Radiative and nonradiative transitions of Pr^{3+} in trichloride and tribromide hosts

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We have measured the fluorescent decay rates of the ^3P states of the Pr^{3+} ion in trihalide crystals as a function of temperature. When extrapolated to 0 K we find that the fluorescent lifetimes of $^3P_0$ are 14.7 ± 1.0 μsec ($Pr_{0.01}La_{0.99}Cl_3$), 11.5 ± 1.5 μsec ($PrCl_3$), 12.0 ± 1.0 μsec ($Pr_{0.01}La_{0.99}Br_3$), and 1.0 ± 0.12 μsec ($PrBr_3$). By combining the fluorescent decay rates with measurements of the quantum efficiency we have been able to extract the rate for nonradiative transfer of excitation between $^3P_1$ and $^3P_0$ in the dilute crystals and have found the results in reasonable agreement with a multiple-optical-phonon transition model. In $Pr_{0.01}La_{0.99}Br_3$ we have observed both fluorescence and laser action from the $^3P_2$ state, although this state has not previously been observed in emission in any host. Finally, we present a summary of the laser transitions which we have observed in these hosts.

I. INTRODUCTION

In an earlier paper[1] (hereinafter referred to as GK) we investigated certain radiative and nonradiative decay processes involving the ^3P states of the Pr^{3+} ion in the trichlorides $PrCl_3$ and $Pr_{0.01}La_{0.99}Cl_3$. Specifically we measured decay rates from $^3P_0$ and $^3P_1$ and set a lower limit on the nonradiative decay rate of the fast relaxing $^3P_2$ states. In this paper we present our work on the analogous tribromide system as well as the results of some extended measurements on the trichlorides.

The analysis of nonradiative decay processes in low-concentration crystals has generally centered on multiphonon relaxation.[2-5] For example, both the $^3P_1$ and $^3P_2$ states of Pr^{3+} in $Pr_{0.01}La_{0.99}Cl_3$ decay quite rapidly by a three-optical-phonon process across an energy gap of ~600 cm⁻¹ (see Fig. 1). In simplified form the n-phonon relaxation rate between states separated in energy by ΔE may be expressed as[5]

$$w^{(n)} = A\alpha^{n-1}\rho_n(1 - e^{-\epsilon_p/kT})^{-n} , \tag{1}$$

where ρ_n is a joint density of phonon-ion states, ϵ_p is the optical-phonon energy, n is the number of phonons required for the process ($n \approx \Delta E/\epsilon_p$), A is a constant, and α is a number proportional to the square of the ratio of the lattice-ion interaction energy to the energy gap. This expression has been tested qualitatively in a number of cases[5] by observing the lifetimes of different states in the same ion-crystal system (ΔE varies) or the lifetime of the same state in different crystals (ϵ_p and α vary). The comparison of relaxation rates between the trichlorides and the tribromides affords us the unique opportunity to study relaxation rates when only ϵ_p changes markedly. This is due to the fact that $LaCl_3$ and $LaBr_3$ have identical symmetry and

nearly equal lattice spacings. Observation of the Pr^{3+} spectrum indicates that the crystal-field splittings (at least those dominated by second- and fourth-order harmonics) are nearly the same in the two cases. The major difference then is that the maximum of the optical-phonon density in $LaBr_3$ is ~150 cm⁻¹ compared to 210 cm⁻¹ in $LaCl_3$.[6,7] Thus, a three-phonon process in the latter crystal would become a four- or five-phonon process in the tribromide.

Thus, one would predict that the $^3P_1$ state, which has a rather poor fluorescent quantum efficiency in the trichloride, should be much more efficient in the tribromide. Similarly the $^3P_2$ state, which had never been observed in fluorescence in any material, may fluoresce in the bromide. Indeed, both of these expectations were confirmed in the course of this work.

II. EXPERIMENT

The experimental apparatus is basically the same as described in GK. Briefly, it consists of a tunable pulsed dye-laser excitation source (pulse width ~4 nsec), a variable-temperature Dewar to hold the crystal, and a spectrometer with a photomultiplier connected to a boxcar integrator. The dye laser was used to selectively excite the $^3P_0$, $^3P_1$, $^1I_6$, and $^3P_2$ states. The fluorescence observed could be either from the state directly excited or from some lower-energy state to which the excitation relaxed.

The fluorescent lifetimes were measured by plotting the intensity-versus-time data obtained from the boxcar on semilog paper and performing a best fit to the data. The sensitivity was such that the time scanned corresponded to two to three lifetimes of the transition. To prevent stimulated emission with a consequent apparant shortening of the lifetime, it was often necessary (particularly at
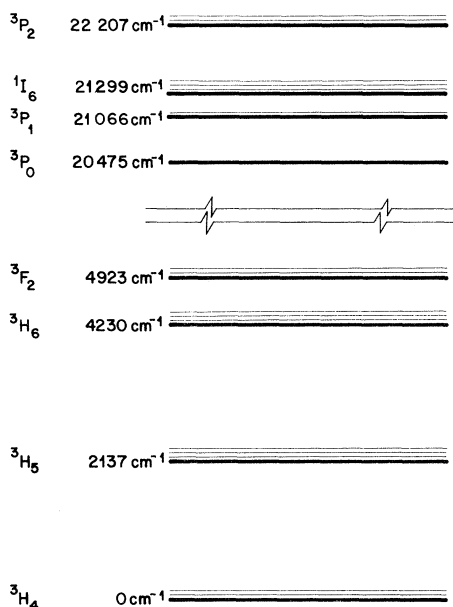
FIG. 1. Partial energy-level diagram for Pr^{3+} in $Pr_{0.01}La_{0.99}Cl_3$. The $^1D_2$, $^1G_4$, $^3F_3$, and $^3F_4$ levels are not shown but lie between $^3P_0$ and $^3F_2$. There are small shifts (≤ 100 cm^{-1}) in the energies of the manifolds for the concentrated crystal and for the bromides.

low temperatures) to greatly reduce the excitation flux. This, of course, diminished the available sensitivity of the experiment.

In order to partition the observed fluorescent decay rates into radiative and nonradiative components it was necessary to measure the quantum efficiency of the fluorescing level. Absolute-quantum-efficiency measurements are always complicated by scattering and geometrical factors and, occasionally, as in the present case, by reabsorp-
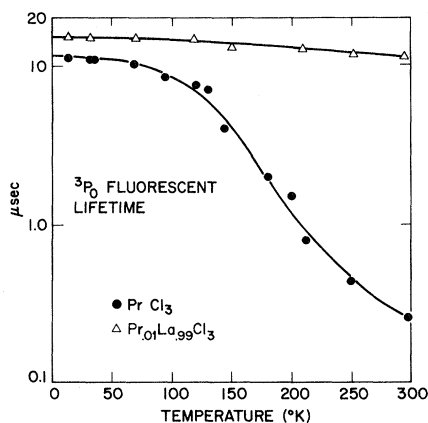

FIG. 2. Variation of the $^3P_0$ fluorescent lifetime of Pr^{3+} with temperature and concentration in the trichloride lattice.
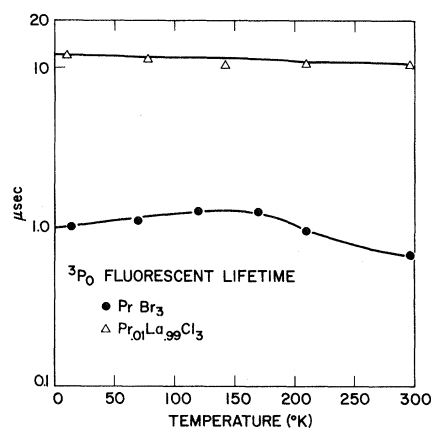

FIG. 3. Variation of the $^3P_0$ fluorescent lifetime of Pr^{3+} with temperature and concentration in the tribromide lattice.

tion. Fortunately, to measure the nonradiative relaxation rate from $^3P_1$ to $^3P_0$ it was necessary to measure only the ratio of fluorescence intensity from $^3P_0$ under direct excitation to $^3P_0$ as compared with excitation to $^3P_1$.

III. RESULTS

A. Dilute crystals

1. $^3P_0$ state

The fluorescent lifetimes of the $^3P_0$ state as a function of temperature for both $Pr_{0.01}La_{0.99}Cl_3$ and $Pr_{0.01}La_{0.99}Br_3$ are plotted in Figs. 2 and 3, respectively. An extrapolation to 0 K gives a lifetime of 14.7 ± 1 μsec for the trichloride and 12.0 ± 1 μsec for the tribromide. In both cases there is a small thermal dependence corresponding to a less than 20% change in the lifetime at room temperature. Part or all of this effect could be due to a small change in the radiative transition rate arising from a variation in the lattice constants with temperature. From this modest change with temperature, the relative brightness of the fluorescence, and the lack of fluorescence from states of lower energy, we conclude that the $^3P_0$ state is essentially 100% quantum efficient for temperatures ≤ 300 K. This is what one would expect for low-concentration crystals since the nearest energy level is ~ 3500 cm^{-1} below $^3P_0$ (or 16 times the optical-phonon energy).

2. $^3P_0$ state

The $^3P_1$ state lies about 600 cm^{-1} above $^3P_0$ (see Fig. 1). When $^3P_1$ is selectively excited, fluorescence from both $^3P_0$ and $^3P_1$ is observed in the tribromide as well as the trichloride. The $^3P_0$ emission in this case is attributed[1] to a multiphonon relaxation from $^3P_1$ to $^3P_0$ and was significantly more intense in $LaCl_3$ than in $LaBr_3$.
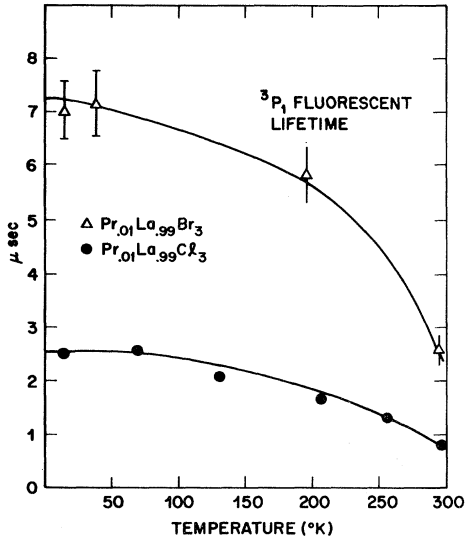
FIG. 4. Fluorescent decay lifetimes of the $^3P_1$ state in $Pr_{0.01}La_{0.99}Cl_3$ and $Pr_{0.01}La_{0.99}Br_3$. In concentrated crystals the $^3P_1$ state did not fluoresce.

In Fig. 4 the variation of fluorescent lifetime of $^3P_1$ with temperature is plotted for both crystals. The values obtained at 0 K are $\tau = 2.5$ μsec for $LaCl_3$ and $\tau = 7.2$ μsec for $LaBr_3$. If the fluorescent lifetime τ is written as a sum of radiative, τ_R, and nonradiative, τ_{NR}, components we have

$$\tau^{-1} = \tau_R^{-1} + \tau_{NR}^{-1} \ , \tag{2a}$$

$$\tau_{NR}^{-1} = \tau_P^{-1} + \tau_Q^{-1} \ , \tag{2b}$$

where τ_{NR} is also partitioned into a transfer component τ_P which consists only of relaxation from $^3P_1$ to $^3P_0$ and a component τ_Q embodying all other nonradiative decay from $^3P_1$. The quantum efficiency of fluorescence from $^3P_0$ when $^3P_1$ is pumped is now just

$$\phi = \tau/\tau_P \ , \tag{3}$$

while as we stated earlier the quantum efficiency of $^3P_0$ when excited directly is assumed to be unity. Consequently, if we measure the ratio of intensity of $^3P_0$ fluorescence for excitation to $^3P_1$ relative to that obtained when exciting $^3P_0$ directly we have a value for ϕ. The results of these measurements are

$$\phi = 0.83 \pm 0.03 \ \text{for} \ LaCl_3$$

and

$$\phi = 0.20 \pm 0.03 \ \text{for} \ LaBr_3 \ .$$

By inserting the values for τ from Fig. 4 we find

$$\tau_P = 3.1 \pm 0.3 \ \mu\text{sec} \ (LaCl_3) \ , \tag{4a}$$

$$\tau_P = 15 \pm 3 \ \mu\text{sec} \ (LaBr_3) \ . \tag{4b}$$

In GK we used Dorman's[8] values for the oscillator

strength of $^3P_1$ to compute τ_R, which when combined with Eq. (2b) gives for $LaCl_3$

$$\tau_{NR} = 2.8 \pm 0.2 \ \mu\text{sec}. \tag{5a}$$

Since the values given in (4a) and (5a) overlap our measurements are consistent with $\tau_Q^{-1} = 0$. We would expect $\tau_Q^{-1} = 0$ for dilute crystals for the same reason we expect 100% quantum efficiency for $^3P_0$ as outlined at the end of the Appendix. However, if we assume that τ_R for $LaBr_3$ scales in the same way as the change in the radiative lifetime of $^3P_0$ for the two crystals we have for the tribromide

$$\tau_{NR} = 9 \pm 2 \ \mu\text{sec}. \tag{5b}$$

This result is outside the range of Eq. (4b) and would imply a τ_Q of 36 μsec, contrary to the chloride case. This perplexing result led us to a more critical analysis of some of the values of the oscillator strength tabulated in Ref. 8.

Under closer scrutiny it became apparent that some of the oscillator strengths were in disagreement with the predictions based on the highly successful Judd[9] theory of forced electric dipole transitions. Specifically, the reported transitions to $^3F_3$ and $^3F_4$ were anomalously weak and the transition rate from $^3P_1$ to the ^3H manifold was significantly smaller than for $^3P_0$ to ^3H instead of being nearly equal as expected from Judd's theory (and atomic theory as well).

In the Appendix we outline the theory of electric dipole transitions in ionic crystals with special emphasis on the Judd theory.[9] Our conclusion, based on this analysis, is that there is a systematic underestimate of the oscillator strength of transitions from $^3P_1$ and of the $^3P_0$-$^3F_4$ transition, with the result that the lifetime of $^3P_0$, as determined from these oscillator strengths, should be 20% shorter; and the radiative lifetimes of $^3P_0$ and $^3P_1$ are approximately equal. From Table II, we obtain a radiative lifetime of $^3P_0$ in $LaCl_3$ of 15 μsec, which is in very good agreement with our observation of 14.7 ± 1 μsec.

From the stated equality of the radiative rates of $^3P_0$ and $^3P_1$ we conclude that $\tau_R = 15$ μsec in $LaCl_3$ and 12 μsec in $LaBr_3$. Consequently from Eq. (2a) we now obtain

$$\tau_{NR} = 3.0 \pm 0.2 \ \mu\text{sec} \ (LaCl_3) \ , \tag{6a}$$

$$\tau_{NR} = 18 \pm 3 \ \mu\text{sec} \ (LaBr_3) \ . \tag{6b}$$

In both cases the agreement with Eqs. (4a) and (4b) is sufficient to conclude that $\tau_Q^{-1} \approx 0$. Therefore we can state that in both the trichloride and the tribromide $^3P_1$ decays nonradiatively only to $^3P_0$, and that τ_P is 5 to 6 times longer at 0 K in the tribromide than in the trichloride, consistent with the higher-order process required.

The temperature dependence of the multiphonon

relaxation rate gives us an important clue to the order n of the process. From Eq. (1) we would calculate that the temperature dependence of the phonon-induced decay is given by

$$\tau_{NR}^{-1}(T) = \tau_{NR}^{-1}(0)(1 - e^{-\epsilon_p/kT})^{-n} \quad . \tag{7}$$

For LaCl$_3$ where $n = 3$ this would imply that

$$\tau_{NR}^{-1}(300\ K)/\tau_{NR}^{-1}(0\ K) = 4 \quad . \tag{8a}$$

The experimental values taken from Fig. 4 and corrected for the radiative decay of $^3P_1$ give

$$\tau_{NR}^{-1}(300\cdot K)/\tau_{NR}^{-1}(0\ K) = 3.9 \pm 0.5 \quad , \tag{8b}$$

which is in excellent agreement for the assumed three-phonon process. For LaBr$_3$, however, $\epsilon_p \approx 150$ cm^{-1} and $\Delta E \approx 600$ cm^{-1} so that we expect $n = 4$. Substituting these values in Eq. (7) we obtain

$$\tau_{NR}^{-1}(300\ K)/\tau_{NR}^{-1}(0\ K) = 13 \quad . \tag{8c}$$

The experimental value for this ratio is 5.3 ± 0.8. This disagreement is probably due to the fact that the actual process is a combination of a three- and four-phonon process. The three-phonon process is still permitted although the value of ρ_n used in Eq. (1) will be rather small at this energy. Nonetheless, the transition rate of the three-phonon decay may still be comparable to the strength of the fourth-order process at low temperature although at sufficiently high temperatures the fourth-order process would dominate. If this conjecture is valid then we would expect a value somewhere between 4 and 13 for the ratio in Eq. (8c).

3. $^3P_2$ state

The $^3P_2$ state of Pr^{3+} is about 1200 cm^{-1} above the $^3P_1$ state. In GK we reported that when the $^3P_2$ state in Pr$_{0.01}$La$_{0.99}$Cl$_3$ was selectively excited, the only observed fluorescence was from the $^3P_1$ state, or the $^3P_0$ state by way of the $^3P_1$ state. The rate of transfer of excitation from $^3P_2$ to $^3P_1$ was shown to be less than 1.5 nsec from the small buildup time required for the $^2P_1$-$^3H_5$ (529 nm) transition to start lasing after the onset of $^3P_2$ pumping. In Pr$_{0.01}$La$_{0.99}$Br$_3$ the behavior is significantly different. In this crystal we observed a weak fluorescence from $^3P_2$ to $^3F_3$ (632 nm) in addition to the strong fluorescence from $^3P_1$. A measurement of the fluorescent decay rate at 20 K of the $^3P_2$ state gave a lifetime of 20 ± 5 nsec. By increasing the excitation power we could obtain laser action at 632 nm which was always accompanied by laser action of the $^3P_1$-$^3H_5$ (530 nm) transition whose threshold was about 2.5 times lower. Measuring the delay in onset of the 530-nm laser output gave results consistent of the $^3P_2$ lifetime quoted above. The laser action from $^3P_2$ disappears for temperatures higher than ~ 70 K indicating a strong phonon enhancement of the decay process.

It is safe to assume that the emission oscillator strengths from $^3P_2$ are comparable for the bromide and chloride. From our failure to see lasing from $^3P_2$ in the chloride, although the pump power was some 100 times above the indirect-pumping threshold for $^3P_1$ lasing, we may infer that the $^3P_2$ to $^3P_1$ relaxation has a lifetime $\leq$ 500 psec. This estimate is admittedly rather crude but it does serve to indicate that the $^3P_2$-$^3P_1$ relaxation has changed much more between the chloride and the bromide than the $^3P_1$-$^3P_0$ relaxation.

In GK the $^3P_2$ to $^3P_1$ relaxation was postulated to proceed via a multiple-phonon transition from the bottom of the $^3P_2$ manifold to the top of the $^1I_6$ manifold ($\Delta E \approx 613$ cm^{-1}) followed by very rapid cascading to the bottom of the $^1I_6$ level and an eventual single-phonon transition from $^1I_6$ to $^3P_1$. The rate-limiting step of this process was found to occur in the multiphonon transition from $^3P_2$ to the $^1I_6$ manifold. For the trichlorides where good crystal-field data are available it was possible to calculate the position of the closest $^1I_6$ level and to show that the energy gap required a three-optical-phonon transition. In the tribromide there is insufficient data to calculate the unobserved $^1I_6$ manifold position but it is unlikely that the $^3P_2$-$^1I_6$ gap will scale with the same consistency as the ^3P intervals.[10] Consequently, in the bromide the $^3P_2$-$^1I_6$ energy difference may well correspond to a higher-than-the-fourth-order transition. In that case the $^3P_2$-$^3P_1$ relaxation may be more drastically changed between chloride and bromide than the $^3P_1$-$^3P_0$ transition.

B. Concentrated crystals

1. PrCl$_3$

In the concentrated crystals PrCl$_3$ and PrBr$_3$ only the $^3P_0$ state fluoresced and the $^3P_0$ lifetime is plotted as a function of temperature in Figs. 2 and 3. It should be noted that the low-temperature intercept of the $^3P_0$ lifetime (11.5 μsec) for PrCl$_3$ is significantly different than reported earlier in GK (4 μsec). This is because in the earlier work the low-temperature measurements were invalidated by stimulated emission from $^3P_0$ although there was never any cavity feedback to cause actual lasing. In the present experiment stimulated emission was eliminated by a series of stringent but very necessary experimental restrictions designed to decrease the excitation density of the $^3P_0$ state by a factor of about 1000. Although the fluorescent signal was much weaker than before, with these precautions the lifetime eventually reached a limiting value of 11.5 ± 1.5 μsec.

The dramatic increase in the $^3P_0$ lifetime as the temperature is lowered cannot be explained as a single-ion–n-phonon process since this behavior does not occur in the analogous dilute crystal. In-

stead it is probably a simultaneous two-ion–n-phonon transition or a three-ion–n-phonon transition. For $^3P_0$ however, there are no really close two-ion energy matches to the energy of $^3P_0$. The closest is a

$$^3P_0 + {}^3H_4\,(\mu = 0) \rightarrow {}^3H_6\,(\mu = 3) + {}^1D_2\,(\mu = 0) - 130 \text{ cm}^{-1} .$$

This process requires absorption of an optical phonon and proceeds from a thermally excited level of the ground state. At low temperatures the population would condense into the lowest $^3H_4$ level thus roughly doubling the energy mismatch, and the number of available optical phonons would decrease thus greatly reducing the transition probability. The combination of such effects may well explain the $^3P_0$ lifetime curve in Fig. 2.

It is also possible, however, that part of the nonradiative concentration-dependent decay may be due to a still-higher-order three-ion process such as $^3H_4 + {}^3H_4 + {}^3P_0 \rightarrow {}^3F_4 + {}^3F_4 + {}^3F_4$, where the energy difference may be quite small for thermally excited levels of $^3H_4$.

2. PrBr₃

The behavior of the $^3P_0$ lifetime in PrBr₃ shown in Fig. 3 was quite unexpected. If the model adduced for the two-ion process in PrCl₃ were correct then one would expect a comparable lifetime in PrBr₃. This is found to be the case only near room temperature. The PrBr₃ data in Fig. 3 clearly show that the relaxation is dominated by a temperature-independent process. This implies an n-ion exchange without phonon participation, i.e., a nearly exact energy match. While this is out of the question for a two-ion process it is conceivable that the energy levels in PrBr₃ are such that the three-ion process mentioned above may be the dominant one.

The problem of the short $^3P_0$ lifetime is not due to stimulated emission as the visible quantum efficiency of this crystal is quite poor so that stimulated emission would have to be into the far red, which would entail a huge and unexpected shift of the oscillator strengths between dilute and concentrated crystals. The PrBr₃ crystals were not of high optical quality and x-ray fluorescence was used to see if this poor quality were due to an impurity which could also explain the temperature-independent decay of $^3P_0$. No rare-earth impurities were in evidence, however, to a concentration of about 0.1%. This limit however, is not sufficient to exclude the possibility that the PrBr₃ crystals had enough impurities or defects so that the excitation could diffuse rapidly to these sites and then decay nonradiatively. Weber[11] has examined such an excitation migration process and has shown that the fluorescent decay would consist of a fast, nonexponential component and an exponential tail character-

istic of a combination of radiative decay and diffusion, where the rate for the latter process is given by

$$\tau_D^{-1} \propto \left(\frac{\sum g_j^2 f_j^2 e^{-\epsilon_j/kT}}{\sum g_j e^{-\epsilon_j/kT} \nu_j^2 \Delta\nu_j} \right)^{3/4} .$$

In the above expression the sum is over the crystal-field levels of the $^3H_4$ manifold which have degeneracies g_j, oscillator strengths to $^3P_0$ of f_j, and linewidths $\Delta\nu_j$. In both PrCl₃ and PrBr₃ most of the oscillator strength between $^3P_0$ and $^3H_4$ is contained in the two lowest-lying crystal-field levels[8] so that the only strong temperature dependence enters through the linewidths $\Delta\nu_j$. These linewidths have been observed to decrease markedly at low temperatures so that the diffusion rate would be expected to increase at low temperatures. Since the experimental observations do not show this trend it must be concluded that excitation diffusion, at least in the present formulation, is not a significant contribution to fluorescent decay. As corroborating evidence we also note that the initial decay was exponential and no fast component was observed, so that the initial decay would have to be as fast as the laser excitation pulse to have escaped detection.

The $^3P_0$ state was not alone in having an unusually short lifetime in PrBr₃. It was also observed that no laser action from $^3P_1$ could be obtained when pumping $^3P_1$, $^1I_6$, or $^3P_2$ although such lasing was rather easily observed in the case of PrCl₃ at low temperatures. Hence the fluorescent lifetime of $^3P_1$ is also much shorter in PrBr₃ than in PrCl₃.

C. Laser transitions in the trihalides

In the course of these experiments a number of laser transitions were observed and the list to date is summarized in Table I. Most of the transitions in the trichlorides have been reported earlier by the authors[12] but these too are reproduced here for purposes of reference. Almost all of the lasers have a threshold that is strongly dependent upon temperature because of nonradiative decay processes and thermal broadening of fluorescence lines. The only laser transition observed at room temperature was the $^3P_0$-$^3F_2$ transition in the concentrated crystals although it should also be observable in the dilute crystals if larger crystals are available to absorb all of the pump light.

ACKNOWLEDGMENTS

APPENDIX: FORCED ELECTRIC DIPOLE TRANSITION IN Pr₀.₀₁La₀.₉₉Cl₃

All the states of Pr^{3+} shown in Fig. 1 are within the $4f^2$ configuration. In the free ion they have

TABLE I. Laser transitions in Pr halides.

Crystal	Energy level excited	Laser transition	Laser wavelength (nm)
$Pr_{0.01}La_{0.99}Cl_3$	$^3P_0$	$^3P_0 - ^3F_2$ ($\mu=2$)	645
		$^3P_0 - ^3H_6$ ($\mu=3$)	616
		$^3P_0 - ^3H_6$ ($\mu=2$)	619
		$^3P_0 - ^3H_4$ ($\mu=3$)	490
	$^3P_1$ $^3P_2$	$^3P_1 - ^3H_5$ ($\mu=2$)	530
$PrCl_3$	$^3P_0$	$^3P_0 - ^3F_2$ ($\mu=2$)	647
		$^3P_0 - ^3H_6$ ($\mu=3$)	617
		$^3P_0 - ^3H_6$ ($\mu=2$)	620
	$^3P_1$ $^1I_6$ $^3P_2$	$^3P_1 - ^3H_5$ ($\mu=2$)	531
$Pr_{0.01}La_{0.99}Br_3$	$^3P_0$	$^3P_0 - ^3F_2$ ($\mu=2$)	647
		$^3P_0 - ^3H_6$ ($\mu=2$)	621
	$^3P_1$	$^3P_1 - ^3H_5$ ($\mu=2$)	532
	$^3P_2$	$^3P_1 - ^3H_5$ ($\mu=2$)	532
		$^3P_2 - ^3F_3$	632
$PrBr_3$	$^3P_0$	$^3P_0 - ^3F_2$ ($\mu=2$)	649
		$^3P_0 - ^3H_6$ ($\mu=2$)	622
	$^3P_1$ $^1I_6$ $^3P_2$	none	...

definite parity and electric dipole transitions within $4f^2$ are forbidden. However, if the crystal lacks a center of symmetry, there are odd harmonics in the crystal field which serve to mix excited configurations such as $4f5d$ and $4f5g$ into the ground configuration. Thus, parity conservation need not hold for the perturbed wave function in cyrstals and electrical dipole transitions will occur. This is the case for $PrCl_3$ and $PrLaCl_3$. In these cases the contributing odd crystalline-field terms are

$$V_{odd} = A_3^3 C_3^{\pm3}(\theta, \phi) + A_5^3 C_5^{\pm3}(\theta, \phi) + A_7^3 C_7^{\pm3}(\theta, \phi) , \quad (A1)$$

where the $C_k(\theta, \phi)$ are spherical harmonics and the $A_k^{|q|}$ are numerical coefficients.

From second-order perturbation theory, the effective dipole moment can be shown to be proportional to

$$\sum_{n'l'\Gamma_\alpha} \frac{\langle (f)^2 \Gamma_i | e\vec{r} | (f)(n'l')\Gamma_\alpha \rangle \langle (f)(n'l')\Gamma_\alpha | V_{odd} | (f)^2 \Gamma_j \rangle}{E(\Gamma_i) - E(\Gamma_\alpha)}$$

$$(A2)$$

where $\vec{r}$ is the position vector and $| (n'l') \rangle$ are the intermediate-state wavefunctions and Γ_i includes all of the other quantum numbers. This expression is too complicated to evaluate exactly but Judd has given a very useful approximate expression, which eliminates the sum over the individual states of the opposite parity manifolds, by introduction of closure techniques. In this approximation the line strength of a transition from the LSJ manifold to the $L'SJ'$ manifold may be written as[9]

$$S_{JJ'} = \sum_{K=2,4,6} T_K |\langle LSJ | |U^{(K)}| | L'SJ' \rangle|^2 \nu , \quad (A3)$$

where $U^{(K)}$ is the unit tensor, and T_K is an effective operator whose form is given by Judd but which in practice is treated as an adjustable parameter. The conclusion is that all of the transitions from the ^3P states can be expressed in terms of just three adjustable parameters, T_2, T_4, and T_6.

The chief difficulty in this approximation lies in the assumption that all of the states of the odd-parity manifold have the same energy which is explicit in the application of closure techniques. Judd argues however, that the T_K in Eq. (A3) would not be expected to vary markedly so long as the excited states of $(f)^2$ are much lower in energy than the centroid of the $(f)(n'l')$ band and in any event would not be expected to vary significantly between different J states of the ^3P manifold. This contention appears to be borne out by the work of Axe[13] and Weber,[14] the latter paper referring to Pr^{3+} in LaF_3.

The problem is that the conclusions drawn from Judd's theory do not agree with the relative values of oscillator strengths found in Table II of the work by Dorman[8] on $PrLaCl_3$ although the agreement in the work by Weber on PrF_3 is excellent. Specifically, if the strong transitions from $^3P_0$ to $^3H_4$, $^3H_6$, and $^3F_2$ are used to fit T_2, T_4, T_6 and all of the remaining transitions from $^3P_0$ and $^3P_1$ are evaluated using these T_K and the reduced matrix elements in Weber[13] then we obtain the results listed in Table

TABLE II. Comparison of oscillator strengths $(\sum f)$ between the experimental results of Dorman (Ref. 8) (column 2) and the predictions of the Judd-theory (Ref. 9) (column 3) fit to the strongest transitions measured by Dorman. The radiative lifetime is proportional to $(\nu^2 f)^{-1}$ and the results of Dorman would predict a lifetime for $^3P_0$ of 18.6 μsec and for $^3P_1$ of 29 μsec. Our experimental value for the lifetime of $^3P_0$ is 14.7 μsec.

Terminal state	$10^6 \sum f$ (Dorman)	$10^6 \sum f$ (Theoretical)	$10^{-4} \nu$ (cm^{-1})	$10^{-8} \nu^2 \sum f$ Theoretical
(a) Oscillator strengths from $^3P_0$, $Pr_{0.01}La_{0.99}Cl_3$
$^3H_4$	52.4	52.4	2.044	218
$^3H_5$	0.59	0	1.83	0
$^3H_6$	7.6	7.6	1.62	20
$^3F_2$	5.4	5.4	1.55	13
$^3F_3$	0	0	...	0
$^3F_4$	1.44	24.9	1.37	46
Total				297
(b) Oscillator strengths from $^3P_1$, $Pr_{0.01}La_{0.99}Cl_3$
$^3H_4$	16.1	18.1	2.105	80
$^3H_5$	11.7	30.8	1.88	108
$^3H_6$	1.4	4.5	1.68	13
$^3F_2$	0.61	1.7	1.61	4.5
$^3F_3$	2.17	17.8	1.48	38
$^3F_4$	1.93	20.3	1.42	41.2
Total				285

II. From Table II, column 5, we would conclude that the lifetimes of $^3P_1$ and $^3P_0$ are essentially equal and that the lifetime of $^3P_0$ should be slightly shorter than stated in Dorman because of the strong contribution of the $^3P_0$-$^3F_4$ transition. The $^3P_0$ lifetime predicted by this correction to Dorman's work now becomes 15. 7 μsec, which is in quite good agreement with our direct measurement of 14. 7 μsec. Note that the equality of $^3P_0$ and $^3P_1$ lifetimes would be expected both from the limiting case of ordinary atomic theory and also from summing Eq.

(A3) over all of the allowed terminal states $|L', S', J'\rangle$ assuming that $^3P_1$ and $^2P_0$ do not differ significantly in energy.

It is difficult to know how much to trust the re-evaluation of hard experimental data but because of the theory's success in other materials we will assume the validity of its conclusions in this work. We note in passing that much of the disagreement could be rectified by a simple error in calibration of the intensity in the extreme red end of the spectrum in the work by Dorman.

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[1] K. R. German and A. Kiel, Phys. Rev. B 8, 1846 (1973). Note Eq. (2) in this work was misprinted; it should read

$$2\lambda_\pm = - (w_{10} + w_{20} + w_{12} + w_{21})$$
$$\pm \{[(w_{10} + w_{13}) - (w_{20} + w_{21})]^2 + 4w_{21} w_{12}\}^{1/2}.$$

[2] B. Barnet and R. Englman, J. Lumin. 3, 37 (1970).

[3] M. D. Sturge, Phys. Rev. B 8, 6 (1973).

[4] S. J. Lin, J. Chem. Phys. 56, 2648 (1972).

[5] H. W. Moos, J. Lumin. 1, 106 (1970).

[6] J. T. Hougen and S. Singh, Proc. R. Soc. A 277, 193 (1964).

[7] I. Richman, R. A. Satten, and E. Y. Wong, J. Chem. Phys. 39, 1833 (1963).

[8] E. Dorman, J. Chem. Phys. 44, 2910 (1966).

[9] B. R. Judd, Phys. Rev. 127, 750 (1962).

[10] This is because states with $J < 3$ are not sensitive to the sixth-order crystal-field term. Measurements of the levels of $^3H_4$, $^3H_5$, and $^3H_6$ indicate that this term is appreciably larger in the chloride as compared to the bromide which would lead to a larger gap between $^3P_2$ and the top of $^1I_6$.

[11] M. J. Weber, Phys. Rev. B 4, 2932 (1971).

[12] K. R. German and A. Kiel, Appl. Phys. Lett. 22, 87 (1973).

[13] J. D. Axe, J. Chem. Phys. 39, 1154 (1963).

[14] M. J. Weber, J. Chem. Phys. 48, 4774 (1968).