Comments and Addenda

Fluorescence linewidths and energy transfer in LaF$_3$(Pr^{3+}, Nd^{3+})[†]

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Fluorescence line narrowing is used to study nonresonant linewidths in the doubly doped LaF$_3$(Pr^{3+},Nd^{3+}) system. The linewidths from the $^3P_0$ to the bottom of the $^3H_6$, $^3H_5$, and $^3F_2$ Stark manifolds are found to increase with Nd^{3+} concentration. This increase is attributed to a residual strain broadening of the narrowed nonresonant transitions and not to a lifetime broadening of the terminal states, as originally assumed. The change in the temporal decay of the $^3P_0$ state with Nd^{3+} concentration is used to discuss the Pr-Nd interaction.

I. INTRODUCTION

The homogeneous and inhomogeneous broadening of spectral lines in 4f and 3d impurity ions in crystalline hosts have been extensively studied over the last decade.[1] With the advent of high-resolution dye lasers, the technique of fluorescence line narrowing[2] (FLN) has recently been applied to these systems to increase our understanding of the ion-ion and ion-ligand interaction.[3-5] FLN is used to reduce the effect of inhomogeneous broadening (and to completely eliminate it for resonant optical transitions, i.e., fluorescence back to the ground state).

II. EXPERIMENTAL DETAILS

We have used FLN to review fluorescent linewidths in the doubly doped LaF$_3$(Pr^{3+}, Nd^{3+}) system. The relevant energy levels for[1] LaF$_3$(Pr^{3+}) and[6] LaF$_3$(Nd^{3+}) are illustrated in Fig. 1. The $^3P_0$ state of Pr^{3+} was directly excited with a pulsed tunable dye laser having a 1.5-GHz spectral width. The resulting fluorescent linewidths to the bottom of the $^3H_5$, $^3H_6$, and $^3F_2$ Stark manifolds[7] for samples containing 1-mole% Pr^{3+} and varying concentrations of Nd^{3+} were measured with either a 1-m grating spectrometer or a pressure scanned Fabry-Perot interferometer. The signals were processed with conventional gated electronics. Sample temperatures were maintained at 9 K in a variable-temperature optical cryostat.

III. LINEWIDTH RESULTS AND DISCUSSION

A previous investigation of this system[8] with broadband lamp excitation revealed an increasing Lorentzian component of the $^3P_0 \rightarrow (^3H_6)_1$ linewidth with increasing Nd^{3+} concentration. This increase was thought to arise from a spin-exchange interaction resulting in the $|(^3H_6)_1; (^4I_{9/2})_1\rangle \rightarrow |(^3H_5)_1; (^4I_{11/2})_2\rangle$ transition.[9] If the transition rate of this cross-relaxation process is comparable to phonon relaxation rates, or to the inverse of the inhomogeneous linewidth, then it will give an observable homogeneous contribution to the $(^3H_6)_1$ linewidth. The high probability for this cross-relaxation mechanism was explained by a strong exchange coupling between impurity ions and the inordinately small value of the energy separation between the $|(^3H_6)_1; (^4I_{9/2})_1\rangle$ and $|(^3H_5)_1; (^4I_{11/2})_2\rangle$ states.

For LaF$_3$ crystals containing molar percentages of 1% Pr^{3+}; 1% Pr^{3+}, 0.5% Nd^{3+}; and 1% Pr^{3+}, 2% Nd^{3+}, the linewidths under narrow-band laser excitation at 9 K are shown in Table I. These widths are significantly narrower than similar transitions in comparably doped crystals pumped broadband. [The $^3P_0 \rightarrow (^3H_6)_1$ broadband-pumped linewidth is approximately 0.7 cm^{-1} in LaF$_3$ (1% Pr).] For each of the three transitions the fluorescent linewidth increases with Nd^{3+} concentration. We cannot explain the increasing width of *each* of the lines as arising from spin-exchange-induced lifetime broadening of the terminal state, as near resonant
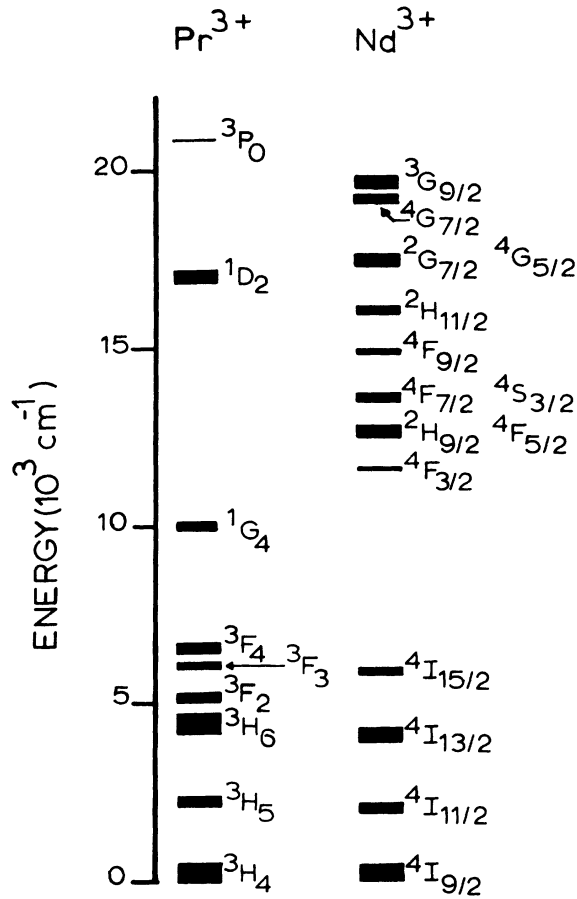
FIG. 1. Energy levels for $LaF_3(Pr^{3+})$ and $LaF_3(Nd^{3+})$.

conditions exist only for the $|(^3H_6)_1; (^4I_{9/2})_1\rangle$
$\rightarrow |(^3H_5)_1; (^4I_{11/2})_2\rangle$ transition. We therefore must
assume that a different mechanism predominates.

For an inhomogeneously broadened system we
can select a set of ions with excited-state ener-
gies within the homogeneous linewidth by excita-
tion with a sufficiently narrow spectral source.
These ions may, however, be at inequivalent lat-
tice sites. This accidental coincidence results
from the multiparameter description of the local
crystalline potential. The distribution of the in-
termediate levels for this set of ions will not nec-
essarily coincide within a homogeneous width.

TABLE I. Linewidths from $^3P_0$ to various terminal
states (cm^{-1}).

Sample	$(^3H_5)_1$	$(^3H_6)_1$	$(^3F_2)_1$
$1 - mole\%\ Pr^{3+}$	0.65	0.34	1.8
$1 - mole\%\ Pr^{3+}, 0.5 - mole\%\ Nd^{3+}$	0.98	0.56	2.2
$1 - mole\%\ Pr^{3+}, 2 - mole\%\ Nd^{3+}$	2.0	0.90	3.1

Thus the nonresonant fluorescence to some inter-
mediate state will in general have an inhomogene-
ous residual width. The residual width is corre-
lated with the amount of local strain broadening.
For example, the residual width of the $^3P_0 \rightarrow (^3H_6)_1$
fluorescence, as well as the full inhomogeneous
linewidth in $LaF_3(Pr^{3+})$, has been shown to in-
crease markedly with Pr^{3+} concentration.[3,5] Such
residual widths are also observed in glassy host
materials.[10,11]

This effect becomes clear if we consider an in-
homogeneously broadened system with ground
state $|g\rangle$, excited state $|e\rangle$, and any intermediate
state $|k\rangle$. By pumping the excited state with a
very narrow laser, we can pick out those ions
with identical (to within the laser plus homogene-
ous width) excited state energies. Consider two
such ions labeled 1 and 2. Thus we require that

$$E_1^e = E_2^e, \tag{1}$$

or

$$E^e + \langle e | V_1 | e \rangle = E^e + \langle e | V_2 | e \rangle, \tag{2}$$

where E^e is the free-ion energy and V_j is the local
crystal potential energy at the location of ion j.
Thus we have

$$\langle e | V_1 | e \rangle = \langle e | V_2 | e \rangle. \tag{3}$$

The crystal potential energy at ion j can be ex-
pressed as

$$V_j = \sum_i \sum_{k,q} A_j^{q,k} r^{k,i} Y_k^q(\theta_i, \phi_i),$$

where the summation is over $0 \le k \le 6$ (for $4f$ elec-
trons), $|q| \le k$, and all $4f$ electrons (i). We em-
phasize the point that Eq. (3) does *not* necessarily
imply that $A_1^{q,k} = A_2^{q,k}$ and thus in general

$$\langle k | V_1 | k \rangle \ne \langle k | V_2 | k \rangle. \tag{4}$$

When ions 1 and 2 undergo radiative transitions to
state $|k\rangle$, the difference in energies between pho-
tons emitted by ions 1 and 2 is

$$\hbar\omega_1 - \hbar\omega_2 = \langle k | V_1 | k \rangle - \langle k | V_2 | k \rangle. \tag{5}$$

In general, the differences between $A_1^{k,q}$ and $A_2^{k,q}$
require that $\hbar\omega_1 \ne \hbar\omega_2$. Thus, by considering a
large number of ions, there will be a distribution
of photons emitted during the $|e\rangle$ to $|k\rangle$ transition,
i.e., a residual inhomogeneous broadening. This
is the accidental coincidence effect. Note that for
the resonant $|e\rangle$ to $|g\rangle$ transition, this effect will
be absent. In this latter case, however, we
might point out that the *homogeneous* linewidth ob-
served is not that of a particular ion site but rath-
er a width averaged over all the accidentally coin-
cident sites.

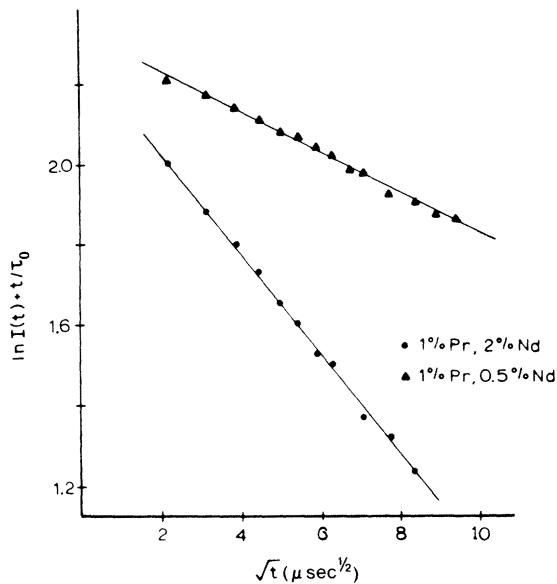We feel that it is just the residual width of these

FIG. 2. Decay of the $^3P_0$ state assuming a dipole-dipole interaction.

nonresonant transitions that increases with Nd^{3+} concentration, and thereby reflects the additional strain broadening introduced by the Nd^{3+} ions. Each of the three transitions show this increase, although lines that are partially homogeneously broadened will be affected less. Although the line shape for these residual widths is expected to be Gaussian, the presence of satellite lines[1,5,12] complicates the actual line shape, often resulting in quasi-Lorentzian wings.

IV. ENERGY TRANSFER

The temporal decay of the $^3P_0$ state was also measured for this set of samples. The observed nonexponential behavior indicates an ion-ion non-radiative relaxation mechanism. The decay curves were fit to the formula of Inokuti and Hirayama[13] for multipolar coupling

$$I(t) = I_0 e^{-t/\tau_0} \exp[-(t\omega_s)^{3/s}],$$

where τ_0 is the radiative lifetime and s reflects the dominate term in the multipolar expansion of the ion-ion Hamiltonian. A slightly better fit was obtained for $s = 6$ (dipole-dipole) than for $s = 8$ (di-

pole-quadrapole) or $s = 10$ (quadraple-quadrapole). Representative decays plotted for a dipolar interaction are shown in Fig. 2.

A comparison of ω_s for $s = 6$, 8, and 10 is given in Table II. The Pr-Pr interaction ($\omega \sim 0.5 \times 10^3$ sec^{-1}) obtained on the 1-mole% singly doped crystal is assumed to be independent of the Nd concentration and has been subtracted to give the Pr-Nd transfer rates. The expected ratio of the transfer rates is just the ratio of the Nd (acceptor) concentrations raised to the $s/3$ power. The agreement with the measured ratio is best for the dipolar case. Considerations such as covalency, shielding by outer-shell orbitals, and induced moments may complicate the simple electric multipole expansion of the ion-ion interaction[14] and will modify the dependence of the transfer rate on the acceptor concentration. We interpret the poor agreement of our transfer rate ratios to the expected values as an indication of the possible importance of these effects.

The actual transfer process is a cross-relaxation mechanism that serves to deplete the $^3P_0$ population. The donor ion makes a nonradiative transition to some intermediate state, and simultaneously an acceptor ion makes a transition into one of its excited states. Energy transfer within the donor-system state has been shown to be van-ishing small at these temperatures and concentrations.[3] The observed gentle variation of the transfer rate with temperature indicates that this cross-relaxation process is mediated by multiphonon emission: The transfer rate for such a process can be written[15]

$$W \propto f_a f_b e^{-\beta(\Delta\epsilon)},$$

where f is the oscillator strength, β is related to the multiphonon orbit-lattice relaxation rate,[15,16] and $\Delta\epsilon$ is the energy of the emitted phonons required by energy conservation. There are ten decay schemes for the Pr-Nd cross relaxation with multiphonon emission less than 2000 cm^{-1}, as compared to two for the Pr-Pr case. Given similar oscillator strengths in both systems ($f \sim 10^{-6}$),[17] larger Pr-Nd cross-relaxation rate is easily accounted for.

The Pr-Nd transfer rates are also of the same order of magnitude of those in $LaCl_3(Pr^{3+}; Nd^{3+})$

TABLE II. $Pr^{3+}-Nd^{3+}$ transfer rates (10^3 sec^{-1}).

S	ω_s (1 − mole% Pr^{3+}, 2 − mole% Nd^{3+})	ω_s (1 − mole% Pr^{3+}, 0.5 − mole% Nd^{3+})	Ratio	Expected ratio
6	17 ± 2	2.2 ± 0.5	7.7 ± 2.7	16
8	31 ± 4	3.1 ± 0.6	$10 \ \pm 3.3$	40
10	67 ± 7	3.9 ± 0.8	$17 \ \pm 5.9$	101

for decays originating from the $^3F_3$ state.[18] The variation of transfer rates with phonon-ion coupling strengths, oscillator strengths, the number of phonons emitted during the transfer process, and the number of possible decay schemes makes any quantitative comparison difficult.

V. CONCLUSIONS

Our linewidth measurements demonstrate the care that is needed in the interpretation of fluorescence line shapes. Even under FLN conditions, it is only the resonant transition back to the ground state which reflects the true homogeneous linewidth, particularly for low-symmetry crystals. The combined effects of accidental coincidence and nearby satellite lines may make any analysis of nonresonant line shapes meaningless.

From our present results and previous work,[3,4] we conclude that multipolar energy-transfer rates are typically too small to contribute to lifetime broadening. However, such transfer processes are easily studied by the temporal decay of the initially excited ions: nonexponential behavior is generally an indication that an ion-ion transfer process is active, but overlapping satellite lines with differing lifetimes may complicate the analysis.[5,19]

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