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1S_0 Level of Pr^{3+} in Crystals of Fluorides*

EUGENE LOH

Hughes Research Laboratories, Malibu, California

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The 1S_0 level of the trivalent praseodymium ion Pr^{3+} in CaF_2 and LaF_3 crystals has been identified in the absorption spectrum and in the excitation spectrum of orange fluorescence. It appears as a small peak near the $4f \rightarrow 5d$ band of Pr^{3+} at $47\,200\text{ cm}^{-1}$ (2120 \AA) in CaF_2 and $46\,900\text{ cm}^{-1}$ (2135 \AA) in LaF_3 . The identification of this peak as a transition to the 1S_0 level rather than as part of the $4f \rightarrow 5d$ transition is based on its small spectral shift when observed in different environments, its low intensity, and its relatively narrow width—all of which are characteristics of a shielded $4f$ transition.

THE rare-earth trivalent praseodymium ion Pr^{3+} has two $4f$ electrons, which, according to the Russell-Saunders coupling, have 13 energy levels.¹ Twelve levels in the visible and infrared region have been experimentally determined in crystals² containing Pr^{3+} and in the vapor state³ of Pr^{3+} . A 1S_0 level in the ultraviolet around $50\,000\text{ cm}^{-1}$ (2000 \AA),¹ however, remains uncertain. Low *et al.*,⁴ reported the observation of this 1S_0 level at $46\,300\text{ cm}^{-1}$ (2160 \AA), by attributing three emission peaks, at 2160 , 2250 , and 3350 \AA , in x-irradiated $\text{CaF}_2:\text{Pr}^{3+}$ at 77°K to transitions from 1S_0 to the 3H_4 , 3H_5 , and 1D_2 levels, respectively. However, the emission spectrum of such x-irradiated $\text{CaF}_2:\text{Pr}^{3+}$ contains several unidentified peaks in the same spectral region which, together with the chosen peaks, may originate from other centers.⁵ The identification of the 1S_0 level from such a complicated emission spectrum is therefore not clear. Crozier⁶ recently observed five sharp and strong absorption peaks around $45\,500\text{ cm}^{-1}$

(2200 \AA) in CaF_2 doped with $10^{-4}\%$ Pr^{3+} at liquid-helium temperature. He concluded that these peaks are due to the $4f \rightarrow 5d$ transition and that the 1S_0 level of the $4f^2$ configuration would be very difficult to identify in this spectral region.

In this work we report the observation of the 1S_0 level of Pr^{3+} in the absorption and excitation spectra of CaF_2 and LaF_3 crystals doped with appropriate amounts of Pr^{3+} . The assignment of a peak in the absorption and excitation spectra to a transition involving the 1S_0 state rather than to $4f \rightarrow 5d$ transitions is based on the properties characteristic of transitions within a well-shielded $4f$ shell, i.e., low intensity, narrow linewidth, and comparative independence of crystal environment. The result of present work indicates the possibility of identifying many higher levels in the $4f^n$ configuration. These levels lie in the region of inter-configurational transition and hence have not been determined.

The 1S_0 level in Pr^{3+} -doped CaF_2 is found to be at $\sim 47\,200\text{ cm}^{-1}$ ($\sim 2120\text{ \AA}$). It is observed as a small absorption peak or hump, depending on the concentration of Pr^{3+} and crystal temperature, between large absorption bands of the interconfigurational transition. The convenient concentration of Pr^{3+} in CaF_2 for observing 1S_0 is in the range between $\sim 10^{-2}$ and $\sim 10^{-10}\%$. Low temperature such as that of liquid nitrogen sharpens the hump to a peak.

The 1S_0 level in Pr^{3+} -doped LaF_3 crystals is found at $46\,900\text{ cm}^{-1}$ ($\sim 2135\text{ \AA}$). It is readily observed in the

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¹ For example, see J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) **A240**, 509 (1957); G. H. Dieke and H. M. Crosswhite, Appl. Opt. **2**, 675 (1963).

² E. Y. Wong, O. M. Stafudd, and D. R. Johnston, J. Chem. Phys. **39**, 786 (1963) and references therein on previous works.

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⁴ W. Low, J. Makovsky, and S. Yatsiv, in *Quantum Electronics III*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), Vol. 1, p. 655; J. Makovsky, W. Low, and S. Yatsiv, Phys. Letters **2**, 186 (1962).

⁵ J. R. O'Connor and J. H. Chen [Phys. Rev. **130**, 1790 (1963)] showed that the commonly Y-contaminated CaF_2 crystals have absorption peaks at 2250 , 3350 , 4000 , and 5800 \AA .

⁶ M. H. Crozier, Bull. Am. Phys. Soc. **9**, 631 (1964).

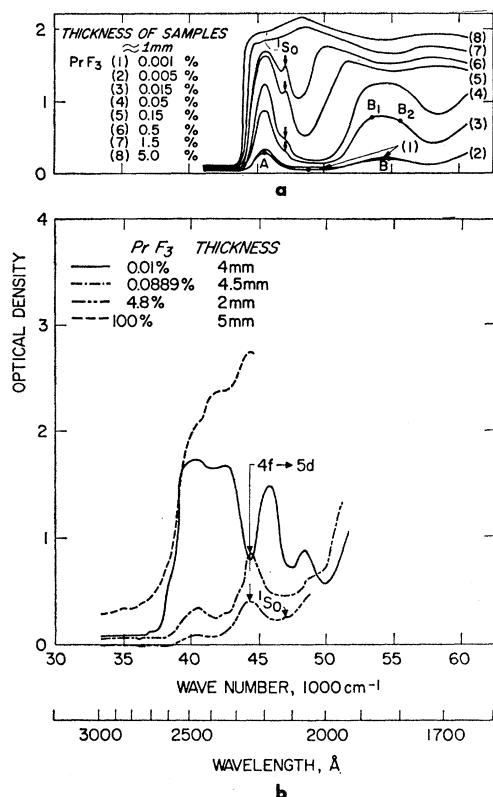


FIG. 1. (a) Ultraviolet absorption spectrum of Pr³⁺-doped CaF₂ crystals at room temperature. (b) Ultraviolet absorption spectrum of Pr³⁺-doped LaF₃ crystals at room temperature.

excitation⁷ spectrum of orange fluorescence of Pr³⁺ as a small excitation peak next to the large $4f \rightarrow 5d$ band [which peaks at 44 600 cm⁻¹ (2245 Å) at room temperature]. The ¹S₀ level has also been observed in the absorption spectrum of Pr³⁺-doped LaF₃. The convenient concentrations of Pr³⁺ in LaF₃ for observing the ¹S₀ level are 0.1 to 5% for excitation measurement and ~5% for transmission measurement.

The concentration effect on the absorption or excitation spectrum of Pr³⁺ in the spectral region of the ¹S₀ level is complex mainly because of the proximity of interconfigurational bands. This is illustrated by the absorption spectra in Figs. 1 (a) and 1 (b) for CaF₂ and LaF₃ crystals, respectively. Figure 1 (a) shows the room-temperature absorption spectrum of CaF₂ crystals doped with PrF₃ from 10⁻³ to 5%. As Pr³⁺ concentration increases, the ¹S₀ absorption first appears as a hump⁸ at 0.015% Pr³⁺ and then develops to a peak at 0.15 and 0.5% Pr³⁺. For Pr³⁺ concentrations below ~10⁻²% the ¹S₀ absorption is too weak to be detectable at both room and liquid-nitrogen temperatures. A

⁷ The excitation spectrum of orange fluorescence of Pr³⁺-doped CaF₂ is highly concentration- and temperature-dependent. No attempt has been made to identify the ¹S₀ level in this complicated excitation spectrum.

⁸ The room-temperature hump sharpens to a small peak at liquid-nitrogen temperature.

typical spectrum of such a dilute sample is that for 10⁻³% Pr³⁺ in Fig. 1 (a). It shows three bands (sharpened at liquid-nitrogen temperatures), one known⁶ $4f \rightarrow 5d$ band (called A) at 45 800 cm⁻¹ (~2180 Å), and two broader bands at 54 800 cm⁻¹ (~1825 Å) (called B) and⁹ 49 000 cm⁻¹ (~2040 Å). As Pr³⁺ concentration reaches a few percent, such as 1.5 and 5% in Fig. 1 (a), the B band masks¹⁰ both the ¹S₀ peak and the A band.

Figure 1 (b) shows the absorption spectrum of LaF₃ crystals doped with from 10⁻² to 100% PrF₃. The ¹S₀ absorption is shown at 46 900 cm⁻¹ (~2135 Å) in the sample with 4.8% Pr³⁺. For dilute samples, e.g., 10⁻² and 10⁻¹% Pr³⁺, the weak ¹S₀ absorption is masked by neighboring strong absorption peaks¹¹ at 45 900 cm⁻¹ (2180 Å) and 48 500 cm⁻¹ (2060 Å).

The ¹S₀ level also appears as a peak in the excitation spectrum of Pr³⁺-doped LaF₃. Figure 2 shows the room¹² temperature excitation spectrum of orange fluorescence of Pr³⁺ in LaF₃ crystals at various concentrations. The ¹S₀ excitation peak persists in samples with concentrations ranging from a fraction of a percent of Pr³⁺ to 100%, i.e., PrF₃. On the other hand, the neighboring $4f \rightarrow 5d$ excitation band at 44 500 cm⁻¹ (~2245 Å) starts to lose its identity above ~10% Pr³⁺ concentration. The persistence of the 46 900 cm⁻¹ (2135 Å) excitation peak at the same wavelength in samples with such a wide range of Pr³⁺ concentrations resembles the behavior of all the lower $4f^2$ levels of Pr³⁺. This constitutes strong evidence for associating it with the ¹S₀ level of Pr³⁺ in LaF₃.

The evidence supporting identification of the spectral features noted in Pr³⁺-doped CaF₂ and LaF₃ crystals as a transition involving the ¹S₀ level of the $4f^2$ configuration is summarized in the paragraphs below.

The ¹S₀ level has small spectral shift in various media. The location of ¹S₀ level is between 47 200 cm⁻¹ (2120 Å)

⁹ It becomes obvious at liquid-nitrogen temperature.

¹⁰ The effect of Pr³⁺ concentration on the behavior of A and B bands [Fig. 1 (a)] is as follows: As the Pr³⁺ concentration increases, the A band increases in intensity and shifts slowly toward the ¹S₀ level at a shorter wavelength. Meanwhile, the B band at 54 800 cm⁻¹ (~1825 Å) first does not change its spectral position appreciably at Pr³⁺ concentrations below 0.005%. From 0.015% Pr³⁺ on, the B band appears to broaden to two bands B₁ and B₂ with apparent peaks at 53 600 cm⁻¹ (~1865 Å) and 55 500 cm⁻¹ (~1800 Å), respectively. The B₁ band increases its intensity faster than the A band and shifts rapidly toward the ¹S₀ band at a longer wavelength. Finally, at Pr³⁺ concentrations above 0.5% the B₁ band masks both ¹S₀ peak and A band.

¹¹ These two absorption peaks 2180 and 2060 Å, together with other absorption peaks at 40 600 cm⁻¹ (2460 Å) and 42 900 cm⁻¹ (2330 Å) [shown by the curve for 10⁻²% Pr³⁺ in Fig. 1 (b)], resemble the absorption peaks at 45 200 cm⁻¹ (2215 Å), 47 400 cm⁻¹ (2111 Å), 39 600 cm⁻¹ (2525 Å), 41 700 cm⁻¹ (2395 Å), respectively, in the $4f \rightarrow 5d$ absorption spectrum [see Ref. 14] of the Ce³⁺ ion in an aqueous solution of the perchlorate. The spectral range of all these peaks falls in the "second" $4f \rightarrow 5d$ band (A₂ band) of Ce³⁺ (II type)-doped alkaline-earth fluorides [see Ref. 16]. Hence, they may be the $4f \rightarrow 5d$ absorption of trace amounts of Ce³⁺ in LaF₃.

¹² The fluorescence is enhanced at liquid-nitrogen temperatures, especially for $4f \rightarrow 5d$ band in heavily doped samples. For example, a tenfold increase in the $4f \rightarrow 5d$ band is observed for 5% Pr³⁺ and a threefold increase for 0.1% Pr³⁺ in LaF₃.

and $46\,700\text{ cm}^{-1}$ (2140 \AA) in various host media, e.g., at $47\,200\text{ cm}^{-1}$ (2120 \AA) in CaF_2 , at $46\,900\text{ cm}^{-1}$ (2135 \AA) in LaF_3 , and at $46\,700\text{ cm}^{-1}$ (2140 \AA)¹³ or $46\,900\text{ cm}^{-1}$ (2135 \AA)¹⁴ in aqueous solution.¹⁵ The apparent peak of the neighboring $4f \rightarrow 5d$ transition, however, has wider range of location, e.g., at $\sim 45\,800\text{ cm}^{-1}$ ($\sim 2185\text{ \AA}$) in $\sim 10^{-20}\%$ Pr^{3+} -doped CaF_2 at room temperature, at $\sim 44\,500\text{ cm}^{-1}$ ($\sim 2245\text{ \AA}$) in Pr^{3+} -doped LaF_3 at room temperature, and above $46\,700\text{ cm}^{-1}$ (below 2140 \AA)¹³ or at $52\,900\text{ cm}^{-1}$ ($\sim 1890\text{ \AA}$)¹⁴ in aqueous solution.¹⁵ It is interesting to note that the $4f \rightarrow 5d$ band in aqueous solution is on the high-energy side of 1S_0 in fluoride crystals. The strong crystal-field effects on d levels in fluorides may be responsible for the lowering¹⁶ of the $4f \rightarrow 5d$ band.

The spectral location of 1S_0 level is insensitive to the concentration of Pr^{3+} and temperature of the crystal.

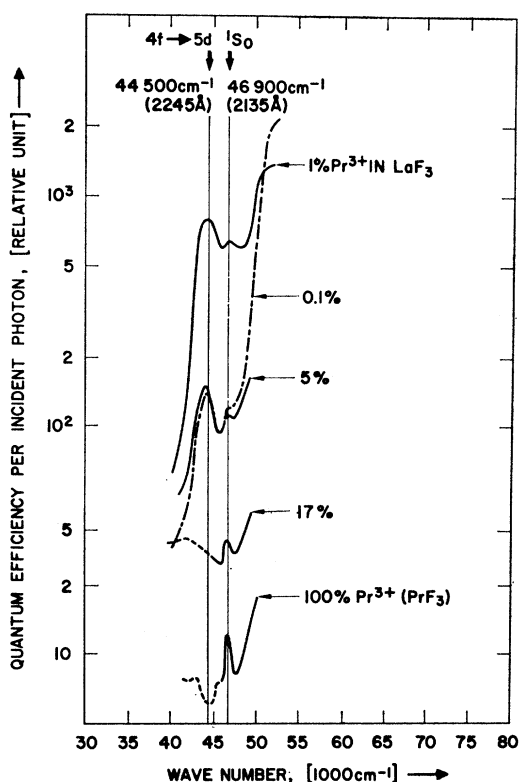


FIG. 2. Excitation spectrum of orange fluorescence of Pr^{3+} -doped LaF_3 crystals at room temperature.

¹³ D. C. Stewart, Atomic Energy Commission Document No. I AECD-2389, Berkeley, 1948 (unpublished).

¹⁴ Chr. Klixbüll Jørgensen and J. S. Brinen, *Mol. Phys.* **6**, 629 (1963).

¹⁵ From the literature, we may assume that the small peak at 2140 \AA (Ref. 13) [or 2135 \AA (Ref. 14)] and the strong band at shorter wavelength, $<2140\text{ \AA}$ (Ref. 13) [or at 1890 \AA (Ref. 14)], in the absorption spectrum of Pr^{3+} perchlorate aqueous solution, are 1S_0 absorption and $4f \rightarrow 5d$ transitions, respectively. This assumption may be made because, according to present data, their spectral structure resembles that of fluoride crystals.

¹⁶ A. A. Kaplyanskiĭ, V. N. Medvedev, and P. P. Feofilov, *Opt. i Spektroskopiya* **14**, 664 (1962) [English transl.: *Opt. Spectry.* (USSR) **14**, 351 (1963)].

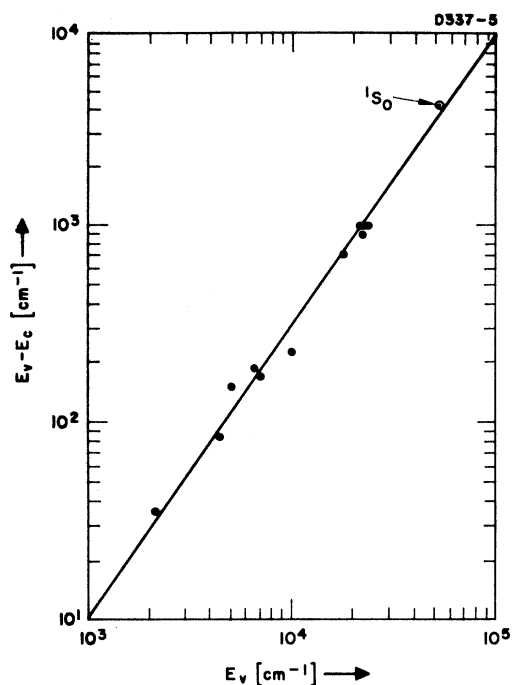


FIG. 3. Difference between corresponding energy levels of Pr^{3+} in vapor state and in crystal versus Pr^{3+} level in vapor state.

In contrast, the peak of the neighboring known $4f \rightarrow 5d$ absorption in CaF_2 [e.g., at $45\,800\text{ cm}^{-1}$ ($\sim 2185\text{ \AA}$) for $10^{-20}\%$ Pr^{3+}] shifts toward longer wavelength¹⁷ as either the Pr^{3+} concentration or the temperature of the crystal decreases. In LaF_3 crystals, this $4f \rightarrow 5d$ absorption or excitation band has the opposite temperature shift, e.g., from $44\,500\text{ cm}^{-1}$ ($\sim 2248\text{ \AA}$) at room temperature to $45\,100\text{ cm}^{-1}$ ($\sim 2219\text{ \AA}$) at liquid-nitrogen temperature. The excitation spectrum of Pr^{3+} in LaF_3 (Fig. 2) shows that the 1S_0 peak persists up to pure PrF_3 , while the $4f \rightarrow 5d$ excitation band loses its identity at $Pr^{3+} \gtrsim 10\%$.

1S_0 absorption is weak and narrow. The 1S_0 peak in Pr^{3+} -doped CaF_2 and LaF_3 is weaker and narrower than the $4f \rightarrow 5d$ band, as shown in Figs. 1 (a), 1 (b), and 2. Compared with other $4f^2$ levels the 1S_0 peak of Pr^{3+} in CaF_2 is narrower than 3P_2 manifold at $22\,500\text{ cm}^{-1}$ (4440 \AA) at both room and liquid-nitrogen temperatures. In the LaF_3 crystal the 1S_0 at room and liquid-nitrogen temperatures is comparable to 1D_2 manifold at $16\,800\text{ cm}^{-1}$ ($\sim 5940\text{ \AA}$) in a 4.8% Pr^{3+} sample at room temperature.

These three properties are, in general, characteristic of the intraconfiguration lines of well-shielded $4f$

¹⁷ For example, the apparent shift of $4f \rightarrow 5d$ band is from $46\,000\text{ cm}^{-1}$ (2175 \AA) for 0.5% Pr^{3+} to $45\,800\text{ cm}^{-1}$ (2185 \AA) for $10^{-20}\%$ Pr^{3+} in CaF_2 . The temperature shift is about -250 cm^{-1} ($+10\text{ \AA}$) as samples are cooled down from room to liquid-nitrogen temperature. This red shift of the apparent peak of $4f \rightarrow 5d$ band with decreasing temperature and Pr^{3+} concentration is consistent with the data of Crozier (Ref. 6) for $10^{-4}\%$ Pr^{3+} at liquid-helium temperature.

electrons in rare earths and we attribute the observed peak to transitions from the 1S_0 level.

It is interesting to compare³ the levels observed for the $4f^2$ configuration of Pr^{3+} in the vapor (E_v) phase with those found in single crystal (E_c). If our value for the 1S_0 level in CaF_2 crystals is compared with the calculated³ value for the vapor, it is found (Fig. 3) that the relation is described by a simple expression: $E_v - E_c \propto E_v^{3/2}$, or $E_c = E_v - 10^{-3.5} E_v^{3/2}$.

Note added in proof. Fortunately, the 1S_0 level of Pr^{3+} sits conveniently on the short-wavelength side of the first $4f \rightarrow 5d$ band in fluorides. Otherwise, it might be difficult to distinguish the 1S_0 absorption from the zero phonon line of $4f \rightarrow 5d$ transition at low temperature, although the former is a weak and the latter is a strong transition. The absorption spectrum of 0.015% Pr^{3+} in

CaF_2 at liquid nitrogen temperature shows a weak 1S_0 peak at $\sim 2120 \text{ \AA}$ and a strong zero phonon peak at $\sim 2240 \text{ \AA}$, both being conveniently located on the opposite sides of the $4f \rightarrow 5d$ band with apparent peak at $\sim 2200 \text{ \AA}$.

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Theory of Rotational Excitation of Homonuclear Diatomic Molecules by Slow Electrons: Application to N_2 and H_2 †

DOUGLAS H. SAMPSON*

Space Sciences Laboratory, General Electric Company, Valley Forge, Pennsylvania

AND

RAYMOND C. MJOLNESS‡

Space Sciences Laboratory, General Electric Company, Valley Forge, Pennsylvania

and

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

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A distorted-wave theory of rotational excitation of homonuclear diatomic molecules with Σ ground states by slow electrons is given. The assumption is made that distortion of only the $l=0$ and $l=1$ partial waves is significant and a simple semiempirical model is used for the potential. Results obtained for H_2 and N_2 using the most recent theoretical and experimental values for the electric quadrupole moments and polarizabilities appear to remove, or very nearly remove, the discrepancies which have existed between theory and the analysis of swarm experiments.

I. INTRODUCTION

IT has been well known for many years that for electron energies below vibrational threshold the observed electron energy losses in homonuclear diatomic molecular gases greatly exceed those due to elastic scattering alone. Early theoretical calculations^{1,2} of the cross section for rotational excitation considering only the short-range electron-molecule interaction yielded energy loss rates smaller than the observed ones. How-

ever, in 1955, Gerjuoy and Stein (G. S.)³ showed that, for the low energies of interest, the long-range part of the electron-molecule interaction is dominant in determining the rotational excitation cross section. Assuming the electron-molecule interaction to be the r^{-3} pure electric-quadrupole interaction for all r and using the Born approximation, they obtained an expression for the rotation excitation cross section which is proportional to Q^2 , where Q is the electric-quadrupole moment of the molecule. Using reasonable values for Q (which was not precisely known in most cases), approximate agreement with observed energy losses was obtained. However, with increase in the precision of the analysis of swarm experiments,⁴ some discrepancies became

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* Present address: Astronomy Department, Pennsylvania State University, University Park, Pennsylvania.

‡ Present address: Theoretical Division, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

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