a model with an excluded volume for neodymium ion around the chromium ion (Fig. 3). The values used in these fits are shown in Table 5.

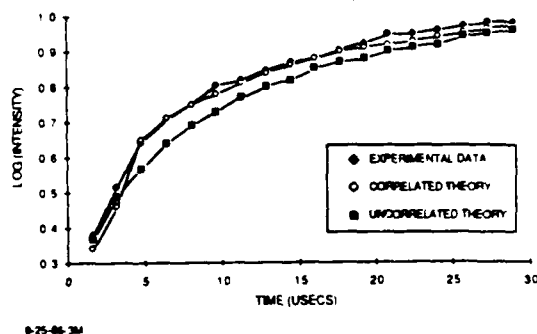


FIGURE 2. Comparison of uncorrelated and correlated theory with experiment for Nd:Cr:GSGG.

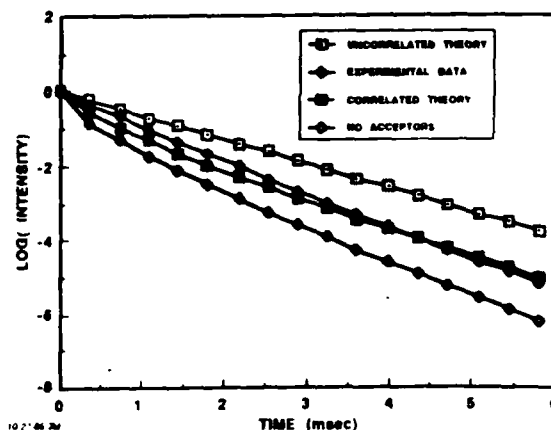


FIGURE 3. Comparison of uncorrelated and correlated theory with experiment for Nd:Cr:YAG.

<u>Parameters</u>	<u>Excluded-Volume Correlated Values</u>	<u>Uncorrelated Values</u>
c/c ₀	.6	.6
r ₀ /r ₁	.88	-

TABLE 5. Parameters for YAG simulations based on the model in Fig. 1a

Once again, the data in Table 4 show that an excluded volume about the chromium ion is appropriate from size considerations. Neodymium is considerably larger than yttrium and the chromium ion is larger than the aluminum ion. To relieve the strain in the crystal, they would tend to locate apart from one another.

In summary, the measured rates of energy transfer in neodymium-chromium-doped crystals can be affected by non-uniform distributions of acceptors and donors. We have explained several anomalous energy transfer data in YAG and GSGG using this approach.

V. Physical Factors Affecting Correlated Placement in Crystals

In the previous sections, we have developed the model of correlated placement of donors and acceptors in various crystals. We have examined the possibility that such correlated pairs may exist in the neodymium-chromium-doped garnets. We must consider whether it is possible to plan crystals with the specific intention of correlating the donor and acceptor ions. This would be especially useful in crystals in which deliberately doping in a macroscopically non-uniform manner would help control thermal gradients; large crystals which must be lightly doped to allow the radiation to penetrate throughout the bulk may also benefit.

The first method to achieve correlation would be by utilizing the mismatch between dopants and sites. A favorable mismatch occurs in GSGG where the Nd^{+3} is bigger than the yttrium site, while the chromium is smaller than the scandium site. Alternatively, in YAG both the Nd^{+3} and Cr^{+3} are bigger than the Y^{+3} and Al^{+3} sites, respectively, and an unfavorable mismatch results. An even more dramatic example of this effect has been noted in Eu:Mn:RbMgF_3 . Shinn et al.¹⁰ find that 95 percent of the Eu^{+2} in this crystal are paired with Mn^{+2} ions; they note that the Eu^{+2} ion (1.12Å) is smaller than the Rb^{+1} ion (1.48Å) it replaces, while the Mn^{+2} ion (0.80Å) is larger than the Mg^{+2} ion (0.65Å).

While Eu:Mn:RbMgF_3 is a dramatic example of a crystal with correlated donor-acceptor placement, the most promising application of such approaches may be in the use of aliovalent crystal doping to provide new laser materials. In most laser materials, one dopes a crystal with an ion in the same valence state (isovalent) as the ion for which it substitutes. In this way, charge neutrality is maintained in the crystal. However, it is known that an ion with a different valence (aliovalent) from the ion for which it substitutes can enter the crystals. In several recent papers, Rotman et al.¹¹ and Schwartz et al.¹² show this to be true in YAG and GSGG, respectively. This can lead to defects in the lattice structure, e.g., positively charged oxygen vacancies can arise to compensate for Ca^{+2} in Y^{+3} sites in YAG. However, if one codopes with an ion which is effectively negative and an ion which is effectively positive, then charge neutrality can be maintained and defects are not formed. For example, codoping into +3 cation sites with both Zr^{+4} and Ni^{+2} allows these ions to enter the crystal lattice without producing defects. Such Zr-Ni pairs tend to be correlated and may even affect the choice of lattice sites of each of the constituents. In fact, Ni^{+2} goes partially into tetrahedral sites in YAG only when codoped with zirconium.

We propose that the possibility of codoping with aliovalent ions opens several new avenues of research for laser materials. If one could find a combination of acceptors and donors which were aliovalent with the ions for which they substitute and which compensated for each other, one would expect these ions to correlate their position in the crystal simply from the effects of coulombic attraction. As shown, ions which lie close together have a much stronger interaction than those which are further apart. Such donor-acceptor combinations provide convenient methods to couple the absorption and emission processes of different ions to provide a whole new range of possibilities for laser materials.

VI. Conclusions

The model for non-radiative transfer has been expanded to include physically significant non-uniform distributions of donors and acceptors. Comparison with time-dependent fluorescent emission data from several neodymium-chromium-codoped garnet lasers indicates that correlation may occur in such materials. Factors leading to enhanced correlations are size and electronic structure effects.

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E. PRESENTATION

The presentation associated with the preceding written work is reproduced here for convenience.

**NON-RADIATIVE TRANSFER BETWEEN CORRELATED
DONOR-ACCEPTOR PAIRS IN SOLID STATE
LASER MATERIALS**

by S.R. Rotman and F.X. Hartmann

INSTITUTE FOR DEFENSE ANALYSES

11/6/86

(SPONSORED BY THE DIRECTED ENERGY OFFICE, DARPA)

**OVERALL
GOAL:**

TO UNDERSTAND THE FACTORS WHICH AFFECT THE EFFICIENCY OF
PRESENT-DAY SOLID-STATE LASERS

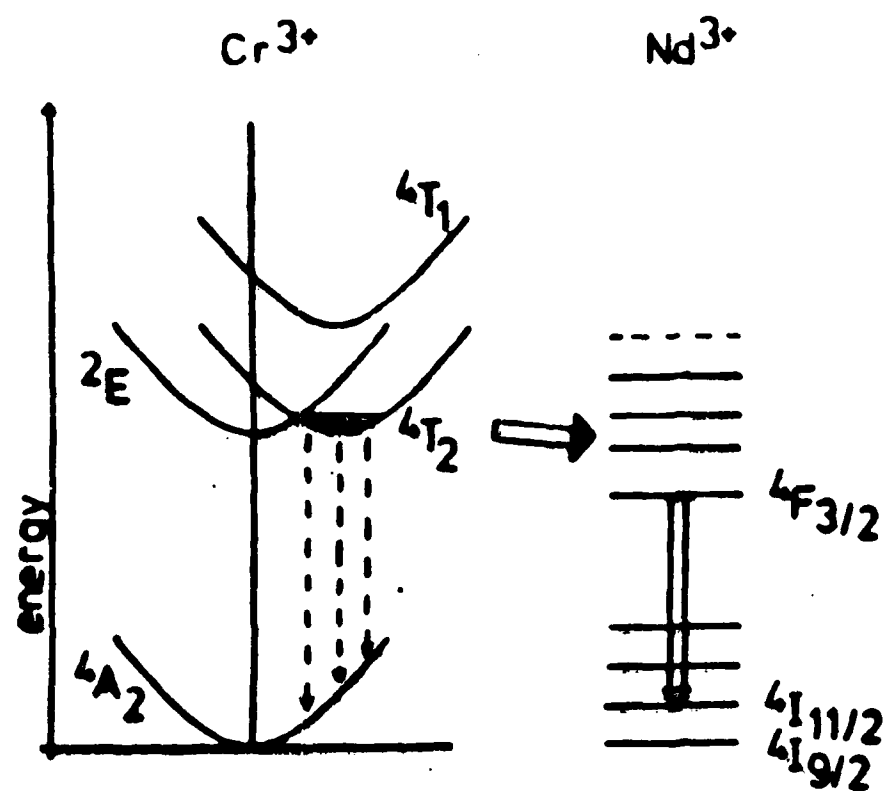
**SPECIFIC
GOAL:**

TO ANALYZE FOERSTER-DEXTER NON RADIATIVE TRANSFER UNDER
CONDITIONS OF DONOR-ACCEPTOR COORDINATION

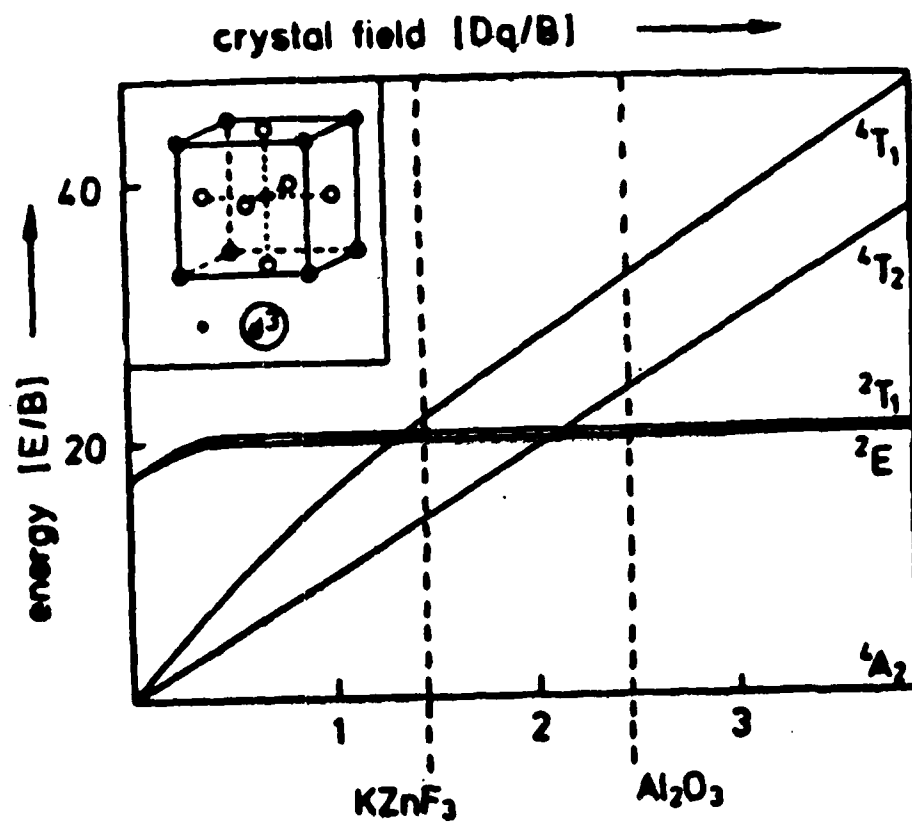
METHOD:

THEORETICAL CALCULATIONS OF SEVERAL DONOR-ACCEPTOR
PLACEMENT MODELS; EXPERIMENTAL EXAMPLES ANALYZED

Energy Levels Of Cr^{3+} And Nd^{3+} In Garnets



Tanabe-Sugano Diagram For Octahedral Cr³⁺



COMPARISON OF YAG AND GGG

Material	Temp. (°K)	Chromium Time Constant	Inter-Ion Transfer Rate	Level Populated
GGG	<100°K	1.44m sec ⁻¹	$2.2 \times 10^{-39} \frac{\text{cm}^6}{\text{sec}}$	Only 2E
YAG	300°K	1.53m sec ⁻¹	$9 \times 10^{-40} \frac{\text{cm}^6}{\text{sec}}$	Only 2E

COMPARISON OF YAG AND GGG

**THE OVERLAP OF THE 2E EMISSION SPECTRA OF Cr⁺³ AND
THE ABSORPTION SPECTRA OF Nd⁺³ ARE SIMILAR FOR
BOTH YAG AND GGG**

ENHANCED TRANSFER IN GGG

QUESTION

- WHY DOES ENHANCED TRANSFER OCCUR IN GGG? (SIZE FACTORS ALONE DO NOT INDICATE THAT CORRELATION SHOULD OCCUR).

ION AND SITE SIZES

<u>ION</u>	<u>SIZE (Å)</u>	<u>SITE</u>
Y+3	1.01	Dod
Nd+3	1.10	Dod
Cr+3	.61	Oct
Sc+3	.81	Oct
Ga+3	.62	Oct
Gd+3	1.05	Dod
Al+3	.53	Oct

ENHANCED TRANSFER IN GSGG

ZHARIKOV'S THEORY

- INSTANTANEOUS TRANSFER OCCURS BETWEEN CHROMIUM AND NEODYMIUM FOR NEAREST NEIGHBORS AND NEXT NEAREST NEIGHBORS DUE TO EXCHANGE INTERACTION

QUESTION

- WHY DOES IT ONLY OCCUR IN GALLIUM GARNETS AND NOT ALUMINATE GARNETS?

DIFFERENCES IN GARNET TRANSFER RATES

- IMPROVED TRANSFER RATE CAUSED BY LOWER OCTAHEDRAL CRYSTAL-FIELD SPLITTING AT CHROMIUM ION SITE

- a) Higher population of $4T_2$ level relative to $2E$ level of
excited chromium ions

(E.V. Zharikov et al. Sov. J. Quant. Elec. 14 (3), 322 (1984)).

DIFFERENCES IN GARNET TRANSFER RATES

- IMPROVED TRANSFER RATE IS CAUSED BY LOWER
OCTAHEDRAL CRYSTAL-FIELD SPLITTING AT
CHROMIUM ION SITE

b) Increased spin-orbit coupling of $4T_2$ state into $2E$ state of the
chromium ion

[B. Struve et al., *Appl. Phys. B* 36, 195 (1985)]

ENHANCED TRANSFER IN GSGG

THEORY

- ENHANCED TRANSFER IS DUE TO CORRELATED DONOR-ACCEPTOR PAIRS IN GSGG

DIFFERENCES IN GARNET TRANSFER RATES

- CORRELATED PLACEMENT OF NEODYMIUM AND CHROMIUM IONS WOULD EFFECT ENERGY TRANSFER RATES**

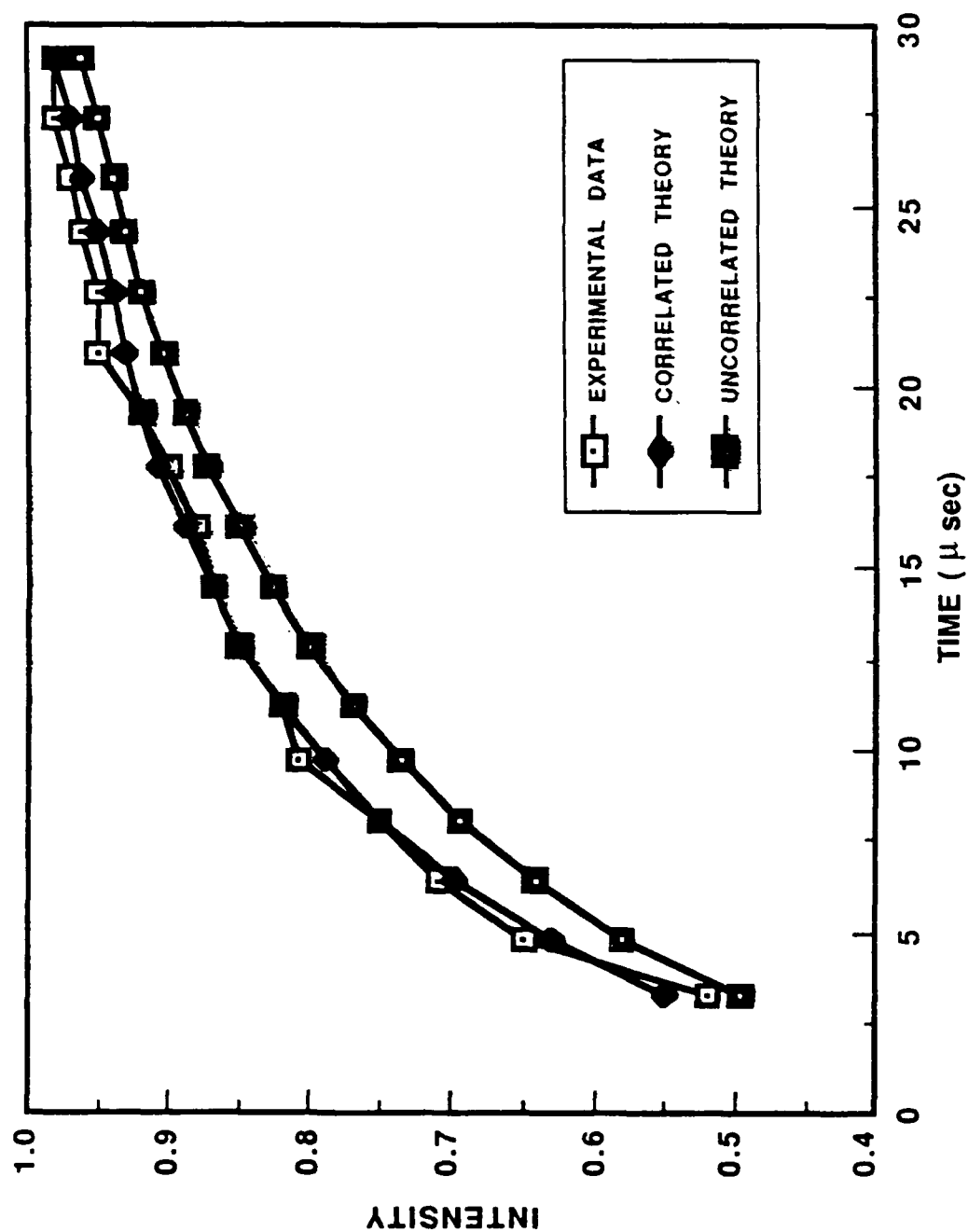
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V.G. Ostroumov, et al,

J. Opt. Soc. Am. B 3 (1), 1986, pp. 81-93

COMPARISON OF THEORETICAL AND EXPERIMENTAL EXCITED ACCEPTOR POPULATIONS FOR Nd:Cr:GSGG



INHIBITED TRANSFER IN YAG

THEORY

- INHIBITED TRANSFER IS DUE TO ANTI-CORRELATED
DONOR-ACCEPTOR PAIRS IN YAG

CONCLUSIONS

- A MODEL FOR CORRELATED PLACEMENT OF DONORS AND ACCEPTORS IN SOLID STATE LASER MATERIALS HAS BEEN ANALYTICALLY CALCULATED
- THE APPLICATION OF THIS THEORY TO Nd:Cr:YAG AND Nd:Cr:GSGG HAS BEEN CONSIDERED

III. ENERGY TRANSFER BETWEEN DEFECTS AND RARE-EARTH IONS IN GARNET CRYSTALS

A. INTRODUCTION

The work on non-radiative transfer between donors and acceptors was extended to energy transfer between defects and rare-earth ions in garnet crystals. This paper makes the proposal that energy can also be transferred directly between dopants and defects as applied to defects in YAG. The work was presented at the XV International Quantum Electronics Conference (IQEC '87) (26 April - 1 May 1987) in Baltimore, Maryland. The paper was jointly written with H.L. Tuller and C. Warde from the Massachusetts Institute of Technology. Since the presentation was made at a poster session, we produce the paper summary here, from session THGG (No. 16).

B. PAPER SUMMARY

TTGG16 Energy Transfer Between Defects and Rare-Earth Ions in Garnet Crystals

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In crystalline solid-state laser materials, defects in the host lattice can act as energy sinks, draining energy from the dopant ions which would otherwise have contributed to the lasing transition. Conversely, in some fluorescent materials, the transfer of energy from defects to dopants can cause an undesirable persistence of luminescence to occur. Understanding and controlling these defects can be critical to the development of a laser or phosphor source.

Defects in rare-earth-doped yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$ or YAG) are known to affect the properties of the rare-earth luminescence driven by electron-beam pumping¹ and, to a lesser extent, flashlamp pumping.² The current hypothesis in the literature¹ concerning the cathodoluminescent spectrum of rare-earth-doped YAG assumes that energy is transferred between the defects and dopant ions through the initial thermal production of excited carriers, initially located at the defect, into the conduction band; their subsequent deexcitation leads to excited states of the rare-earth ion.

We propose that energy can also be transferred directly between the dopants and defects through a Foerster-Dexter nonradiative transfer mechanism. The degree of overlap of the emission spectrum and the dopant's absorption spectrum determines the magnitude of the nonradiative energy transfer. In particular, the temperature dependence of the cathodoluminescence of cerium-doped, terbium-doped, and europium-doped YAG and the temporal decay of excited states of these materials can be understood by this latter model.

The model one assumes for energy transfer is important for understanding the nature of the defects in YAG. We show that electrons localized at oxygen vacancies in the crystals are responsible for the defect luminescence in YAG and the observed energy transfer properties. Implications for garnet laser development are discussed.

¹D.J. Robbins, B. Cockayne, J.L. Glasper, and B. Lent, *J. Electrochem. Soc.* **126**, 1213 (1979).

²S.R. Rotman and C. Warde, *J. Appl. Phys.* **58**, 522 (1985).

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