Spectral energy transfer in PrF$_3$, PrCl$_3$

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Time-resolved fluorescence line narrowing is used to study spectral energy transfer in PrF$_3$ and PrCl$_3$. The excitation spectrum of PrF$_3$ in the region of the $(^3H_4) \rightarrow ^5P_0$ absorption indicates that several strong satellite lines accompany the main transition, their origin being ascribed to different Pr$^{3+}$ ions lying in strongly perturbed lattice sites. The spectral transfer within the inhomogeneously broadened main transition is measured, where the energy mismatch is about 2 cm$^{-1}$. This process is characterized by a strong ($\sim T^{-1}$) dependence of the transfer probability on sample temperature. The growth of the full inhomogeneous emission profile accompanies a uniform decay of the donor line shape. A transfer process between the lowest-energy satellite ions is also measured. Here the energy mismatch is 32 cm$^{-1}$ resulting in a weak temperature dependence for the transfer rate. Both the intraline and intersatellite transfer are characterized by simple exponential rate equations. Recent calculations of phonon-assisted transfer probabilities are compared to our measurements, with the intersatellite transfer ascribed to a “one-phonon direct” process whereas the transfer within the main transition occurs by a “one-phonon second-order” mechanism. In PrCl$_3$ the transfer times are faster than the 15-nsec response time of our detection system indicating a much stronger ion-ion coupling.

I. INTRODUCTION

The static spectral properties of the fluorescence and absorption lines of rare-earth ions in crystals have been extensively studied with crystal-field and phonon relaxation theories having had great success in explaining the position, number, and widths of these spectral lines. Much experimental work has also been devoted to the dynamics of energy transfer between different species of (3d) and/or (4f) ions doped into the same host.\textsuperscript{1} Detailed analysis of these experiments allows the indirect study of energy transfer between ions of the same species.

Energy transfer \textit{within} an inhomogeneously broadened optical transition of a single species has recently been observed in several impurity-doped crystalline and amorphous hosts\textsuperscript{2-8} using the technique of time-resolved fluorescence line narrowing. These time-resolved fluorescence spectra show directly the spectral transfer from the initial set of excited ions (donor system) to the ions comprising the full inhomogeneous distribution (acceptor system). The temperature dependence of the transfer probability has indicated the phonon-assisted nature of this process.

The optically active ions in stoichiometric crystals have been discussed by many authors using an excitonic description for the collective excitation of the electronic states. This concept of delocalized or collective excitation is useful when the perturbation energy caused by strains or defects in the crystal is much less than the ion-ion coupling. For a weakly coupled system with a large inhomogeneous linewidth, a localized or single-ion description is more appropriate. In this article we consider two such stoichiometric crystals, PrF$_3$ and PrCl$_3$.

We have measured the excitation spectrum of PrF$_3$ in the region of the $(^3H_4) \rightarrow ^5P_0$ absorption which indicates several “satellite lines” accompanying the main transition. These lines presumably arise from Pr$^{3+}$ ions situated in strongly perturbed lattice environments and suggest the inhomogeneous broadening mechanism active in this crystal. Our experiments have determined that inhomogeneous broadening is indeed responsible for the width of main absorption line, and time-resolved fluorescence studies have revealed a two-phonon-assisted spectral transfer\textsuperscript{9} of a similar character to that observed in LaF$_3$:Pr$^{3+}$. An energy-transfer process between the different satellite ions is also measured. Here the energy mismatch is large and a weak temperature dependence for the transfer rate indicates a one-phonon mechanism.\textsuperscript{10,11}

We have correlated our results with recent microscopic theoretical descriptions\textsuperscript{8-11} of phonon-assisted spectral transfer. The temperature and energy mismatch dependences of the transfer rate are used to identify the dominant ion-phonon coupling term responsible for the transfer process. Phonon phase terms are shown to be responsible for the increase in the intraline transfer temperature dependence over that in LaF$_3$:Pr. The observed exponential dynamics are shown to be consistent with a macroscopic description of energy transfer including back-transfer terms.

In view of our results in PrF$_3$, we have attempted to observe spectral energy transfer in PrCl$_3$. The
characteristic transfer times are faster than our 15-nsec instrumental response time indicating the probable excitonic nature of the electronic states in this crystal.

II. EXPERIMENTAL DETAILS

The PrF₃ crystal was provided by Optovac, Inc. and was of "high optical quality." Observation of the fluorescence filament under well-focused laser excitation indicated little internal scattering arising from macroscopic flaws. The PrCl₃ crystal was obtained from Johns Hopkins through R. Sarup. Careful crystal handling resulted in a minimum of surface deterioration due to its hygroscopic properties.

The crystal was excited with a high-resolution, pulsed, pressure-tunable dye laser¹² as indicated in Fig. 1. Lasing is achieved by pumping the dye with a Molecron UV-400 nitrogen laser having a peak power of approximately 200 kW at a 40-Hz repetition rate and a 10-nsec pulse width. Coumarin 102, diluted to a 10⁻²² mol/L concentration in high-purity ethanol is appropriate for exciting the (¹⁰⁰)→³P₀ absorption at 4778 Å in PrF₃. Inserting an intracavity etalon with a 3.6-mm spacer narrowed the laser spectral width from 1 cm⁻¹ to 1.0 GHz and an Intracavity Glan-Thompson prism was used to control the polarization of the beam.

The crystal was mounted in a variable temperature helium cryostat along with a carbon-glass resistance thermometer. A dc heater and electronic controller maintained a 0.05-K temperature stability. Careful thermal sinking minimized the uncertainty in the temperature measurements and no heating from the laser excitation was observed.

The PrF₃ fluorescence was focused onto the entrance slit of a Spex 1-m spectrometer. When appropriate, the fluorescence was spatially rotated by placing a dove prism between the sample and the entrance slit. The 30-μm slit widths used throughout gave a 0.9-cm⁻¹ resolution. An RCA 7265 photomultiplier tube with an S-20 cathode and a 7-nsec FWHM single-photon response time was used to detect the fluorescence. The high gain of this tube alleviated the need for additional signal amplification.

A PAR model 162/164 boxcar integrator measured the photomultiplier output with a 15-nsec gate width, and an external trigger generator provided the necessary synchronization between the laser pulse and the opening of the boxcar gate. Careful grounding and shielding reduced the rf pickup from the nitrogen laser to less than 1% of full scale. The boxcar output was then normalized to the dye-laser intensity, with the ratio displayed on an X-Y recorder. A total system response time of 15 nsec was measured for a 10%–90% rise in the fluorescence signal.

III. THEORETICAL REVIEW

The microscopic theory of energy transfer developed by Forster,¹³ Dexter,¹⁴ and Miyakawa¹⁵ has been applied to many studies of energy transfer between different species of ions. More recent discussions¹⁶–¹⁸ have been of a more fundamental nature in that they treat the ion-ion and ion-lattice interactions on equal footing. The temperature and energy mismatch dependences of the transfer probability arise in a natural way. We present here a synopsis of the relevant transfer probabilities calculated using perturbation theory.

The probability for the transfer of electronic excitation from ion 1 to ion 2 involving the emission or absorption of a single phonon of energy

\[ E = \hbar \omega_{\alpha, \beta} \text{ is }^{10,11} \]

\[ W_{1 \rightarrow 2} = \frac{2 \pi}{\hbar^2} \int \frac{d \omega}{2 \pi} \frac{1}{2 M \nu_{\alpha, \beta}} \left[ \Delta f^{(1)} - \Delta f^{(2)} e^{i (\pi \omega_{\alpha, \beta}} \right] \]

\[ \times \left( \epsilon_{\alpha, \beta} + \gamma \right) \delta (E_1 - E_2 - \hbar \omega_{\alpha, \beta}) , \tag{1} \]

where \( J \) is the ion-ion (exchange, multipolar) coupling between ions 1 and 2, \( \overline{R}_{\alpha, \beta} \) is their spatial separation, and \( \gamma \) is 1(0) for phonon emission (absorption). The quantity \( \Delta f^{(j)} \) is the difference in the ion-lattice coupling between the initial and final electronic states for ion \( j \), i.e.,
\[ \Delta f^{(l)} = \langle j^* | H_{\text{la}}^{(l)} | j \rangle - \langle j | H_{\text{la}}^{(l)} | j \rangle. \]

The temperature dependence for this process is
\[ n_{a, b}^2 + 1 = \frac{1}{(e^{\omega_b/kT} - 1) + 1}, \]
and indicates a strong energy mismatch asymmetry for \( \Delta E \approx kT \).

Recently, Holstein, Lyo, and Orbach\(^1\) have calculated transfer probabilities for several higher-order phonon-assisted processes. Their "one-phonon second-order" process appears to dominate the spectral transfer within the main absorption line in PrF\(_3\). For this mechanism the transfer rate is
\[ W_{1 \rightarrow 2} = \frac{2\pi}{\hbar} \sum_{\vec{k}, \vec{k'}} J^2 \left| \frac{\Delta f}{\hbar\omega_{\vec{k}} - \Delta E} \right|^2 \left( \frac{\Delta f}{\hbar\omega_{\vec{k}} - \Delta E} \right) \times (n_{\vec{k}} - 1) \langle \epsilon \mid n_{\vec{k'}} \rangle \langle \epsilon \mid n_{\vec{k'}} \rangle \times \delta(\hbar\omega_{\vec{k}} - \hbar\omega_{\vec{k'}} - \Delta E) \],

where \( \langle \epsilon \rangle \) is an angular average of a phonon-phase interference term
\[ h(\vec{k}, \vec{k'}) = |e^{i(\vec{k} \cdot \vec{R}_{12} + \vec{k'} \cdot \vec{R}_{12})} - 1 - e^{i(\vec{k} - \vec{k'}) \cdot \vec{R}_{12}}| \].

For \( kR \gg 1 \) and \( k'R \gg 1 \), a \( T^3 \) temperature dependence is predicted with the rate being only weakly dependent on the energy mismatch \( \Delta E \) for \( \Delta E \approx kT \).

Other higher-order phonon-assisted processes are characterized by a strong (varying as \( 1/\Delta E^2 \)) dependence on the energy mismatch. For a small \( \Delta E \), one might have a rapid spatial migration of the excitation with little spectral transfer. The importance of such a process depends on the probability of finding an ion with a small enough \( \Delta E \) within a suitable distance through which the ion-ion coupling can act.

The validity of the time-dependent perturbation approach used in these calculations must be carefully considered. The ion-lattice coupling \( (H_{\text{la}}) \) is sufficiently weak for the well-shielded 4\( f \) electrons to use the pure electronic wave functions \( |j\rangle \) and \( |j^*\rangle \). A second limitation involves the strength of the ion-ion coupling relative to the ion-lattice interaction. We require that the phonon-assisted transfer times be longer than the vibrational relaxation time of the ion in order for the transfer to be an incoherent process. Without a dephasing mechanism such as phonon relaxation, one must instead consider a coherent description for energy transfer. It is this vibrational relaxation or dephasing rate which determines how rapidly the electronic wave functions lose coherence and result in a homogeneous or lifetime broadening of the optical lines observed at finite temperatures. The homogeneous width arising from phonon relaxation varies from an extrapolated value of \( 5 \times 10^{-7} \text{ cm}^{-1} \) at 6 K to \( 4 \times 10^{-8} \text{ cm}^{-1} \) at 20 K for the \( (^5H_{1}) - ^3P_0 \) transition in LaF\(_3\):Pr\(^{3+}\). This corresponds to relaxation rates of \( 1 \times 10^{5} \) to \( 1 \times 10^{7} \) sec\(^{-1} \), respectively. We anticipate our measured transfer rates by saying that the criteria for an incoherent phonon-assisted process are generally met for PrF\(_3\).

We have also considered the nature of \( J \) the ion-ion coupling mechanism. Following Kushida\(^2\) we have calculated\(^3\) an electric dipole-dipole interaction strength of \( J \approx 7 \times 10^{-8} \text{ cm}^{-1} \) for two nearest-neighbor Pr\(^{3+}\) ions in LaF\(_3\). The quadrupole coupling terms vanish due to the \( |\Delta J| = 2 \) selection rule. A magnetic dipole coupling requires \( |\Delta S| = |\Delta L| = 0 \) and hence also vanishes.

Exchange can also couple two nearby rare-earth ions. A direct exchange process involving the overlap of the 4\( f \) wave functions should be negligible due to their small radial extent. A more plausible mechanism involves the mixing of the 4\( f \) and 5\( d \) wave functions at the two ion sites, with a direct exchange occurring for the 5\( d \) wave functions.\(^4\) Estimates of the interaction strength for such a process are difficult to undertake. There is also a superexchange\(^5\) process in which the Pr ions interact through a mutual exchange coupling with intervening fluorine ions. The coupling strength varies with the number and type of paths connecting the ions.

There are other considerations\(^6\) which enter into the already complicated description of the ion-ion coupling. The linear and nonlinear screening of the 4\( f \) electrons by the outer-electron orbitals will serve to modify the range dependence of the interaction. The role of the intervening ligands in producing induced moments, overlap, and bonding covalency is not properly understood and may influence the nature of the ion-ion coupling strength.

Radiative processes can also lead to energy transfer within an inhomogeneously broadened line. It has recently been demonstrated\(^7\) that this radiative mechanism can be estimated by replacing the nonradiative ion-ion coupling \( J \) by \( J' = \lambda A/2\pi R_c \), where \( \lambda \) is the transition wavelength, \( A \) is the radiative decay probability for the \( ^3P_0 - (^5H_{1}) \) transition, and \( R \) is the ion-ion separation. Assuming that this decay probability is approximately \( A = 0.3 \times 10^{-13} \text{ sec}^{-1} \), we estimate \( J' = 1 \times 10^{-6} \text{ cm}^{-1} \) as compared to a dipolar nonradiative \( J = 7 \times 10^{-2} \text{ cm}^{-1} \). Since it enters as \( J'^3 \) in the transfer rate, we assume that radiative phonon-assisted transfer is negligible in our system.

The microscopic transfer rates can be related to the observed spectral dynamics by macroscopic rate equations. Consider the \( k \)-th donor ion; initially excited at time \( t = 0 \), located at position \( \vec{R}_k \) and having an excited-state energy of \( E_k \). If \( P_k(t) \)
is the probability of finding this $k$th ion in its excited state at time $t$, then the time rate of $P_k(t)$ is
\[
\frac{dP_k(t)}{dt} = -W_{at} P_k(t) - P_k(t) \sum_{j=1}^{N} W_{jk}(\bar{R}_{jk}, \Delta E_{jk}) + \sum_{j=1}^{N} P_j(t) W_{jk}(\bar{R}_{jk}, \Delta E_{jk}).
\] (6)

The first term is the decay of ion $k$ due to “single-ion” processes such as radiative or multiphonon de-excitation. Next is the term describing the probability for the transfer of excitation from ion $k$ to its $N$ neighbors each of which is located at $\bar{R}_j$, and the final term is involved with the transfer from the neighbors back to ion $k$. The solution to this equation depends on the environment of the donor ion and the form of the single-ion transfer probability $W_{jk}(\bar{R}_{jk}, \Delta E_{jk})$. One must then average over all the possible donor configurations to obtain the macroscopic behavior of the donor ensemble.

IV. EXCITATION SPECTRUM

The excitation spectrum of PrF$_3$ in the region of the $({^2H}_{15}, {^3P}_2$) absorption was measured at 6 K and is shown in Fig. 2. In order to obtain a signal proportional to the fraction of ions that absorb at a particular wavelength, the excitation volume sampled must have a thickness much less than the absorption length. Using a 1.0-GHz excitation source, the shortest absorption length is about 100 $\mu$m. By magnification of the fluorescent image onto the narrow spectrometer slits, the first 3 $\mu$m of the excitation volume was observed. The spectrometer was placed in zeroth order and the fluorescence intensity was plotted as the dye laser was spectrally scanned.

The prominent feature in the excitation spectrum is at 4778 Å which we label $A_0$ and will refer to as line center or the main transition. Other strong lines are $A_1$ and $A_2$ at 20 and 18 cm$^{-1}$ on the high-energy side of line center, respectively, and $A_3$ and $A_4$ at 30 and 62 cm$^{-1}$ on the low-energy side. The width of $A_0$ is about 2.0 cm$^{-1}$ FWHM and is comparable to the width of the rest of the features.

The satellite lines ($A_1 \cdots A_4$ in Fig. 2) that accompany the main transition ($A_0$) are Pr$^{3+}$ ions located in strongly perturbed lattice environments. Their identification as Pr$^{3+}$ ions follows from the comparison of their fluorescence spectra to that of the $A_0$ ions and to those of Pr$^{3+}$ ions in PrF$_3$ films and in LaF$_3$: Pr$^{3+}$.11 A strong crystal-field perturbation due to these ions being located at or near irregular lattice sites is presumably responsible for their energy states being shifted from the $A_0$ value. These irregular lattice sites are assigned to vacancies, interstitial ions, impurities, or other lattice defects and have been observed in other crystals with high concentration of optically active ions.30,31 We note that the high optical quality of the crystal probably rules out any large macroscopic defects. The satellite lines were also independent of the geometric position of the dye-laser excitation, again indicating the microscopic nature of the defects.

The existence of these lattice defects also points to the inhomogeneous nature of the main transition $A_0$. An ion located at a “normal” lattice site and having a nearby lattice irregularity will see a slightly distorted crystalline environment, hence will have its energy levels slightly shifted. The randomness in defect to normal site distance and orientation, thus leads to an inhomogeneous broadening of the ions at these locations.

V. MEASUREMENT OF ENERGY-TRANSFER RATES

A direct measurement of the probability for the transfer of excitation from ion 1 to ion 2 implicitly assumes a method exists for distinguishing between the two ions. The most experimentally accessible characteristic is their difference in excited-state energy. Thus, we will be concerned with investigating the transfer rate between ions 1 and 2 whose excited states are separated by an energy mismatch $\Delta E_{12}$. This requirement limits the possible process for spectral-energy transfer to those having a frequency shifting mechanism, i.e., a phonon-assisted process.

We operationally define the donor system as that ensemble of ions excited at time $t = 0$ by the pulsed dye laser. The energy spread of this ensemble is the sum of the dye-laser width and the averaged homogeneous width of the ions. The population of this donor ensemble is monitored by observing

![Fig. 2. Excitation spectra of PrF$_3$ in the region of the $({^2H}_{15}, {^3P}_2$) absorption.](image-url)
the fluorescence characteristic of these ions. As
time evolves following the initial pulsed excita-
tion, energy is transferred from the donor en-
semble to the acceptor ensemble. We measure
this process by observing the growth of the fluo-
rescence characteristic of the acceptor population
for times $t > 0$. The transfer probability is ex-
tracted by monitoring the donor and acceptor
fluorescence at different time delays after the laser
pulse excitation.

A. Transfer within the main absorption line

We now present our measurements of the spectral
energy transfer within the main $(^3H_m)_1 - (^3P_0)$ transi-
tion; that is, the $A_0$ set of sites indicated by the
excitation scan. The mere existence of line nar-
rowing and the fact that the narrowed component
tunes with the laser across the absorption profile,
demonstrates the inhomogeneous character of this
line. In order to excite a small fraction of Pr ions
within this $\sim 2\text{ cm}^{-1}$ linewidth, the dye laser was
used in its intermediate resolution configuration
where the spectral width is about 1.0 GHz (0.03
$\text{ cm}^{-1}$). As mentioned previously, the resonant
$^3P_0 - (^3H_m)_1$ fluorescence for the $A_0$ ions is weak
due to some reabsorption and a small branching
density for this transition. We therefore used the
much stronger but nonresonant $^3P_0 - (^3H_m)_1$ fluores-
ence to monitor the population of the donor and ac-
ceptor ions despite the residual inhomogeneous
broadening due to the accidental coincidence ef-
fect of nonresonant transitions. This residual
broadening does not complicate the direct obser-
vation of the energy-transfer process, and nonreson-
ant transitions have been used to study similar
processes in LaF$_3$:Pr$^{3+}$.5

Time-resolved emission spectra showing the in-
trafine spectral-energy transfer in PrF$_3$ are il-
lustrated in Fig. 3. Here the laser is pumping
those ions whose absorption is 2 $\text{ cm}^{-1}$ on the
high-energy side of line center. The growth of the
acceptor population at the expense of the donors is
clearly demonstrated by these spectra. At a
1-$\mu$s delay, the donor population has almost
vanished and the acceptor fluorescence begins to
decay through other deexcitation channels.

These scans point out the spectral characteristics of the energy-transfer process. The profiles of the
donor and acceptor fluorescence are seen to rise
and fall uniformly. We observe no distinguishable
broadening or other change in the line shape of the
donor fluorescence with time. These character-
istics are similar to those observed in the lower-
concentration LaF$_3$:Pr$^{3+}$ studies.3,5

The dynamics and temperature dependence for
this process were measured by pumping at the
edge of the absorption line and using the spectro-

FIG. 3. Time-resolved $^3P_0 - (^3H_m)_1$ emission spectra of the $A_0$ ions.

meter to separate the donor from the acceptor
line shape. That is, by fixing the spectrometer
at the wavelength of the donor fluorescence and
then scanning the delay of the boxcar integrator,
the time evolution of the donor population is easily
extracted. Similarly, we can monitor the acceptor
population by moving the spectrometer to the ac-
ceptor fluorescence wavelength.3,5

The time development of the donor and acceptor
ions is shown in Fig. 4, where we have scanned
the boxcar gate while using the spectrometer to
isolate the donor and acceptor fluorescence. The
dye laser is now 4 $\text{ cm}^{-1}$ on the low-energy side of
line center and the sample temperature is 15 K.
The rise of the acceptor fluorescence intensity
from a value of zero at $t=0$ is evidence that we
have adequately spectrally isolated the donor and ac-
ceptor fluorescence.

In Figs. 5 and 6 we illustrate semilog graphs of
the same donor and acceptor fluorescence as

FIG. 4. Spectral dynamics of the $A_0$ donor and ac-
ceptor emission.
shown in Fig. 4. The transfer rates are calculated using simple rate equations for the donor and acceptor excited-state populations. The time evolution of these populations is assumed to be described by

$$\frac{dN_d}{dt} = -W_d N_d - W_{d\rightarrow a} N_d$$  \hspace{1cm} (7)

and

$$\frac{dN_a}{dt} = +W_{d\rightarrow a} N_d - W_a N_a,$$  \hspace{1cm} (8)

with the initial conditions $N_d(t=0) = N_0$ and $N_a(t=0) = 0$. Here $W_{d\rightarrow a}$ is the donor to acceptor spectral-transfer rate, and $W_d$ and $W_a$ are the rates for other decay channels for the donor and acceptor ions, respectively. The solution to these differential equations is easily shown to be

$$N_d(t) = N_0 \exp \left[ - (W_{d\rightarrow a} + W_d) t \right],$$  \hspace{1cm} (9)

and

$$N_a(t) = \frac{N_0 W_{d\rightarrow a}}{W_{d\rightarrow a} + W_d} \left( e^{-W_a t} - e^{-(W_d + W_{d\rightarrow a}) t} \right)$$  \hspace{1cm} (10)

A justification of this simple rate-equation description as well as the processes responsible for $W_d$ and $W_a$ is discussed in Sec. VI.

The tail of the acceptor fluorescence in Fig. 5 is fit to $W_a = 1.1 \times 10^6$ sec$^{-1}$ and $\Delta(t)$ is then graphically evaluated as shown. In Fig. 6 a straight-line fit on this semilog graph of $\Delta(t)$ gives $W_{d\rightarrow a} + W_d = 6.8 \times 10^6$ sec$^{-1}$ which agrees very nicely with the value extracted from the donor fluorescence of $6.6 \times 10^6$ sec$^{-1}$. In order to extract $W_{d\rightarrow a}$ we now assume that $W_a = W_p$ based on the fact that the donor and acceptor ions are in very similar environments and that their distances to traps or satellite ions as well as their ion-lattice coupling strengths are almost identical. The nearly-temperature-independent$^{34}$ value of $W_d = W_p = (1.1 \pm 0.2) \times 10^6$ sec$^{-1}$ is then subtracted from $W_{d\rightarrow a} + W_d$ to evaluate $W_{d\rightarrow a}(T, \Delta \nu)$. For the data points discussed above, we have $W_{d\rightarrow a}(15 \text{ K}, -4 \text{ cm}^{-1}) = 5.7 \times 10^6$ sec$^{-1}$, with an estimate $0.5 \times 10^6$-sec$^{-1}$ error arising from the combined uncertainties in $W_{d\rightarrow a} + W_d$ and $W_a$.

Using this analytic technique, we have conducted an evaluation of the donor to acceptor transfer rate in the 6–20 K temperature range. Data was taken with the laser pumping 2 cm$^{-1}$ on the high-energy side of line center ($\Delta \nu = 2$ cm$^{-1}$) and 4 cm$^{-1}$ on the low-energy side ($\Delta \nu = -4$ cm$^{-1}$). The temperature and energy mismatch dependence of this transfer rate are illustrated in Fig. 7. This figure indicates the strong relationship of the transfer probability on sample temperature. Also important is the weak dependence on the magnitude and sign of $\Delta \nu$, the rates for $\Delta \nu = 2$ cm$^{-1}$ and $\Delta \nu = -4$ cm$^{-1}$ being almost identical within the experimental
FIG. 8. Power-law fit to the $A_3 \rightarrow A_4$ spectral-transfer rate. The straight line indicates a $T^{4.3}$ relationship.

error. These two facts are suggestive of the "one-phonon second-order" process. By plotting the results on log-log coordinates a power-law fit to the temperature dependence is obtained. The straight line in Fig. 8 indicates a relationship of

$$W_{A_3}(T) \approx (4.5 \pm 1.5) \times 10^1 \ T^{4.3 \pm 0.5} \ \text{sec}^{-1}.$$  

B. Transfer among the satellite ions

The excitation spectra of PrF$_3$ indicates the presence of several strong satellite lines accompanying the main $^{3}P_0 \rightarrow ^{3}H_4$ transition. By selectively exciting one of the unique sets of satellite ions, we observe the dynamics of the energy transfer to other sets of satellite ions. Here, the dye laser was used with a 1-cm$^{-1}$ spectral width since high resolution is not required.

The lowest-energy absorption is that of the $A_4$ ions at 4792.3 Å. With the dye laser tuned to this absorption, prominent fluorescence lines were observed at 4792.3, 4806.5, and 4811.0 Å ($T = 5.9$ K). The rise time of the fluorescence intensity is less than the 15-nsec instrumental response time. Because of this fast rise time and the close correlation with the expected wavelengths, these lines must then be components of the $^3P_0 \rightarrow ^{3}H_4$ transitions of the $A_4$ ions.

The next-higher-energy absorption is that of the $A_3$ ions at 4785.0 Å. With the dye laser now tuned to this absorption, a new set of fluorescence lines are observed. These are at 4784.9, 4799.8, and 4804 Å. Again the lines have rise times of less than 15 nsec, and are clearly the $^3P_0 \rightarrow ^{3}H_4_{1,2,3}$ transitions of the $A_3$ ions. In addition, as the $A_3$ ions are pumped the transitions of the $A_4$ ions are also observed, but now exhibit a markedly slower rise time. This rise time is characteristic of an energy-transfer process from the $A_3$ ions to the lower-energy $A_4$ ions.

The same rate equations are assumed for the intra- and intersatellite transfer as for the intraline transfer, with the donor and acceptor ions redefined as those comprising the $A_3$ and $A_4$ distributions, respectively. In Fig. 9 we illustrate the dynamics of the $A_3 \rightarrow A_4$ transfer process. The upper curve is the 4806.5 Å $^3P_0 \rightarrow ^{3}H_4_{2}$ fluorescence of the $A_4$ ions after direct excitation and is exponential over more than one decade. The lower curve is the same fluorescence of the $A_4$ ions following laser excitation of the $A_4$ ions. The growth of this fluorescence is given by $\Delta(t)$ and we illustrate this $\Delta(t)$ along with the temporal decay of the $A_3$ donor fluorescence in Fig. 10. The applicability of the simple rate equations is demonstrated by the exponential behavior in both Figs. 9 and 10.

To investigate the role of phonons in this 32-cm$^{-1}$ energy-transfer process from the $A_3$ sites to the $A_4$ sites, we consider the decay of the $A_3$ donor emission as compared to $\Delta(t)$ derived from the $A_4$ acceptor fluorescence.

FIG. 9. Dynamics of the $A_4$ emission for excitation of the $A_3$ and $A_4$ ions.

FIG. 10. Decay of the $A_3$ donor emission as compared to $\Delta(t)$ derived from the $A_4$ acceptor fluorescence.
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FIG. 11. Temperature dependence of the A₂→A₄ transfer process. The straight lines indicate [exp(ΔP/0.77)−1]⁻¹, where ΔP = 32 cm⁻¹ for W₄→₃+W₄ and 22 cm⁻¹ for W₆.

A₄ sites, we have analyzed the dynamics of the 4806.5-Å acceptor fluorescence at several different temperatures. The temperature dependence of the extracted rates is illustrated in Fig. 11. This weak temperature dependence and the fact that the energy mismatch between the A₄ and A₄ ions is 32 cm⁻¹, lead us to postulate that the responsible mechanism is the “one-phonon direct” process. Finally, in regard to the A₂→A₄ transfer, we note that in the temperature range studied, no A₂→A₄ transfer was observed since such a process would require the absorption of a 32 cm⁻¹ phonon.

We now turn to the other sets of ions observed in the excitation spectra. When the line center or A₄ sites are directly excited, the observed fluorescent lines increase in number. Qualitatively, the A₄→A₃ and A₄→A₄ transfer processes can be identified although their rates are much slower than the A₃→A₄ rate as indicated by the weak intensity of the A₃ and A₄ fluorescence. The large number of lines observed and their finite widths [especially the strong A₄ fluorescence to the (⁹H₄) and (⁹H₃) states] makes spectral isolation of the A₄→A₃ and A₄→A₄ transitions impractical.

The fluorescence spectrum when the A₁ and A₂ ions are directly pumped with the dye laser has also been observed. Their coupling to the A₄ and A₄ sites is strong as evidenced by the intensity of the A₁ and A₄ fluorescence with only a very weak A₄ fluorescence. At 6 K we measure a rate for W₄→₃+W₄ of 7.3 × 10⁷ sec⁻¹ for the A₁ sites and 6.7 × 10⁸ sec⁻¹ for the A₂ sites. No detailed temperature dependence was taken, but qualitatively the deexcitation rate for these ions is again only weakly temperature dependent.

C. Transfer in PrCl₃

We have also considered energy transfer in the PrCl₃ lattice. Here the Pr⁺⁺ ion sees a C₃h site symmetry, and hence, not all the 2J + 1 degeneracy is removed by the static crystal field. The ground state is now a doublet (twofold degenerate) as opposed to PrF₃ where all of the states are singlets.

The experimental techniques are similar to those used in the PrF₃ investigation. Much of the work was done however in a liquid-helium immersion Dewar where the sample temperature was about 2 K. The tendency of PrCl₃ to lase was minimized by defocusing the incident laser beam. Using either a 1-m grating spectrometer or a pressure-scanned high-resolution Fabry-Perot interferometer, the fluorescence lines originating from the ⁵P₆(μ = 0) and terminating on the ⁹H₄(μ = 3), ⁹H₄(μ = 2), or the ⁹F₄(μ = 2) were observed.

The measured linewidths for these various transitions were in essential agreement with those of German and Kiel, with transitions terminating on doublets significantly broader than the singlet lines. These authors have attributed the doublet widths to fluctuations modulating the doublet splitting far above the ordering temperature of ~0.4 K.

The important characteristic of the fluorescence transitions for our energy-transfer studies was the observation that the spectral location of the fluorescence did not change when the wavelength of the dye laser was shifted, nor were any spectral dynamics observed. We interpret our results as indicating that the transfer between Pr ions in this crystal is much faster than the 15-nsec response time of our detection system. This measurement allows us to put an upper limit on the single-ion to single-ion transfer time of about τ ≤ 5 × 10⁻⁸ sec at 2 K. This is almost three orders of magnitude faster than the extrapolated value for PrF₃ at 2 K for transfer within the main A₄ distribution.

VI. DISCUSSION

The spectral transfer within the inhomogeneously broadened A₁ ion distribution was experimentally characterized by a Tₚ⁻¹ temperature-dependent and energy-mismatch-independent transfer rate. Also important was the uniform rise of the full inhomogeneous emission profile with the dynamics described by simple rate equations. Before treating these observations, we first discuss the processes responsible for W₄ and W₆.
In order to separate the transfer rate $W_{e\alpha}$ from the measured values of $W_{e\alpha} + W_d$ we have assumed $W_d = W_{e\alpha}$ for the intraline transfer. In very low concentration systems, $W_d$ and $W_{e\alpha}$ represent radiative decay rates that are nearly constant across a reasonably narrow homogeneous line. Although this radiative decay rate may be somewhat higher in PrF$_3$ than the $2 \times 10^3$-sec$^{-1}$ rate measured$^{27,28}$ for LaF$_3$:Pr it is probably too low to account for either $W_d$ or $W_{e\alpha}$. A two-ion cross-relaxation process to the $^7G_{\alpha}$ manifold has been discussed by Brown et al.$^{27}$ as a relaxation channel for the $^3P_0$ state in LaF$_3$:Pr and such multi-ion transitions may be a dominant deexcitation process in concentrated Pr$^{3+}$ systems.$^{27}$ Using the PrF$_3$ energy levels,$^{19}$ a two-ion transition of the form $^3P_{0\alpha} - ^7G_{\alpha}$ requires the emission of a 160-cm$^{-1}$ phonon, and hence should be nearly temperature independent in the temperature region studied. A transfer to the $A_3$ and $A_4$ ions can also serve to deplete the $A_0$ distribution. Again, this process should have a weak temperature dependence due to the large (30 and 62 cm$^{-1}$) energy mismatches. In addition, since the $A_3$ and $A_4$ acceptor emission is weak upon excitation of the $A_0$ ions, a slow rate for this process is expected. Although our measurements do not establish the exact nature of the intrinsic donor and acceptor decay, their similar crystalline fields and energy levels support our assumption that $W_d = W_{e\alpha}$ for the intralinear transfer.

The dynamics for the intralinear transfer were well described by simple exponential rate equations. From Eq. (6), the decay of the $k$th donor ion is a solution to

$$\frac{dP_k(t)}{dt} = -P_k(t) \sum_j W_{kj} - P_k(t) \sum_m W_{kn} + \sum_j P_j(t) W_{kj},$$

where $W_{kj}$ and $W_{kn}$ are the incoherent spatial transfer and back-transfer rates and $W_{kn}$ is the two-ion cross-relaxation rate. For PrF$_3$, where every ion site is occupied by a Pr$^{3+}$ ion, it is the back-flow term that will lead to a nonexponential solution and not the donor configurational averaging. It can be shown$^{28}$ that by including the back transfer from the first set of nearest-neighbor acceptors, an approximate solution at short delays to Eq. (11) is

$$P_k(t) = \exp\left(\sum_m - W_{km}\right) \times \exp\left(\sum_j - W_{kj} + \ln(\cosh W_{kj})\right).$$

Using the lattice structure of PrF$_3$ and assuming that $W_{kj} = W_0(R_{o\alpha}/R_{kj})^6$ and $W_{kn} = W_0(R_{o\alpha}/R_{kn})^6$, where $R_0$ is the nearest-neighbor separation and $W_0$, $W_0'$ are chosen to model our measured decay probability, our computer computations indicate that Eq. (12) does not significantly deviate from an exponential over the first 1.5 decades. We feel these results model well the observed exponential transfer dynamics, and thereby justify their description by simple rate equations [Eqs. (7) and (8)].

The spectral characteristics of the transfer within the $A_0$ distribution are described by the uniform decay of the donor-emission profile and a uniform growth of the full $A_0$ inhomogeneous line shape. This observation is consistent with the weak dependence of the "one-phonon second-order" process on the energy mismatch. Also important is the energy distribution of acceptors around the initially excited donor ion. Our spectral observations are explained by assuming that the average donor ion is surrounded by an ensemble of acceptors, the majority of whose energy states span the full inhomogeneous line shape.

The origin of the inhomogeneous broadening of the $A_0$ ions is the presence of lattice defect centers mentioned previously. Ions closest to the defect centers are presumably the strongly perturbed satellite ions. Ions slightly further out may lie in the broad background observed in the excitation scan. Going out a few more lattice spacings away from the defect center, the ions belonging to $A_0$ distribution are encountered. The energy of the $j$th $A_0$ ion can be written as

$$E_j = E_j^0 + \sum_i \langle \phi_i | V(\vec{R}_n - \vec{R}_j) | \phi_j \rangle,$$
energy. Recent energy-transfer measurements in dilute ruby\textsuperscript{7,8} appear to show that a coherent spatial diffusion coexists with the slower spectral transfer, suggesting a less-than-random distribution in energy. Since there is no evidence at present to support the existence of spatial transfer as distinct from the observed spectral transfer in PrF\textsubscript{3}, we shall ignore these effects and assume that a microscopic randomness occurs in this system.

In Fig. 12 we illustrate the temperature dependence of the intraline transfer in PrF\textsubscript{3} along with those for 5\% LaF\textsubscript{3}:Pr\textsuperscript{3+} (Ref. 3) and 20\% LaF\textsubscript{3}:Pr\textsuperscript{3+} (Refs. 4 and 41) which are shown with a fit to a T\textsuperscript{-3} dependence. The somewhat steeper relationship for the PrF\textsubscript{3} curve arises from the phonon-phase terms \( \langle k \rangle \) of Eqs. (4) and (5). For a fixed value of \( k \) and \( k' \), as the ion-ion separation decreases the temperature dependence changes from T\textsuperscript{-2} for \( kR \) and \( k'R \ll 2\pi \) to a T\textsuperscript{-1} relationship when \( kR \) and \( k'R \ll \frac{1}{2} \pi \).\textsuperscript{12} We have completed a more detailed calculation of the temperature dependence for this process by integrating Eq. (4) using a Debye phonon spectrum. The results\textsuperscript{22} indicate a nearly T\textsuperscript{-1} dependence for PrF\textsubscript{3} as compared to the measured T\textsuperscript{-4} relationship. The calculated temperature dependence is very sensitive to the detailed nature of the phonon spectrum which may explain this discrepancy. We feel that the T\textsuperscript{-4} relationship for the 5\% and 20\% LaF\textsubscript{3}:Pr\textsuperscript{3+} and the slightly steeper T\textsuperscript{-4} fit to the PrF\textsubscript{3} results demonstrate the role of the phonon-phase terms in the "one-phonon second-order" transfer process.

The intersatellite transfer between the \( A_3 \) and \( A_4 \) ions was experimentally characterized by a weak dependence of \( W_{A_3} + W_{A_4} \) on sample temperature and again, simple rate equations for the temporal evolution of the donor and acceptor emission. For this problem, however, the separation of the transfer rate from \( W_{A_3} + W_{A_4} \) is more difficult than for the intraline transfer since the acceptor decay rate now shows a measurable temperature dependence. Due to the shifted energy levels the energy mismatch may be altered from the line-center values, causing a different temperature dependence of the \( A_3 \) and \( A_4 \) ions for a cross-relaxation process. Nearby lattice defects may also serve to quench the donor and acceptor emission. The dissimilar lattice environments of the \( A_3 \) and \( A_4 \) ions is further reason for not allowing us to assume \( W_{A_3} = W_{A_4} \). Although the temperature dependence of \( W_{A_3} \) and \( W_{A_4} \) might not be identical, it is clear from Fig. 11 that if they are roughly the same, subtracting a slowly rising form for \( W_{A_3} \) from \( W_{A_3} + W_{A_4} \) should put \( W_{A_3} \) on a curve similar to that expected for a one-phonon direct process involving a 32-cm\textsuperscript{-1} energy mismatch.

We have also pumped into the wing of the \( A_3 \) satellite ion absorption to measure the spectral transfer among the \( A_3 \) ions. No transfer to the center of the \( A_3 \) emission profile was observed and an upper limit of 0.5 \times 10\textsuperscript{5} sec\textsuperscript{-1} was placed on the \( A_3 \rightarrow A_3 \) transfer rate compared to the \( A_3 \rightarrow A_4 \) rate of approximately 10 \times 10\textsuperscript{5} sec\textsuperscript{-1} and the \( A_3 \rightarrow A_5 \) rate of 2 \times 10\textsuperscript{6} sec\textsuperscript{-1} at 10 K. This suggests that the spatial separation between the \( A_3 \) ions is larger than the \( A_3 \rightarrow A_4 \) or \( A_3 \rightarrow A_5 \) separation.

These results are consistent with a model where the different satellite lines arise from Pr\textsuperscript{3+} ions located at different distances or orientations from the same impurity, interstitial, or vacancy defect. This model is similar to that used by Green et al.\textsuperscript{43} in MnF\textsubscript{2}, where a one-to-one correspondence can be established between the distance of a Mn ion from an impurity and its energy levels. We can also use this model to explain the exponential transfer dynamics between the \( A_3 \) and \( A_4 \) ions. The probability of finding the \( k \)th \( A_3 \) donor ion excited at time \( t \) can be found from

\[
\frac{dP_k(t)}{dt} = -P_k(t)\sum_j W_{kj} - P_k(t)\sum_i W_{ik} \tag{14}
\]

where we have neglected the slow single-ion decay rate. Here, \( W_{kj} \) is the \( A_3 \rightarrow A_j \) transfer rate, \( W_{ik} \) is the two-ion cross-relaxation rate and we have set
the $A_4 \rightarrow A_3$ back-transfer rate to zero. The solution is simply

$$P_3(t) = \exp \left( -\sum_j W_{kj} + \sum_{kn} W_{kn} \right). \quad (15)$$

We must now average over all the $A_3$ donor environments. Assuming a fixed $A_3 \rightarrow A_4$ separation and noting that all $A_3$ ions are uniformly surrounded by other Pr$^{3+}$ ion to which they can cross relax, then the configurational average of Eq. (15) becomes

$$\langle P_3(t) \rangle = \exp \left( -\sum_j W_{kj} + \sum_{kn} W_{kn} \right)$$

$$= \exp \left( -W_{k'j} + W_{kj} \right), \quad (16)$$

which is the form of our simple rate equations for the donor ($A_3$) fluorescence.

Using the weak temperature dependence of the $A_3 \rightarrow A_4$ transfer rate and its large (32 cm$^{-1}$) energy mismatch, we have identified the dominant transfer mechanism as the one-phonon direct process. A calculation of the magnitude transfer rate using Eq. (1) is most difficult due to a lack of knowledge about the relevant ion-lattice matrix elements. Making a long-wavelength approximation ($kR \ll 2\pi$) and assuming $(\Delta f^{(1)} - \Delta f^{(2)})^2 = 1 \times 10^9$ cm$^{-2}$ and a dipolar coupling strength of $J = 7 \times 10^2$ cm$^{-1}$ our estimate for the transfer probability is over an order of magnitude slower than the measured rate. This comparison must be viewed in light of the necessarily crude assumptions needed to complete the calculation.

Our results in PrCl$_3$ indicate a very rapid transfer process in this system. Our lower limit of $W \geq 2 \times 10^7$ sec$^{-1}$ at 2 K compares with the values of $10^7$ sec$^{-1}$ deduced by Krauts and Moos and the faster $7 \times 10^6$ sec$^{-1}$ extrapolated by Gandrud and Moos. The similar ion-lattice coupling for PrF$_3$ and PrCl$_3$ suggests a much larger ion-ion interaction strength in the latter system. For this situation, an excitonic description of the optically active ions may be more appropriate.

At present we are unable to determine whether the width of the singlet $^3P_0 - ^3H_6(\mu = 3)$ transition, 0.5 cm$^{-1}$, arises mainly from residual inhomogeneous broadening or reflects a true exciton bandwidth. If the latter were solely responsible a dispersion of 0.5 cm$^{-1}$ would indicate a coherent interion transfer rate of $10^{10}$ sec$^{-1}$ assuming six nearest neighbors. This is certainly consistent with the larger of the above estimates. However, since the presence of defects and other rare-earth impurities are likely to contribute to a residual width also of this order, it is likely that there is both an inhomogeneous and a dispersive component to the linewidth. Their relative magnitudes must await further experimentation with lower-concentration samples.

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33Using the spectrometer to deconvolute the donor and acceptor emission requires the excitation be far enough into the wing of the line where the acceptor concentration is minimal.
34The 15-K value of $W_d$ was measured as $(1.3 \pm 0.2) \times 10^8$ sec$^{-1}$.
41The 20% curve is an average of the points measured in Ref. 4.
42Also, for $1/2kR$ or $1/2kR \approx \pi$, an additional spatial dependence for the transfer rate arises from these phase terms.