

Luminescence Decay by Energy Migration and Transfer: Observation of Diffusion-Limited Relaxation*

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The time dependence of the luminescence decay following pulsed excitation is examined for a system in which excited paramagnetic ions decay by a combination of intrinsic relaxation processes, direct energy transfer to acceptor ions, and energy migration. Three limiting cases are considered: direct energy transfer in the absence of diffusion, rapid diffusion, and diffusion-limited relaxation. Investigations of the transient europium fluorescence from a chromium-doped europium phosphate glass, where excited Eu^{3+} ions form the donor system and Cr^{3+} impurities act as energy acceptors, are reported which illustrate these limiting cases. By varying the temperature and Cr^{3+} concentration, transient fluorescence behavior characteristic of diffusion-limited relaxation is studied. The data are analyzed to determine the probability for direct $\text{Eu}^{3+} \rightarrow \text{Cr}^{3+}$ energy transfer, the critical transfer distance for energy exchange, and the diffusion constant D for energy migration through the europium system. D varies with temperature as levels having greater probabilities for resonant Eu^{3+} - Eu^{3+} energy transfer become thermally populated. In the diffusion-limited relaxation case the decay rate is predicted to be proportional to $D^{3/4}$; this $3/4$ power law is verified.

I. INTRODUCTION

Transfer of electronic excitation between paramagnetic ions in solids has been studied extensively. In addition to intrinsic decay processes, excited donor ions have been found to relax (i) by direct interaction and energy transfer to acceptor ions or (ii), if the acceptor concentration is small and the intrinsic decay is slow, by migration of the excitation among donor ions until it comes into the vicinity of an energy acceptor where direct interaction and transfer occur. The first is a one-step process involving resonant energy transfer between donors and acceptors. The theory for this process was developed initially by Förster¹ and by Dexter² for multipolar coupling and later extended for exchange coupling by Inokuti and Hirayama.³ Relaxation of electronic excitation by migration is a multistep process involving resonant energy transfer from one ion to another ion of the same species in a random-walk manner and finally to an imperfection which acts as a quenching center. This process was originally proposed by Botden⁴ to account for concentration quenching of luminescence; the theory for such processes was developed by Dexter and Schulman.⁵ Many features of the above theories of energy transfer have been substantiated by numerous experimental investigations in various organic and inorganic solid matrices. A representative but necessarily limited sampling of this rich literature is provided in Refs. 6-12.

In this paper luminescence decay by a combination of one-step direct relaxation to acceptors and multistep excitation migration is considered. Since migration effectively extends the range of energy transfer, this physical situation is one of interest

for the development of sensitized luminescent and laser materials. The effects of diffusion on energy transfer have been treated by Yokota and Tanimoto.¹³ There has been, however, a paucity of experimental results which clearly illustrate these effects. The present study of the transient europium fluorescence from a chromium-doped europium phosphate glass, where excited Eu^{3+} ions form the donor system and Cr^{3+} impurities act as energy acceptors, has provided a unique opportunity to examine this case.

Experimental studies of energy transfer frequently involve an examination of the donor luminescence intensity and lifetime as a function of donor and acceptor concentrations. Observation of the time evolution of the donor luminescence decay following flash excitation provides additional distinguishing features helpful in identifying the dominant relaxation mechanism.⁶⁻¹³ The forms of luminescence decay curves expected for several different interaction models of energy transfer have been discussed.^{3,7,13} The analysis of the data in many instances is nontrivial and care is required to obtain meaningful quantitative results.

In solids where both direct energy transfer and energy migration to acceptors are active, the form of the luminescence decay is more complex. The characteristics of the donor system relaxation can, however, be discussed conveniently in terms of three limiting cases: (A) direct relaxation—no diffusion, (B) fast diffusion, and (C) diffusion-limited relaxation.¹⁴ The theory of energy migration and transfer and the form of the luminescence decay for these three limiting cases are reviewed below. Experiments on the transient decay of the Eu^{3+} fluorescence in a Cr^{3+} -doped $\text{Eu}(\text{PO}_3)_3$ glass are then reported under a variety of conditions which

illustrate the limiting cases above. The data are analyzed to determine the probability for direct $\text{Eu}^{3+} - \text{Cr}^{3+}$ energy transfer, the critical transfer distance for energy exchange, and the coefficient for diffusion within the Eu^{3+} system and its dependence on temperature.

II. THEORY

Consider a system of energy donors and energy acceptors; the latter are assumed to be distributed randomly throughout the material and to be present in low concentrations such that the distance between acceptors is very much greater than the distance between donors. A small number of donor ions are initially excited by a short pulse of radiation at time $t = 0$. The distribution of excited donors is assumed to be uniform and their number small compared to the total number of donor ions. This condition of weak initial excitation is such that the probability of a neighboring donor being unexcited is essentially unity.¹⁵ Let the donor excitation density $\phi(\vec{r}, t)$ denote the probability of finding a donor at position \vec{r} in an excited state at time t . In the absence of acceptors and energy diffusion within the donor system, $\phi(t)$ decays simply as $\exp(-t/\tau_0)$, where τ_0^{-1} is the intrinsic donor decay rate due to radiation and internal quenching.

A. Direct Relaxation—No Diffusion

When acceptor ions are present, donor ions in the vicinity of acceptors may interact with them via exchange or multipolar forces and transfer energy directly. The transfer rates for different donor-acceptor pairings vary greatly since the strength of the donor-acceptor coupling generally decreases rapidly with separation. If the probability for direct energy transfer to an acceptor at a distance R_n from a donor is $w(R_n)$, then

$$\phi(\vec{r}, t) = e^{-t/\tau_0} \sum_{n=1}^{N_a V} e^{-w(R_n)t}, \quad (1)$$

where $N_a V$ is the total number of acceptors in the sample volume V . A physically observable macroscopic signal will be proportional to a statistical average of ϕ over the ensemble of ions given by

$$\Phi(t) = \int \phi(\vec{r}, t) d^3r. \quad (2)$$

Knowing the form of the donor-acceptor coupling, the detailed distribution of all ions would in principle be required to solve Eq. (2). By assuming a random distribution and orientation of acceptors, the angular dependence of the transfer rate can usually be averaged out, thereby leaving only a dependence of separation.⁷

For multipolar interactions, the transfer rate constant is proportional to an inverse power of the donor-acceptor separation, that is, $w(R) = CR^{-s}$. This covers the familiar cases of dipole-dipole

($s = 6$), dipole-quadrupole ($s = 8$), and quadrupole-quadrupole ($s = 10$) coupling. The general solution for Φ for multipolar coupling is

$$\Phi(t) = \Phi(0) \exp\left[-t/\tau_0 - \frac{4}{3}\pi\Gamma(1 - 3/s)N_a R_0^3 (t/\tau_0)^{3/s}\right], \quad (3)$$

where $\Phi(0)$ is the initial excitation and R_0 is the critical transfer distance $(C\tau_0)^{1/s}$ defined as that separation at which the probability for energy transfer between a donor-acceptor pair is equal to the intrinsic decay probability τ_0^{-1} . Solutions for the decay function when energy transfer occurs by exchange coupling have also been given by Inokuti and Hirayama.³

The donor luminescence intensity is proportional to $\Phi(t)$. When donor-acceptor energy transfer is active, the luminescence decay does not exhibit a simple exponential dependence on time. For multipolar interactions, the decay at earlier times ($t \ll \tau_0$) is proportional, from Eq. (3), to $1 - \alpha t^{3/s}$, where $\alpha = \frac{4}{3}\pi\Gamma(1 - 3/s)N_a R_0^3 \tau_0^{-3/s}$. With time, the number of donors having unexcited acceptors within the critical transfer radius diminishes. The luminescence then originates increasingly from excited donors which are farther removed from acceptors and for which the intrinsic decay rate is more competitive with energy transfer. The over-all decay is therefore characterized by an initial nonexponential portion followed by an exponential decay at a rate governed by the intrinsic decay rate. Examples of such luminescence time dependences are well documented in the literature.^{6,12}

B. Fast Diffusion

If resonant energy transfer between donor ions is possible, excitation may migrate through the donor system until it comes into the vicinity of an acceptor where direct relaxation by donor-acceptor energy transfer can occur. When the average donor separation is small and the probability for resonant energy exchange between donors is large, energy diffusion can be very rapid, leading to a spatial equilibrium within the donor system. The rate-limiting step for the donor relaxation may then be the donor-acceptor transfer rate or the acceptor relaxation rate. Because of the fast diffusion, variations in the transfer times for different donor-acceptor pairs are effectively averaged out and the donor system exhibits a simple exponential decay. Examples of this behavior for rare-earth ions in crystals have been studied by Gandrud and Moos.⁹

C. Diffusion-Limited Relaxation

When the rate of energy diffusion within the donor system to acceptors is slow but still comparable to the intrinsic decay rate, the decay of the total donor system is composed of competing processes. Those

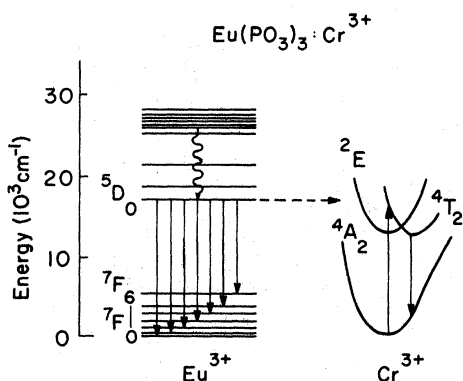


FIG. 1. Lower energy levels of Eu^{3+} and schematic configuration coordinate diagram for Cr^{3+} in $\text{Eu}(\text{PO}_3)_3$ glass. Energy transfer from Eu^{3+} to Cr^{3+} occurs via the 5D_0 state of Eu^{3+} .

excited donors near acceptors relax predominantly by direct ion-pair energy transfer; those more distant donors, however, must first diffuse into the vicinity of an acceptor before relaxation occurs. The time evolution of the donor excitation density $\Phi(t)$ in this case is found by solving a diffusion equation of the form

$$\frac{\partial \phi(\vec{r}, t)}{\partial t} = D \nabla^2 \phi(\vec{r}, t) - \sum v(\vec{r} - \vec{r}_n) \phi(\vec{r}, t) - \frac{1}{\tau_0} \phi(\vec{r}, t). \quad (4)$$

In Eq. (4), D is the diffusion constant (which in this simple treatment is taken to be isotropic)¹⁶ and $v(\vec{r} - \vec{r}_n)$ is the probability for energy transfer from an excited donor to the n th acceptor at position \vec{r}_n . Analytical and numerical solutions to this type of equation have been given in connection with the problem of relaxation of nuclear magnetization by spin diffusion to fast-relaxing paramagnetic impurities.¹⁷

When the acceptor concentration is low, only a small fraction of the total number of excited donors are within the critical transfer distance of an acceptor. In this limit, where the average distance between acceptors $N_a^{-1/3} \gg R_0$, the donor decay will be governed principally by intrinsic relaxation and by diffusion-limited relaxation to acceptors. The decay at long times after the excitation pulse is described by an exponential function of time with a characteristic lifetime

$$1/\tau = 1/\tau_0 + 1/\tau_D, \quad (5)$$

where $1/\tau_D$ is the decay rate due to diffusion. Solutions for τ_D have been obtained for the case where the donor-acceptor interaction $v(\vec{r} - \vec{r}_n)$ arises from dipole-dipole coupling and is of the form $C|\vec{r} - \vec{r}_n|^{-6}$. The resulting rate is given by¹⁸

$$1/\tau_D = 4\pi N_a D \rho, \quad (6)$$

where ρ is a length defined by

$$\rho = 0.68 (C/D)^{1/4}. \quad (7)$$

This solution applies when $d \ll \rho \ll a$, where d is the donor-donor separation and a is the distance between acceptors.

As the acceptor concentration is increased, the above approximations break down. A larger fraction of the donors are then within the critical interaction range of acceptors and energy migration becomes less essential. Yokota and Tanimoto¹³ have obtained a general solution for the donor decay function including both diffusion within the donor system and donor-acceptor energy transfer via dipole-dipole coupling. Their expression is

$$\Phi(t) = \Phi(0) e^{-t/\tau_0} \times \exp \left[-\frac{4}{3} \pi^{3/2} N_a (Ct)^{1/2} \left(\frac{1 + 10.87x + 15.50x^2}{1 + 8.743x} \right)^{3/4} \right], \quad (8)$$

where $x = DC^{-1/3} t^{2/3}$. At earlier times in the decay, when $t \ll C^{1/2} D^{-3/2}$, diffusion is unimportant; Eq. (8) reduces to Eq. (3) for $s=6$ and a nonexponential time dependence is predicted. In the other limit as $t \rightarrow \infty$, Eq. (8) reduces to an exponential function of time with a lifetime approximately equal to that given in Eqs. (5) and (6). This changing time-dependent decay behavior is a distinguishing characteristic of diffusion-limited relaxation. Examples of such decays and their dependence on acceptor concentration and diffusion constant are observed in the experiments below.

III. EXPERIMENTS

The system studied was an europium metaphosphate glass having a composition $\text{Eu}(\text{PO}_3)_3$ which was doped with trivalent chromium impurities. Excited Eu^{3+} ions constitute the donor system; Cr^{3+} ions act as energy acceptors. The latter were assumed to be randomly distributed in the samples and were added in nominal concentrations ranging up to 1 mole %. Since the optical spectra and fluorescence kinetics of both Eu^{3+} and Cr^{3+} ions in this glass were reported in detail elsewhere,¹⁹ only those spectral features of importance for energy transfer are reviewed below.

The lower-energy-level scheme for Eu^{3+} is shown in Fig. 1. The absorption and emission spectra of $\text{Eu}(\text{PO}_3)_3$ glass arise from transitions between the $4f^6$ levels and are generally similar to spectra observed previously for Eu^{3+} impurities in other glasses. The optical linewidths are large, owing to the nonuniform local fields characteristic of glasses.

Excited Eu^{3+} ions in $\text{Eu}(\text{PO}_3)_3$ glass decay rapidly ($< 5 \mu\text{sec}$) to the metastable 5D_0 level from which

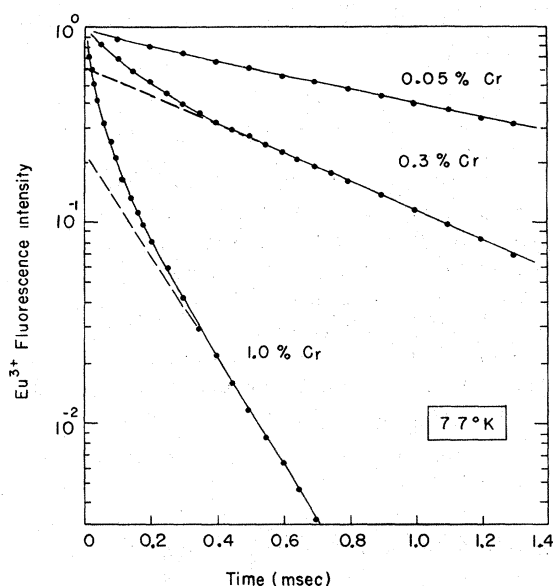


FIG. 2. Variation in the time dependence of the Eu^{3+} fluorescence decay from Cr^{3+} -doped $\text{Eu}(\text{PO}_3)_3$ with increasing Cr content.

fluorescence is observed to levels of the 7F multiplet. In undoped samples at low temperatures, the measured fluorescence lifetime as 2.1 msec, which is equal, within experimental error, to the radiative lifetime of 5D_0 predicted from measurements of integrated absorption coefficients and relative fluorescence intensities.¹⁹ Self-quenching of Eu^{3+} fluorescence via exchange interactions frequently occurs in crystals containing high concentrations of Eu^{3+} ions.⁸ The absence of self-quenching in $\text{Eu}(\text{PO}_3)_3$ glass indicates that exchange coupling between Eu^{3+} ions is weak.

The fluorescence spectrum of Cr^{3+} ions in $\text{Eu}(\text{PO}_3)_3$ and other phosphate glasses²⁰ consists of broad-band emission in the near-infrared rather than the usual ${}^2E \rightarrow {}^4A_2R$ -line emission characteristic of the $3d^3$ configuration. This emission is attributed to Stokes-shifted ${}^4T_2 \rightarrow {}^4A_2$ transitions which are indicated in the schematic configuration coordinate diagram in Fig. 1. The lifetime of the Cr^{3+} emission was $\approx 25 \mu\text{sec}$ at 77°K and decreased with increasing temperature. At all temperatures investigated (77–700°K), the Cr^{3+} lifetime was very much shorter than the Eu^{3+} lifetime; hence Cr^{3+} impurities are well suited to serve as fast-relaxing energy sinks for Eu^{3+} excitation.

The ${}^5D_0 \rightarrow {}^7F_J$ Eu^{3+} emission occurs predominantly in the 600–700-nm region and overlaps the broad ${}^4A_2 \rightarrow {}^4T_2$ absorption band of Cr^{3+} , a requirement for efficient energy transfer. Energy transfer from Eu^{3+} to Cr^{3+} was confirmed from the appearance of Eu^{3+} lines in the excitation spectrum of the Cr^{3+} fluorescence. Both radiative and nonradia-

tive energy transfer were observed. Pulsed selective excitation experiments established that excited Eu^{3+} ions decay to the 5D_0 state before transfer to Cr^{3+} ions occurred.¹⁹

The Eu^{3+} fluorescence from undoped $\text{Eu}(\text{PO}_3)_3$ glass decays exponentially following pulsed excitation. When chromium impurities are added, however, the decay initially deviates from a simple exponential dependence. This is illustrated in Fig. 2, where semilogarithmic plots of the Eu^{3+} decay for three different Cr^{3+} concentrations are shown. The initial nonexponential portion of the decay is attributed to relaxation by direct $\text{Eu}^{3+} - \text{Cr}^{3+}$ energy transfer. This short-time behavior for the 1% Cr sample can be fitted approximately by a $t^{1/2}$ law indicative of dipole-dipole coupling; the data, however, were not considered to be sufficient to establish conclusively the multipolar nature of the energy transfer. At lower Cr concentrations a smaller fraction of the excited Eu^{3+} ions are within the effective interaction sphere of Cr^{3+} energy sinks. Direct relaxation therefore contributes less to the over-all decay and the nonexponential portion of the decays in Fig. 2 becomes correspondingly smaller.

The final portions of the decays in Fig. 2 are exponential. Note that as the chromium concentration is decreased, the decay time of the exponential portion increases. This is characteristic of diffusion-limited relaxation since the average distance required for energy to migrate to a Cr^{3+} sink is increased. As the number of Cr^{3+} impurities goes to zero, the total time dependence of the Eu^{3+} fluorescence decay approaches a single exponential with a lifetime given by the intrinsic decay time.

The over-all decay of the Eu^{3+} fluorescence becomes faster and approaches a predominantly single exponential time dependence with increasing temperature. This is illustrated in Fig. 3, where the fluorescence decay from a sample containing 0.3% chromium is shown for three different temperatures. As discussed later, the Eu^{3+} diffusion constant increases with temperature. The behavior in Fig. 3 is therefore characteristic of the approach to the fast-diffusion limit.

The final portion of the Eu^{3+} fluorescence decay was exponential for all cases investigated. The characteristic relaxation time for this part of the decay is plotted as a function of temperature in Fig. 4 for an undoped and several different chromium-doped samples.

IV. DISCUSSION

The lifetime of the 5D_0 state of an Eu^{3+} ion is governed by a sum of probabilities for several competing decay processes. These include (i) radiative decay, (ii) nonradiative decay by multi-

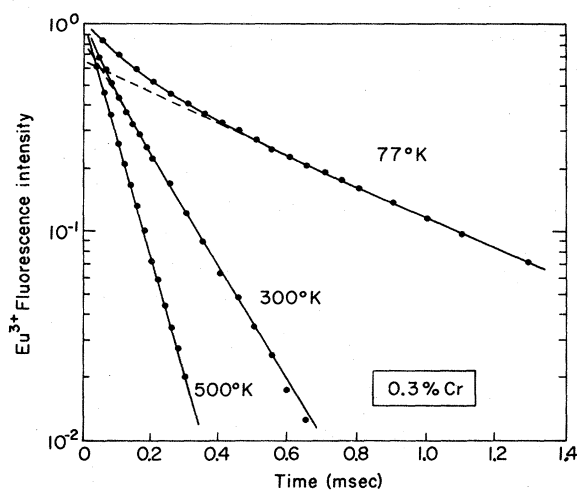


FIG. 3. Variation in the time dependence of the Eu^{3+} fluorescence decay from Cr^{3+} -doped $\text{Eu}(\text{PO}_3)_3$ with increasing temperature.

phonon emission or self-quenching, and (iii) energy transfer to Cr^{3+} or other impurities. The predicted radiative decay rate of the 5D_0 state in $\text{Eu}(\text{PO}_3)_3$ glass¹⁹ is 435 sec^{-1} and is included as a temperature-independent limit in Fig. 4. The measured lifetime of the undoped sample is seen to approach this purely radiative rate at low temperatures; hence the rate of nonradiative decay by multiphonon emission or self-quenching must be small. The increasing decay rate of the undoped sample at higher temperatures could arise from an increased importance of these processes or from additional phonon-assisted radiative transitions. The temperature dependence of the lifetime at elevated temperatures, however, is slower and unlike that generally observed for multiphonon emission²¹ or self-quenching.

The similarity of the temperature dependences of the exponential parts of the decay for the undoped and chromium-doped samples²² suggests that they may both be associated in part with relaxation via migration to energy sinks. Spectrochemical analysis of the undoped sample revealed that chromium was present as an unintentional impurity in only one part per million (this order of magnitude was in agreement with that based upon a search for Cr^{3+} emission). This concentration is too small to account for the observed decay rate. Other transition-metal ions, however, were present in the undoped sample in concentrations totaling in the order of 100 parts per million¹⁹ and some, such as V and Fe, could, depending upon their valence state, serve as quenching centers for excited Eu^{3+} ions. Since these impurities were probably common to all samples studied, the intrinsic relaxation time τ_0 of the 5D_0 state in the absence of Cr^{3+} impurities was

taken to be that measured for the "undoped" sample.

A. Temperature Dependence of Diffusion

The additional decay rate due to relaxation by diffusion to Cr^{3+} impurities was found from Eq. (5) for the 0.05% Cr sample where the approximation $d \ll a$ used in deriving the solutions for diffusion-limited relaxation is well satisfied. This rate is plotted as a function of temperature in Fig. 5. The observed temperature variation of τ_D may arise from changes in either D or C , because, from Eqs. (6) and (7), the rate is given by

$$1/\tau_D = 8.5N_a C^{1/4} D^{3/4}. \quad (9)$$

Since τ_D^{-1} is dependent on only the $\frac{1}{4}$ power of C and changes in the Eu^{3+} - Cr^{3+} coupling with temperature are expected to be small, changes in the diffusion constant D are the most promising source of the temperature dependence in Fig. 5.

The process of energy diffusion within the Eu^{3+} system, considered in terms of its basic step, involves the decay of one ion from a crystalline Stark level $i \rightarrow f$ accompanied by the simultaneous excitation of a nearby ion from $i' \rightarrow f'$. Let $P_{if, i'f'}$ be the probability for this ion-pair process. For the Eu^{3+} system, $i=f' = {}^5D_0$. If $f=i'$, the process is a resonant one; if $f \neq i'$, the creation or annihilation of one or more vibrational quanta is required to conserve energy.

At low temperatures only the 7F_0 ground state is populated and the only resonant transitions giving rise to diffusion are ${}^5D_0 \rightleftharpoons {}^7F_0$. As the temperature

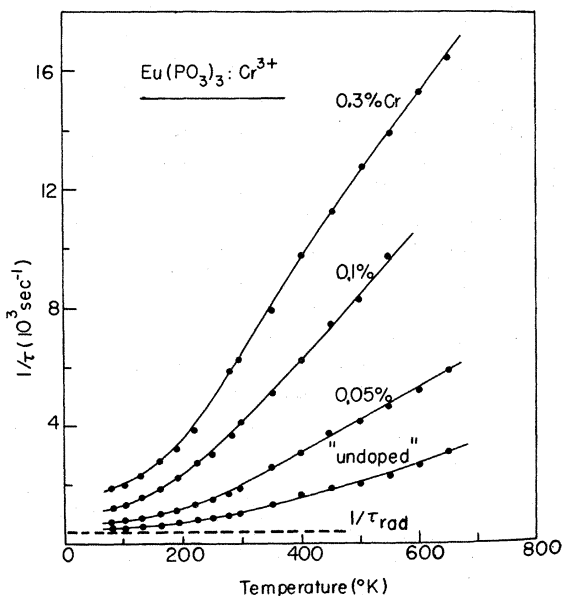


FIG. 4. Temperature dependence of the Eu^{3+} fluorescence lifetime for an undoped (see text) and three chromium-doped samples of $\text{Eu}(\text{PO}_3)_3$.

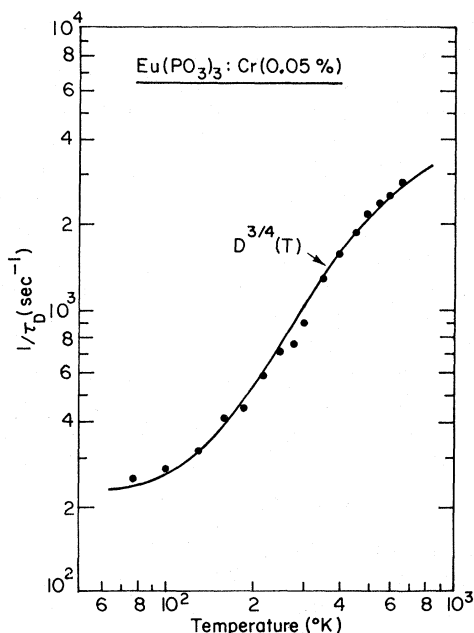


FIG. 5. Comparison of the temperature dependences of the rate τ_D^{-1} attributed to diffusion to Cr^{3+} impurities and the europium energy diffusion constant D in $\text{Eu}(\text{PO}_3)_3$ glass calculated assuming only resonant multipolar processes.

is increased, however, Stark levels of higher-lying 7F_J manifolds become thermally populated and additional resonant transition pairs become possible. The diffusion constant D for Eu^{3+} is therefore proportional to

$$\sum_{f,i'} n_i P_{if,i'f'} \quad (10)$$

where n_i is the number of ions in the i th level at energy E_i . Since the rates of thermal equilibration between closely spaced Stark levels of rare-earth ions such as the 7F_J levels of Eu^{3+} are generally very much faster than energy transfer or fluorescence decay rates,²¹ use of a Boltzmann distribution

$$n_i = N g_i e^{-E_i/kT} / \sum_j g_j e^{-E_j/kT} \quad (11)$$

is justified. The probability P^{12} for multipolar coupling of ions 1 and 2 is given by

$$P_{if,i'f'}^{12} \propto \left(\frac{g_f}{g_i} \right) \frac{f_{if} f_{i'f'}}{\nu^2} \int F_{if}^1(\nu) F_{i'f'}^2(\nu) d\nu \quad (12)$$

In Eq. (12), the f 's are the oscillator strengths of the transitions and the line-shape functions $F(\nu)$ are normalized such that $\int F(\nu) d\nu = 1$. For resonant processes between like ions, the overlap integral is approximately equal to the inverse linewidth $\Delta\nu_{if}$. Thus, combining Eqs. (10)–(12) for $i' = f$,

$$D \propto \sum_f \frac{g_f e^{-E_f/kT}}{\sum_f g_f e^{-E_f/kT}} \left(\frac{g_f}{g_i} \right) \frac{f_{if}^2}{\nu_{if}^2 \Delta\nu_{if}} \quad (13)$$

If the frequencies, linewidths, and probabilities of all resonant transitions were equal, D would be temperature independent. Measurements of the fluorescence intensities of the 5D_0 – 7F_J transitions show, however, that the oscillator strengths are not equal.¹⁹ The strongest transitions are to the 7F_1 , 7F_2 , and 7F_4 states; of these, the first two states become significantly populated near or above ambient temperatures. Using the energy levels, oscillator strengths, and estimated linewidths for Eu^{3+} in $\text{Eu}(\text{PO}_3)_3$, the temperature dependence of D predicted by Eq. (13) was calculated. Since, from Eq. (9), $1/\tau_D \propto D^{3/4}$, the $3/4$ power of D is plotted in Fig. 5.

The agreement between the temperature dependence predicted from Eq. (13) and the measured variation of $1/\tau_D$ is quite satisfactory and the dependence of $1/\tau_D$ on the $3/4$ power of D is well verified. This result is perhaps surprisingly good in view of the neglect of nonresonant processes in the diffusion and of any temperature dependence associated with $\Delta\nu$ or C . It emphasizes, instead, the dominant importance of the strength and number of the Eu^{3+} – Eu^{3+} resonant transitions in determining the net diffusion rate.

The linewidths of optical transitions in $\text{Eu}(\text{PO}_3)_3$, although broad at low temperatures as is typical for rare-earth ions in glasses, do, in addition, exhibit broadening with increasing temperature. This can affect the rate of Eu^{3+} energy diffusion in two ways. For resonant transfer processes involving perfect spectral overlap, an increasing linewidth reduces the coupling probability in Eq. (12) and thereby decreases D . In glasses, however, the observed lines are usually inhomogeneously broadened due to site-to-site variations in the ligand fields. Adjacent Eu^{3+} ions may therefore see different local environments and have slightly different energies. Thermal line broadening tends to overcome this energy mismatch. This second effect increases the spectral overlap and thereby enhances diffusion.²³ Since these two processes change the diffusion rate differently, they may be partially self-compensating, thus contributing to the good fit obtained using Eq. (13).

B. Magnitudes of C , R_0 , and D

The Eu^{3+} – Cr^{3+} energy transfer involves a pair of simultaneous energy-conserving transitions in which an excited Eu^{3+} ion decays from 5D_0 to a level of 7F and a neighboring Cr^{3+} ion is excited from 4A_2 to 4T_2 . Although the exact multipolar or exchange nature of the Eu^{3+} – Cr^{3+} transfer process is uncertain, forced electric-dipole transitions are possible for the two ions. In lieu of evidence fa-

ving other mechanisms, we examine the transfer probability for dipole-dipole coupling given by

$$P_{dd}(\text{Eu}^{3+}-\text{Cr}^{3+}) = \frac{3h^4 d^4 \Sigma_{\text{Cr}}}{4\pi R^6 n^4 \tau_{\text{Eu}}} \left(\frac{\mathcal{E}_0}{(\sqrt{\kappa}) \mathcal{E}_{\text{eff}}} \right)^4 \int \frac{F_{\text{Eu}}(E) F_{\text{Cr}}(E) dE}{E^4} = CR^{-6}. \quad (14)$$

Σ_{Cr} is the integrated absorption cross section $\int \sigma(E) dE$, R is the Eu-Cr separation, τ_{Eu} is the intrinsic Eu^{3+} lifetime, n is the refractive index, and the F 's in the overlap integral are normalized line-shape functions for the Eu^{3+} emission and Cr^{3+} absorption. The constant C was evaluated from Eq. (14). The overlap integral was determined from measurements of the Eu^{3+} fluorescence spectrum and the absorption spectrum for the 0.3% Cr sample. The term $\mathcal{E}_0/(\sqrt{\kappa}) \mathcal{E}_{\text{eff}}$, which is the effective field correction in the material, was taken to be unity. The resulting value for C was $\approx 4 \times 10^{-38} \text{ cm}^6/\text{sec}$.

C was also found by fitting the initial portions of the 77°K decay curves in Fig. 2 to Eq. (8). For the 0.3% Cr sample, again assuming dipole-dipole coupling, a value of $C \approx 6.3 \times 10^{-38} \text{ cm}^6/\text{sec}$ was derived. In view of the assumptions made and experimental uncertainties, the agreement with the previous result for C is considered satisfactory.

The critical transfer distance for dipole-dipole coupling is defined by $R_0 = (C\tau_0)^{1/6}$, where τ_0 is the radiative lifetime of Eu^{3+} . Using a value of $C = 5 \times 10^{-38} \text{ cm}^6/\text{sec}$ yields $R_0 = 22 \text{ \AA}$. At Cr^{3+} concentrations of $> 0.33 \text{ at. \%}$, all Eu^{3+} ions are within the critical transfer distance of a chromium quenching center.

The diffusion constant was found from Eq. (9). While it is not sensitive to the value of C , it is dependent on the concentration of Cr^{3+} acceptors. Using the nominal chromium concentrations and $C = 5 \times 10^{-38} \text{ cm}^6/\text{sec}$, a diffusion constant of $D \approx 6 \times 10^{-10} \text{ cm}^2/\text{sec}$ is obtained at 300°K. This small diffusion constant is a consequence of (i) the particular $4f^6$ energy level scheme and transition probabilities of Eu^{3+} and (ii) the property that in a glass the ligand fields at adjacent Eu^{3+} ions are sufficiently different to make energy diffusion transitions nonresonant. Since excitation migrates a distance $(DT)^{1/2}$ in a time T , this D value corresponds to energy migration of 78 Å in 1 msec.

The above values of C and D can be used to test

the applicability of the solutions in Eqs. (5) and (6). Using the value of D at 77°K and assuming the temperature dependence of C is negligible, the length parameter ρ from Eq. (7) is 12 Å. Since $d \approx 5.7 \text{ \AA}$ and $a \geq 30 \text{ \AA}$ for all samples studied, the criterion $d \ll \rho \ll a$ is satisfied. Because of the increase in diffusion rate with increasing temperature, this is no longer true at temperatures $\gtrsim 300 \text{ °K}$ and one approaches the fast-diffusion case (B). This is reflected in the time dependence of the fluorescence decay. As noted earlier, the time domain in which nonexponential decay is expected is for $t \ll C^{1/2} \times D^{-3/2}$. Using values of C and D at 77°K, $t \ll 650 \text{ \mu sec}$. At 500°K, however, nonexponential behavior is predicted only for $t \ll 4 \text{ \mu sec}$. This is beyond the time resolution used in Fig. 2.

V. CONCLUDING REMARKS

Energy migration and transfer to quenching centers in glasses have been reported and discussed previously.²⁴ Here we have shown that studies of the transient luminescence can provide additional information that is useful in distinguishing the physical processes active in the relaxation. By varying the acceptor concentration and the diffusion rate, the relative contributions and importance of long-range interactions and diffusion were established and the limiting cases of fast diffusion and diffusion-limited relaxation were displayed. Precise, quantitative calculations and predictions of the transfer rates and diffusion rates in glass hosts are difficult to make, however. It is therefore of interest to perform similar investigations of energy migration and transfer in crystalline hosts which are more amenable to such calculations. Since in crystals the diffusion rates within the donor system will generally be faster, observations and measurements in a different time scale may be required. Alternatively, the diffusion rate may be reduced by diluting the donor system or by one of the several temperature-dependent effects discussed in this paper.

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Ion Energy Distributions in Field-Ion Microscopy

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Two currently proposed theories, resonance tunneling and surface-plasmon creation, are critically compared for the interpretation of the energy distributions of field-emitted ions measured by Jason. The properties of the spacings and intensities of the peaks of the observed oscillatory energy distribution curves are explicable in terms of an ion-surface-plasmon inelastic scattering mechanism. Some of the most important features are incompatible with the resonance tunneling effect: (i) The spacings are relatively insensitive to the chemical nature and to the pressure of the imaging gas as well as to the tip crystal face used as ion source; (ii) different metal tips, i. e., W, Pt, and Mo, produce the same peak spacings; (iii) the peak intensities strongly depend on field strength. A detailed theoretical study of a model ion-plasmon interaction Hamiltonian shows that, as a result of the strong dependence of peak spacings and intensities on field strength, field-ion emission could provide a new experimental method for investigating selectively surface collective excitations of metals. The ion-plasmon scattering effects also have important consequences for the energy distributions of ions in field desorption or evaporation and place a limitation on the mass resolution of the atom-probe microscope.

I. INTRODUCTION

This paper is concerned with the description of energy exchange processes between the ions and the electronic plasma modes at the metal tip in field-ion microscopy.

Energy distributions of field-emitted ions have been measured by Jason¹ over the range of fields normally used for the microscope operating in the imaging mode. Similar, though statistically less saturated, distributions have been obtained^{2,3} by mass-spectrometry analysis of field-evaporated ions, i. e., in the "atom-probe" configuration. In Jason's experiments, the energy distributions show well-resolved oscillatory structure which has been

attributed^{1,4} to the resonant tunneling of electrons from the imaging gas atoms to the metal tip during the ionization process. In the atom-probe measurements, an assumed mass resolution of less than 1% has led to an interpretation of some of the broad mass spectra in terms of the formation of metastable compound ion molecules^{2,3} due to the interaction between the metal-tip atoms and the imaging or residual gases.

In the present paper, it is proposed that multiple excitations of surface plasmons in the metal tip occur together with associated discrete energy losses of the imaging gas ions. It will be shown that such a process may constitute a necessary and sufficient mechanism for the origin of the struc-