Ultraviolet Absorption Spectra of Pr^{3+} Ion in Alkaline-Earth Fluorides

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The ultraviolet absorption spectra of Pr^{3+} in CaF_2, SrF_2, and BaF_2 have been measured at room and liquid-nitrogen temperatures. These spectra are similar to those of Ce^{3+} reported previously except that Pr^{3+} absorptions generally occur at higher photon energies. This general similarity between the uv absorption spectra of Ce^{3+} and Pr^{3+} in solids indicates that the crystal field is dominant in the higher configurations, $5d$ and $6s$, of rare-earth ions in solids. For Pr^{3+} in CaF_2 the three interconfigurational transitions are: (1) $4f\rightarrow5d$ between 44 000 and 69 000 cm^{-1}; (2) a possible $4f\rightarrow6s$ at $\sim$76 000 cm^{-1}; (3) a charge transfer $F^-(2p^6)\rightarrow Pr^{3+}(6s)$ near $\sim$80 000 cm^{-1}. Other effects, such as vibronics in the lowest $4f\rightarrow5d$ band and their concentration dependence, the effect of cluster formation on $4f\rightarrow5d$ bands, and the crystal effect on the free-ion data, are all similar to the previously reported data on Ce^{3+} in alkaline-earth fluorides. The cross section of $^1S_0$ absorption of Pr^{3+} in CaF_2 is estimated to be concentration-independent, which is consistent with the shielded character of $4f\rightarrow4f$ transitions. Absorption to the $^1S_0$ state and the vibronics are also observed in BaF_2:Pr^{3+}.

I. INTRODUCTION

As a direct approach to the study of interconfigurational transitions of trivalent rare-earth ions in solids, we have previously presented the ultraviolet-absorption spectra of the simplest rare-earth ion $Ce^{3+}(4f^1)$ in alkaline-earth fluorides.[1] The spectra[1] of Ce^{3+} show three types of transitions: $4f\rightarrow5d$ narrow bands, a broad and weak $4f\rightarrow6s$ band, and the charge transfer of $F^-(2p^6)\rightarrow Ce^{3+}(6s)$ appearing as the apparent red shift of the absorption edge of the host crystal.

For comparison with the work on Ce^{3+}, we present here the uv absorption data of Pr^{3+} in alkaline-earth fluorides. $Pr^{3+}(4f^2)$ follows $Ce^{3+}(4f^1)$ in the rare-earth series. Except for the latter, it has the lowest $4f\rightarrow5d$ transition energy[2] among trivalent rare-earth ions. Therefore Pr^{3+} may show as many interconfigurational transitions as Ce^{3+} within the transparent region of the host crystal. Pr^{3+} is also one of the few trivalent rare-earth ions whose free-ion[3] data became available recently. The free-ion data are useful[1] in comparing the corresponding data of interconfigurational transitions in solids.

The uv absorption spectra of Pr^{3+} are similar to those of Ce^{3+}: (1) The $4f\rightarrow5d$ bands of Pr^{3+} are shifted $\sim$13,000 cm^{-1} upward in energy from the corresponding bands of Ce^{3+}. The relative oscillator strengths of these bands of Pr^{3+} in CaF_2 are concentration-dependent because of cluster[1] formation as in the case of Ce^{3+} in CaF_2 or SrF_2. The lowest $4f\rightarrow5d$ band of Pr^{3+} in CaF_2 and BaF_2 also develops vibronic structures at low temperature. (2) A possible hump at $\sim$76,000 cm^{-1} in the absorption spectra of Pr^{3+} in CaF_2 suggests the presence of $4f\rightarrow6s$ absorption of Pr^{3+}. In CaF_2:Ce^{3+} the $4f\rightarrow6s$ absorption[1] of Ce^{3+} is indicated by a weak and broad band with maximum at $\sim$70 000 cm^{-1}. (3) The apparent red shift of the absorption edge of the host crystal with increasing Pr^{3+} concentration suggests also the charge transfer[1] of $F^-(2p^6)\rightarrow Pr^{3+}(6s)$. These general similarities between the uv absorption spectra of Ce^{3+} and Pr^{3+} in solids indicate that the crystal field is dominant in the higher configurations $5d$ and $6s$ of rare-earth ions in solids.

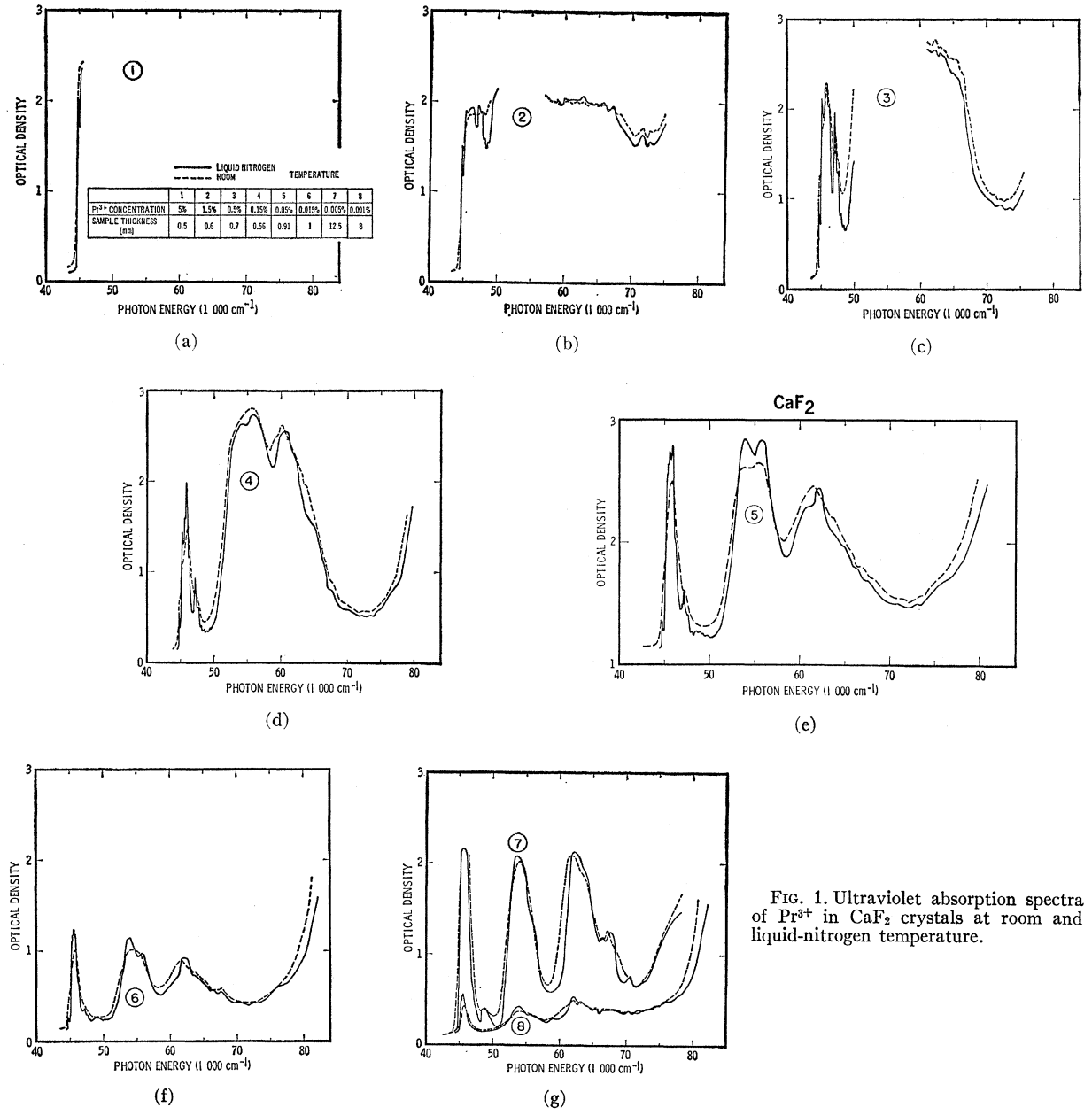
There are, however, two complications occurring in the uv absorption spectra of Pr^{3+}. First is the coincidental appearance of the $^1S_0$ level,[4] the highest $4f\rightarrow4f$ transition of Pr^{3+}, in the lowest $4f\rightarrow5d$ band of Pr^{3+} in CaF_2, and BaF_2. This may complicate the interpretation of the vibronic structure in this band at low temperature. Second is the lack of structure in the lowest $4f\rightarrow5d$ of Pr^{3+} in SrF_2. Neither vibronic structure nor $^1S_0$ absorption is noticeable in Pr^{3+} doped SrF_2. The structure may be smeared out by some strain of unknown origin in SrF_2 crystals.

We shall discuss the uv absorption spectra of Pr^{3+} in the order of increasing energy: $4f\rightarrow5d$, $4f\rightarrow6s$, and charge transfer $F^-(2p^6)\rightarrow Pr^{3+}(6s)$.

II. $4f\rightarrow5d$ ABSORPTION OF SINGLE-ION Pr^{3+} IN ALKALINE-EARTH FLUORIDES

The uv absorption spectra of Pr^{3+} in CaF_2, SrF_2, and BaF_2 crystals are shown in Figs. 1, 2, and 3, respectively. The spectra cover various concentrations of Pr^{3+} and were taken at both room and liquid-nitrogen temperatures. The spectra of Pr^{3+} in these three host crystals are similar in general. As in the case[1] of BaF_2:Ce^{3+}, BaF_2:Pr^{3+} appears to be the simplest. Its spectra consist of two regions of absorption, a lowest band A below 50 000 cm^{-1} and a high-energy band between 61 000 and 67 000 cm^{-1}, called region B, as shown by curve 3 for BaF_2:0.005% Pr^{3+} in Fig. 3. The spectra of SrF_2:Pr^{3+} and CaF_2:Pr^{3+} are very similar to each other. They have additional absorption bands in the intermediate spectral region called C, between 50 000 and 61 000 cm^{-1}. It will be shown later that as the concentration of Pr^{3+} in CaF_2 increases, the absorption in the intermediate region C increases while

[1] E. Loh, Phys. Rev. **154**, 270 (1967).
[2] E. Loh, Phys. Rev. **147**, 332 (1966).
[3] J. Sugar, J. Opt. Soc. Am. **55**, 1058 (1965). H. M. Crosswhite, G. H. Dieke, and Wm. J. Carter, J. Chem. Phys. **43**, 2047 (1965).
[4] E. Loh, Phys. Rev. **140**, A1463 (1965).



	1	2	3	4	5	6	7	8
Pr^{3+} CONCENTRATION	5%	1.5%	0.5%	0.15%	0.05%	0.015%	0.005%	0.001%
SAMPLE THICKNESS (mm)	0.5	0.6	0.7	0.56	0.91	1	12.5	8

FIG. 1. Ultraviolet absorption spectra of Pr^{3+} in CaF_2 crystals at room and liquid-nitrogen temperature.

that in the lowest-band A and high-energy bands B decreases. Following the example[1] of Ce^{3+}, we propose that bands A and B characterize the $4f \rightarrow 5d$ absorption of single-ion Pr^{3+} while bands in region C are attributed to $4f \rightarrow 5d$ absorption of cluster-ion Pr^{3+} in these crystals.

We first discuss the single-ion absorption. The absorption of cluster-ion Pr^{3+} will be discussed later in connection with the concentration dependence of Pr^{3+} absorption in CaF_2. From the interpretation[1] of the $4f \rightarrow 5d$ absorption of single-ion Ce^{3+} in alkaline-earth fluorides, we assume also a tetragonal environment around Pr^{3+} due to the nearest-neighbor interstitial F^- as charge compensator. We assign the lowest band as transitions from $4f$ to $|x^2-y^2\rangle$ and three humps[5] in B as transitions from $4f$ to $|2z^2-x^2-y^2\rangle$, $|xy\rangle$ and $|yz\rangle$, and $zx\rangle$ in the order of increasing energy.

Table I summarizes the experimental data[5] for the $4f \rightarrow 5d$ transitions at liquid-nitrogen temperature. The

[5] The humps in the band B between 61 000 and 67 000 cm^{-1} in Pr^{3+} spectra are not as prominent, and therefore their spectral locations are not as accurate, as the corresponding peaks (Ref. 1) of Ce^{3+} in the bands between 47 000 and 56 000 cm^{-1}. In the high-energy region uv spectra are frequently of marginal quality because the quality of the crystal, the constancy of detecting phosphors, and the cleanness of the experiment are critical in the vacuum uv region. The stability of uv sources becomes more important at energies above 60 000 cm^{-1}, where the hydrogen source emits line, instead of continuous, spectra.

data are assigned as components of $5d$ orbitals in a tetragonal environment. The right portion of the table lists the centroids of e_g, t_{2g}, and $5d$ of Pr^{3+} as deduced from the experimental data. Values of crystal-field strength 10 Dq are listed in the last column of the table as the energy difference between e_g and t_{2g}.

The effects of low temperature on the $4f \rightarrow 5d$ absorption spectra are the sharpening of absorption bands, the increase in separation between the two e_g bands, $|x^2-y^2\rangle$ and $|2z^2-x^2-y^2\rangle$, and the appearance of vibronic structure in the lowest band $|x^2-y^2\rangle$. Figure 4, with an enlarged energy scale for clarity, shows the vibronic structure in the $|x^2-y^2\rangle$ band of Pr^{3+} in CaF_2 for the concentration range from 0.001% to 5% at liquid-nitrogen temperature. The locations of humps in the spectra are tabulated in the first part of Table II for the low-concentration region from ~0.015% to ~0.05% and in the second part of Table II for the medium-concentration range from ~0.15% to ~0.5%. The data in this table shows that the vibronics consist of two frequency intervals. A larger interval ω_1 appears between "major humps" at ν_j, marked by long lines in Fig. 4, and a smaller interval ω_2 separates "minor humps" at ν_i, marked by short lines in Fig. 4, within the interval ω_1. Wagner and Bron[6] in analyzing their vibronic data of divalent rare-earth ions in alkali halides have interpreted ω_1 and ω_2 as the out-of-phase and in-phase, respectively, resonance frequencies of pseudolocalized vibrations occurring at the divalent rare-earth defect in the monovalent host crystal. They also related ω_1 as being slightly larger than the longitudinal optical branch ν_{LO} of the host lattice and ω_2 as being slightly lower than the transverse acoustical

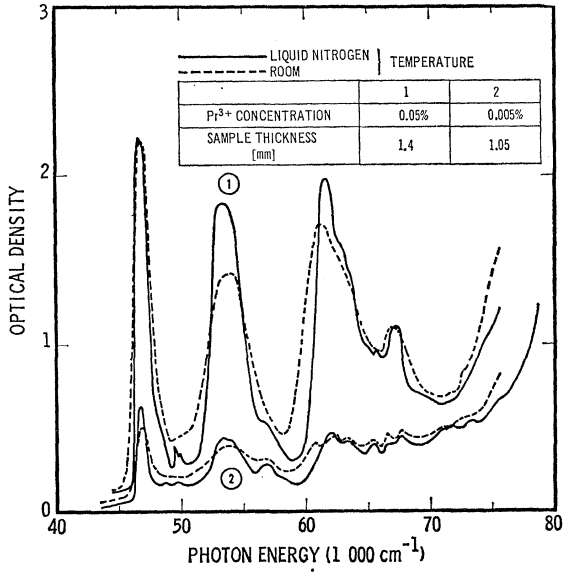


FIG. 2. Ultraviolet-absorption spectra of Pr^{3+} in SrF_2 crystals at room and liquid-nitrogen temperature.

[6] M. Wagner and W. E. Bron, Phys. Rev. **139**, A223 (1965).

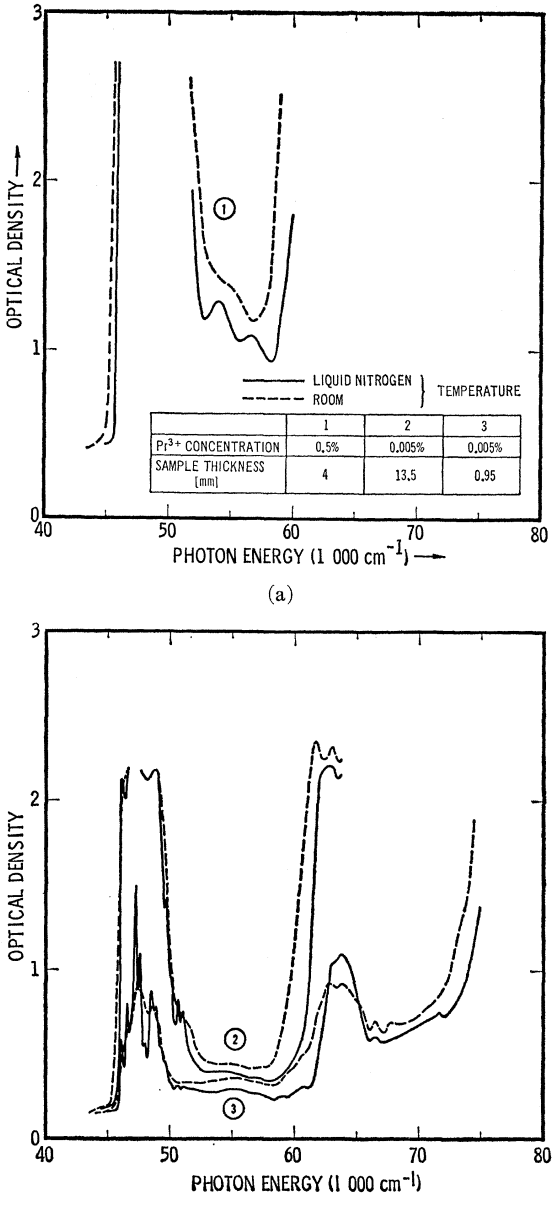


FIG. 3. Ultraviolet-absorption spectra of Pr^{3+} in BaF_2 crystals at room and liquid-nitrogen temperature.

branch[7] ν_{TA} of the host crystal. Values of ω_1, ~460 $cm^{-1} = \nu_{LO}$, and ω_2, ~150 cm^{-1}, for samples in the low Pr^{3+} concentration region, (see the first part of Table II or curve 8 to 5 in Fig. 4) are about the same as the corresponding values[1] of 0.005% Ce^{3+} in CaF_2 which have been interpreted[1] by the vibronic model[6] of Bron and Wagner. As concentration of Pr^{3+} in CaF_2 is raised to the medium-concentration region, 0.15% to 0.5%, the "major humps" remain at ν_j (as shown by curves 3 and 4 in Fig. 4 or the second part of Table II) and the value of $\omega_1 \approx 450$ cm^{-1} persists. The interval ω_2,

[7] This quantity was called ν_{ac} in Refs. 1 and 7.

TABLE I. $5d$ Levels and crystal-field strength 10Dq for single-ion Pr^{3+} in alkaline-earth fluorides.

Host crystal	Experimental data (10^3 cm^{-1}) assigned as tetragonal components of $5d$ orbital				Deduced values (10^3 cm^{-1})			
					Cubic		Spherical	Crystal-field strength
	x^2-y^2	$2z^2-x^2-y^2$	xy	yz and zx	e_g	t_{2g}	$5d$	10Dq
CaF_2	45.6	62	65	67.6	53.8	66.7	61.6	12.9
SrF_2	46.8	61.8	63.5	67.2	54.3	66	61.3	11.7
BaF_2	47.3	63	63.8	66.5	55.2	65.6	61.4	10.4

TABLE II. Vibronic structure of Pr^{3+} in alkaline-earth fluorides at liquid-nitrogen temperature (frequency in 10^3 cm^{-1}).

	ν_j	ω_1 ($=\Delta\nu_j$)	ν_{LO}	ν_i	ω_2 ($=\nu_i-\nu_j$ or $\Delta\nu_i$)	ν_{TA}	ν_{TO}
			0.015% to 0.05% Pr^{3+} in CaF_2				
44.76[a]							
	45[b]						
				45.17	0.17	0.07[c]	
				45.32	0.15		
	45.46	0.46	0.46[c]				
				45.62	0.16		
				45.75	0.13		
	45.89	0.43					
				46.05	0.16		
				...			
	46.34	0.45					
	46.78[b]	0.44					
				47.02	0.24[d]		
	47.19[e]	0.41					
				47.44	0.25[d]		
	47.64	0.45					
	48.03	0.39					
	48.47	0.44					
	48.92	0.45					
			0.15% to 0.5% Pr^{3+} in CaF_2				
44.78[a]	45[b]						
				45.27	0.27		0.26[c]
	45.45	0.45	0.46[c]				
				45.68	0.23		
	45.90	0.45					
				46.12	0.22		
	46.33	0.43					
				46.59	0.26		
	46.78	0.45					
				47.02	0.24		
	47.19[e]	0.41					
				47.44	0.25		
	47.64	0.45					
	48.03	0.39					
	48.44	0.41					
	48.9	0.46					
	49.35	0.45					
			0.005%[f] Pr^{+3} in BaF_2				
46.11[a]	46.56						
	46.92	0.36	0.33				
	47.24[e]	0.32					
	47.6	0.36					
	48	0.4					
	48.52	0.52					
	48.88	0.36					
	49.33	0.45					
	49.67	0.34					
	50.17	0.5					
	50.68	0.51					
	51.06	0.38					

[a] This low-energy peak is strong. It is, however, not separated by ω_1 from other major humps. In CaF_2 it is only $\sim$200 cm^{-1} lower in energy from the next major hump. This peak shifts upward in energy with increasing Pr^{3+} concentration. It is also observed in CaF_2 by M. H. Crozier [Bull. Am. Phys. Soc. **9**, 631 (1964)].

[b] It becomes obvious at 0.5% Pr^{3+} concentration, curve 3 in Fig. 4.

[c] The lattice data are taken from W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howorth, Phys. Rev. **127**, 1950 (1962). From their infrared data, the deduced value of $\nu_{TA}=71$ cm^{-1} for CaF_2 seems to be anomalously lower than that of SrF_2 and BaF_2 with $\nu_{TA}=99$ and 94 cm^{-1}, respectively.

[d] Here the value of ω_2 is close to ν_{TO} as in the region of medium concentration of Pr^{3+}.

[e] $^1S_0$ absorption.

[f] The absorption spectrum of 0.01% Pr^{3+} in BaF_2 is similar.

however, expands to $\sim$250 cm^{-1} and consequently only one "minor hump" can be contained in each major interval ω_1. It is interesting to note that $\omega_2 \approx 250$ cm^{-1} in the medium-concentration region is close to the transverse optical-branch frequency $\nu_{TO} = 260$ cm^{-1} of CaF_2.

We speculate on the origin of the increase of ω_2 from its value near ν_{TA} at low Pr^{3+} concentration to that near ν_{TO} at medium Pr^{3+} concentration as follows. At low concentrations of Pr^{3+} in CaF_2, the frequency ω_2 corresponds to the in-phase resonance of Pr^{3+} with respect to four substitutional F^- ions which are in the same general direction from Pr^{3+} as its charge compensator—interstitial F^-. This is similar to the situation of divalent rare-earth ions in the charge-compensated monovalent alkali halides as proposed by Bron and Wagner.[6] As Pr^{3+} concentration in CaF_2 increases, the direct effect on Pr^{3+} from its charge compensator is gradually diminished because of the proximity of other interstitial F^- from the neighboring Pr^{3+} ions such as those in the cluster.[1] The presence of two or more charge compensators around Pr^{3+} will suppress the in-phase resonance, with frequency $\omega_2 \approx \nu_{TA}$, at rare-earth defects because of the disappearance of a preferential direction. In this stiffened environment of Pr^{3+} due to the presence of several neighboring interstitial F^- ions in the region of medium Pr^{3+} concentration, ω_2 tends to associate with a higher resonance frequency such as the transverse optical branch ν_{TO}. By the same reasoning, we may expect that ω_2 of divalent rare-earth ions (RE^{2+}) in alkali halides will also increase from the value near ν_{TA} to that near ν_{TO} as RE^{2+} concentration in a monovalent host increases. Some variations of ω_2 for RE^{2+} in alkali halides as listed in Table III of Ref. 6 may be attributed to such changes in local environment around the RE^{2+}. In Sm^{2+}-doped CaF_2, where there is no preferential direction around RE^{2+} because of the absence of the charge compensator, ν_{TO} instead of ν_{TA} is known[8] to be a prominent vibrational level.

The absorption spectra of the lowest $4f \rightarrow 5d$ absorption of Pr^{3+} in BaF_2 at liquid-nitrogen temperature are shown in Fig. 5. The spacings between humps are all larger than 300 cm^{-1} ($> \nu_{TO} > \nu_{TA}$). This indicates that the vibronics observed are not "minor peaks" but "major peaks". The last part of Table II summarizes the peaks in the lowest $4f \rightarrow 5d$ absorption spectra of BaF_2:Pr^{3+} (from Fig. 5) and shows that values of $\omega_1 = \Delta\nu_j$ for BaF_2:Pr^{3+} are not as regular as those for CaF_2:Pr^{3+} listed in the other parts of the table.

The spectra of the lowest $4f \rightarrow 5d$ absorption of Pr^{3+} in SrF_2 have no structure at liquid-nitrogen temperature and are shown in Fig. 6. It is possible that some strains of unknown origin may mask the low-temperature structure.

Previously[4] we have identified the $^1S_0$ level of Pr^{3+}

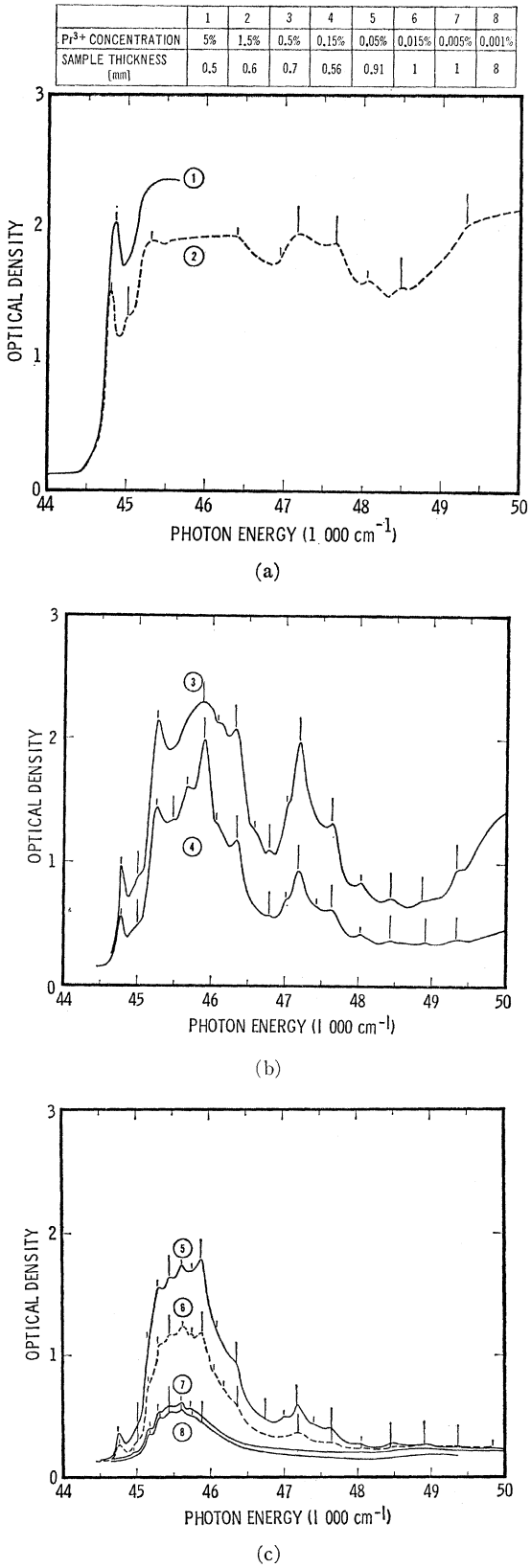


FIG. 4. Lowest $4f \rightarrow 5d$-absorption spectra of Pr^{3+} in CaF_2 crystals at liquid-nitrogen temperature.

[8] D. L. Wood and W. Kaiser, Phys. Rev. **126**, 2079 (1962). W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, *ibid.* **127**, 1950 (1962).

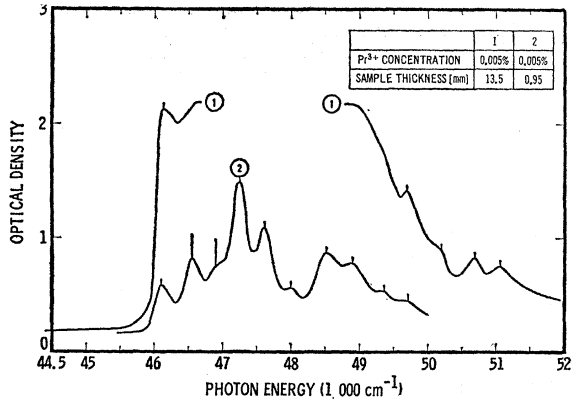


FIG. 5. Lowest $4f \rightarrow 5d$-absorption spectra of Pr^{3+} in BaF_2 crystals at liquid-nitrogen temperature.

in CaF_2 and LaF_3 crystals. At room temperature, it is a small peak at $\sim$47 000 cm^{-1} near the lowest $4f \rightarrow 5d$ absorption band. The identification[4] of this peak as a transition to the $^1S_0$ level rather than as part of the $4f \rightarrow 5d$ transition was based on its shielded character as a $4f \rightarrow 4f$ transition. In the present work we shall show $^1S_0$ absorption in CaF_2 and BaF_2 more clearly at liquid-nitrogen temperature. In CaF_2 the $^1S_0$ level is at $\sim$47 200 cm^{-1}, as shown by curves 6 to 2 in Fig. 4 for Pr^{3+} concentration 0.015 to 1.5%, respectively, and is followed by a series of vibronics. In BaF_2 crystal $^1S_0$ absorption of Pr^{3+} appears at $\sim$47 240 cm^{-1} and is followed by a series of similar vibronic peaks as shown in Fig. 5 for 0.005% Pr^{3+}. The close resemblance between spectra in these two host crystals near and above 47 000 cm^{-1} supports the identification of $^1S_0$ absorption. We have also estimated the values of the oscillator strength of $^1S_0$ absorption for varying concentration of Pr^{3+} in CaF_2, from curve 6 for 0.015% to curve 3 for 0.5% in Fig. 4. They are approximately proportional to the product of Pr^{3+} concentration times the sample thickness. On the other hand, the main absorption of the lowest $4f \rightarrow 5d$ band, at photon energy below $\sim$47 000 cm^{-1} in Fig. 4, decreases with the increasing concentration of Pr^{3+} due to the cluster formation as in the case[1] of Ce^{3+} in CaF_2. This concentration independence of the absorption cross section of $^1S_0$ level is again indicative of the shielded character of $4f \rightarrow 4f$ transition.

III. CONCENTRATION DEPENDENCE OF $4f \rightarrow 5d$ ABSORPTION OF Pr^{3+} IN CaF_2—THE EFFECT OF CRYSTALLINE ENVIRONMENT ON Pr^{3+} ABSORPTION IN ALKALINE-EARTH FLUORIDES

As in the case of Ce^{3+} in Ref. 1, the uv absorption spectra of Pr^{3+} in CaF_2 depends on the concentration of Pr^{3+} especially in the region of $4f \rightarrow 5d$ transitions.[9]

[9] The uv absorption of cluster-ion Pr^{3+} in our CaF_2 samples appears to be more prominent than that of Ce^{3+} in Ref. 1 as indicated by comparing the absorption spectra of Pr^{3+} and Ce^{3+} at comparable concentrations. The smaller ionic size of Pr^{3+} may enhance the cluster formation of Pr^{3+}-interstitial F^- pairs.

Figure 1 shows this concentration effect in a series of uv absorption spectra at varying concentrations from 0.001% to 5%. With increase in Pr^{3+} concentration, the $4f \rightarrow 5d$ bands corresponding to the previously assigned single-ion absorption of Pr^{3+} decrease in intensity while the bands in the intermediate-energy region C grow steadily. Following the example[1] of Ce^{3+}, we suggest that the absorption in region C is due to Pr^{3+} in the cluster formed from several pairs of Pr^{3+}-interstitial F^- (charge compensator). We assign the hump at 61 000 cm^{-1} as the t_{2g} band and the composite band with peaks at 54 000 and 56 000 cm^{-1} as e_g band, split by superchange with neighboring Pr^{3+}, of cluster-ion Pr^{3+}. These absorption bands are shown most clearly by curves 5 and 6 in Fig. 1 for 0.05 and 0.015% Pr^{3+}, respectively, at liquid-nitrogen temperature. The crystal-field strength, 10 Dq, based on this assignment is about 6000 cm^{-1}, half that of single-ion Pr^{3+} in CaF_2, and the reduction is due to higher symmetry around the cluster-ion Pr^{3+}. The centroid of the $5d$ levels of the cluster-ion is at $\sim$59 200 cm^{-1}. This is about 2400 cm^{-1} lower than that of single-ion Pr^{3+} (see Table I) in CaF_2 and the difference is presumably due to slightly larger dielectric screening around the cluster ion.

The cluster-ion absorption of Pr^{3+} in BaF_2 is very weak, as mentioned previously. It starts to become evident in a 4-mm-thick BaF_2 sample containing 0.5% Pr^{3+} as shown by two absorption peaks of e_g at 54 000 and 56 700 cm^{-1}, curve 1 in Fig. 3. As in the case[1] of Ce^{3+}, we speculate that the large interstitial size available in the BaF_2 lattice does not encourage cluster formation from Pr^{3+}-interstitial F^- pairs.

IV. POSSIBLE $4f \rightarrow 6s$ ABSORPTION OF Pr^{3+} IN CaF_2

The uv absorption spectra of Pr^{3+} in CaF_2 at photon energies higher than that of $4f \rightarrow 5d$ are summarized in Fig. 7 for concentrations from 0.001% to 1.5%.

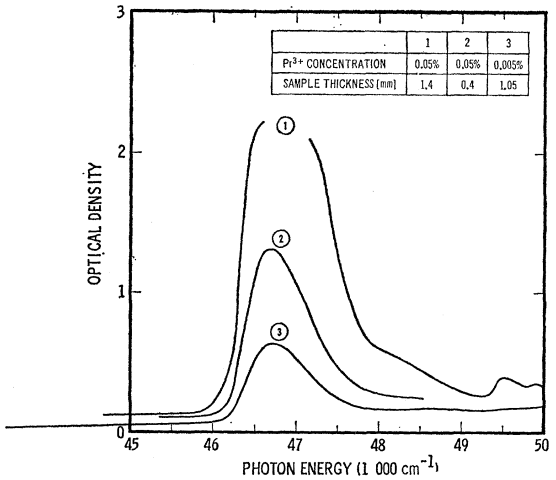
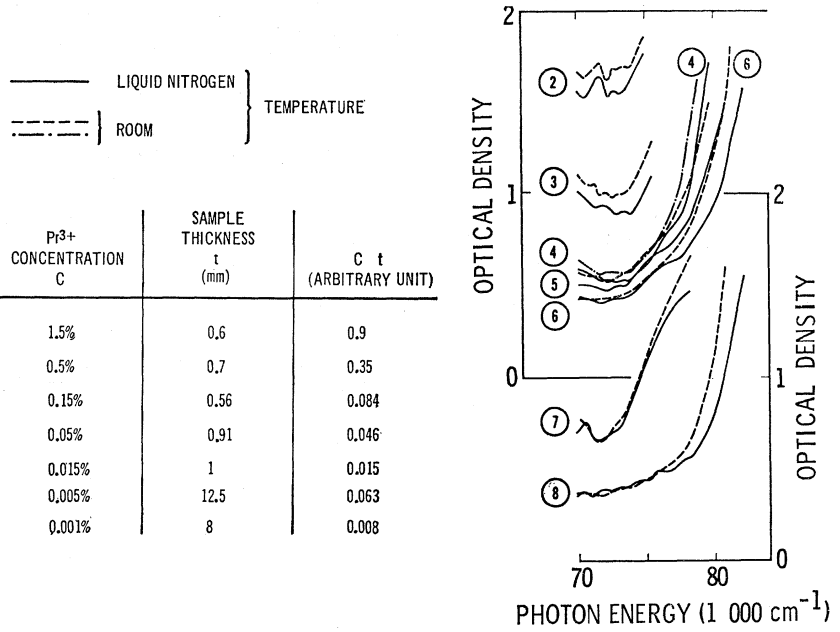


FIG. 6. Lowest $4f \rightarrow 5d$-absorption spectra of Pr^{3+} in SrF_2 crystals at liquid-nitrogen temperature.



	Pr^{3+} CONCENTRATION C	SAMPLE THICKNESS t (mm)	C t (ARBITRARY UNIT)
(2)	1.5%	0.6	0.9
(3)	0.5%	0.7	0.35
(4)	0.15%	0.56	0.084
(5)	0.05%	0.91	0.046
(6)	0.015%	1	0.015
(7)	0.005%	12.5	0.063
(8)	0.001%	8	0.008

FIG. 7. Ultraviolet-absorption spectra of Pr^{3+} in CaF_2 crystals near the absorption edge of CaF_2.

At liquid-nitrogen temperature a hump at ~76 000 cm^{-1} seems to be present in samples of sufficient Pr^{3+} concentration (curve 7 for 0.005% to curve 4 for 0.15% Pr^{3+} in Fig. 1 or Fig. 7). The absorption at this hump may be assigned to the $4f\rightarrow 6s$ transition of Pr^{3+} in CaF_2 which is similar to that[1] of Ce^{3+} with maximum at ~70 000 cm^{-1}.

Table III compares the locations of the interconfigurational transitions $4f\rightarrow 5d$ and $4f\rightarrow 6s$ of free-ion[3] Pr^{3+} with that of single-ion Pr^{3+} in CaF_2. The last column in the table shows the ratio of the transition energy of the free ion to that of single-ion Pr^{3+} in CaF_2. These ratios are comparable to the corresponding values[1] of Ce^{3+}.

V. RED SHIFT OF ABSORPTION EDGE OF CaF_2:Pr^{3+}

The absorption edge of CaF_2 has an apparent red shift as Pr^{3+} concentration increases. This is demonstrated, for example, by comparison of the higher apparent edge absorption of curve 5 (0.05% Pr^{3+}) with that of curve 6 (0.015% Pr^{3+}) where samples with comparable thickness but differing by a factor of 3 in concentration ratio were chosen. Following the example[1] of Ce^{3+}, we interpret this apparent red shift of the absorption edge of the host crystal as charge transfer from $F^-(2p^6)$ to $Pr^{3+}(6s)$.

TABLE III. Energy of centroid of $4f\rightarrow 5d$ and $4f\rightarrow 6s$ of free-ion Pr^{3+} and single-ion Pr^{3+} in CaF_2.

Transition	Free-ion Pr^{3+} Pr^{3+} (cm^{-1})	Single-ion Pr^{3+} in CaF_2 (cm^{-1})	(Free-ion Pr^{3+}) (Single-ion Pr^{3+} in CaF_2)
$4f\rightarrow 5d$	68 100	61 600	1.1
$4f\rightarrow 6s$	102 300	76 000	1.35

VI. CONCLUSION

The uv absorption spectra of Pr^{3+} in alkaline-earth fluorides are similar to those[1] of Ce^{3+} except that Pr^{3+} absorption generally occurs at higher energies. This general similarity between the uv absorption spectra of Ce^{3+} and Pr^{3+} in solids indicates that the crystal field is dominant in the higher configurations $5d$ and $6s$ of the rare-earth ions in solids. For Pr^{3+} in CaF_2, the three interconfigurational transitions are: (1) $4f\rightarrow 5d$ between 44 000 and 69 000 cm^{-1}; (2) a possible weak $4f\rightarrow 6s$ absorption at ~76 000 cm^{-1}; and (3) a charge-transfer absorption $F^-(2p^6)\rightarrow Pr^{3+}(6s)$ near ~80 000 cm^{-1}. Other effects such as vibronics in the lowest $4f\rightarrow 5d$ band and their concentration dependence, the effect of cluster formation on the $4f\rightarrow 5d$ bands, and the crystal effect on the free-ion data are all similar to those of Ce^{3+} in alkaline-earth fluorides. The cross section of $^1S_0$ absorption of Pr^{3+} in CaF_2 is estimated to be concentration-independent, which is consistent with the shielded character of the $4f\rightarrow 4f$ transition. The $^1S_0$ absorption and the vibronics are also observed in BaF_2:Pr^{3+}.

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