

## Vibronic Structure in the Absorption Spectrum of the $Ce^{+3}$ Ion in $CaF_2$ †

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A high-resolution absorption spectrum of the lowest  $4f \rightarrow 5d$  transition of  $Ce^{+3}$  in  $CaF_2$  is presented showing a rich vibronic structure. The observed structure leads to an entirely different interpretation of the spectrum from that proposed by Loh.

### I. INTRODUCTION

Vibronic structure in the electronic transitions of doubly ionized rare-earth ( $R^{+2}$ ) impurities in  $CaF_2$  has been known for many years.<sup>1,2</sup> In photon absorption, the structure arises from an event in which a phonon is created simultaneously with the electronic transition. The phonon frequencies may correspond either to local modes of oscillation involving the impurity ion and its nearest neighbors, or to delocalized modes of the host crystal, depending on the amount of lattice distortion and electron-phonon coupling.<sup>3</sup> Loudon<sup>4</sup> has shown that both local and nonlocal phonon modes can be observed simultaneously. In the case of the  $R^{+2}$  ions, most of the vibronic lines can be associated with pure-host-crystal frequencies as observed by Raman or infrared spectroscopy.<sup>5</sup>

More recently, vibronic structure in the lowest  $4f \rightarrow 5d$  transition of the  $Ce^{+3}$  ion impurity in  $CaF_2$  has been reported by Loh<sup>6</sup> and Schlesinger and Whippey.<sup>7</sup> The crystal environment is more complicated than in the case of the  $R^{+2}$  ions because each  $Ce^{+3}$  ion must be accompanied by a charge-compensating ion in the neighborhood. However, the spectra reported above appear to be much simpler than in the case of the  $R^{+2}$  ions, and Loh has interpreted the structure in terms of just two frequency components which he associates with the delocalized acoustical ( $\omega_{ac}$ ) and longitudinal optical ( $\omega_{LO}$ ) frequencies of the host crystal<sup>8</sup> according to the analysis of Bron and Wagner.<sup>3</sup> Loh's value for  $\omega_{ac}$  in  $CaF_2$  is greater by more than a factor of 2 than that for pure  $CaF_2$ , suggesting that further unresolved vibrational structure may be present.

In this paper, we report new higher-resolution absorption spectra which show substantially more vibrational structure than has been observed by Loh. The resolved peaks lead to an entirely different interpretation of the spectrum from that proposed by Loh.

### II. EXPERIMENTAL

Our crystals were supplied by Optovac Inc. They were cleaved into plates 1.10 mm thick and placed in a "home-made"<sup>9</sup> cryostat.

The cryostat is properly mounted at the exit slit of the McPherson (model No. 225) vacuum-uv spectrograph. A double-beam adaptor specially developed in our laboratory<sup>9</sup> enables the recording of the absorption spectra of doped samples in reference to nominally pure  $CaF_2$ . The spectrum presented in this work was recorded with sample and reference  $CaF_2$  at liquid-helium temperature.

### III. RESULTS AND DISCUSSION

The  $Ce^{+3}$  absorption spectrum at liquid-helium temperature in the neighborhood of 3000 Å is shown in Fig. 1. The transition energies are listed in Table I, with the numbering of the peaks corresponding to their order of appearance in Fig. 1. The energies are accurate to about  $\pm 5 \text{ cm}^{-1}$ .

The gross appearance of the spectrum is similar to that observed by Loh.<sup>6</sup> The strong peak 13 at 3085 Å and the two weaker peaks 14 and 15 at 3039.5 and 2996 Å are spaced from the sharp zero-phonon peak at 3132 Å by regular intervals of 485  $\text{cm}^{-1}$ . This is in reasonable agreement with the value 460  $\text{cm}^{-1}$  reported by Loh and undoubtedly is

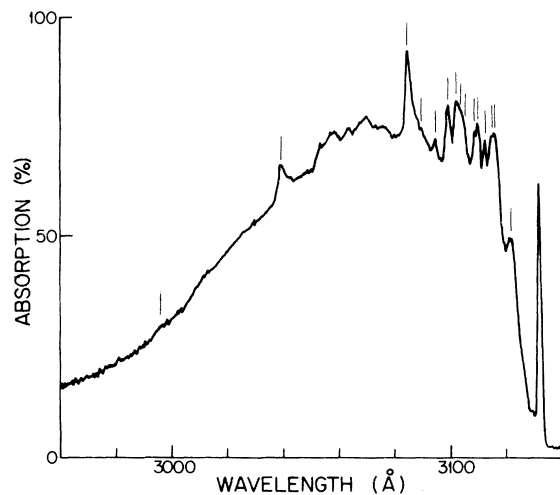


FIG. 1. Absorption spectrum of  $CaF_2:Ce^{+3}$  (impurity concentration 0.01 at.%) in the vicinity of 3000 Å. Sample thickness: 1.10 mm,  $T = 5 \pm 1^\circ K$ .

TABLE I. Wavelengths and frequencies of peaks in the  $\text{CaF}_2:\text{Ce}^{+3}$  spectrum.

Peak No.	$\lambda$ (Å)	$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )
0	3132	31 923	
1	3122	32 025	102
2	3116.5	32 082	159
3	3115.5	32 092	169
4	3113	32 118	195
5	3110.5	32 144	221
6	3109	32 159	236
7	3106	32 190	267
8	3104	32 211	288
9	3103	32 221	298
10	3099.5	32 257	334
11	3095.5	32 299	376
12	3090	32 357	434
13	3085	32 409	486
14	3039.5	32 894	971
15	2996	33 371	1448

associated with the  $\omega_{\text{LO}} = 463\text{-cm}^{-1}$  frequency<sup>8</sup> of the  $\text{CaF}_2$  host crystal. As shown by Bron and Wagner,<sup>3</sup> the value encountered in impurity vibronic spectra should be slightly greater than the host crystal frequency, in agreement with our result.

On a finer scale, our spectrum shows a large number of additional peaks. Loh's interpretation accounts for only two of the twelve peaks between 3132 and 3085 Å listed in Table I (peaks labeled 1–12). The same structure, though less pronounced, appears to be repeated in the next large interval between peaks 13 and 14. If

this is the case, then the latter structure arises from combinations of phonon frequencies 1–12 with 13.

In Table II we have attempted to correlate the first 13 phonon frequencies (column 2) with those observed in  $\text{CaF}_2:\text{R}^{+2}$  vibronic spectra (columns 3 and 4) and in pure  $\text{CaF}_2$  (columns 5 and 6). In common with the  $\text{R}^{+2}$  data, most of the frequencies can be associated with one of those observed in the first- or second-order Raman spectrum of pure  $\text{CaF}_2$ . In making the comparison, it should be noted that the Raman data were taken at room temperature.<sup>5</sup> The increase of phonon energies with decreasing temperature can be approximately allowed for by adding about  $10\text{ cm}^{-1}$  to the values listed in Table II. The lowest phonon frequency  $102\text{ cm}^{-1}$  in  $\text{CaF}_2:\text{Ce}^{+3}$  is in good agreement with the value  $96\text{ cm}^{-1}$  observed in  $\text{CaF}_2:\text{Tm}^{+2}$  and may be associated with the acoustical mode  $\omega_{\text{ac}} = 71\text{ cm}^{-1}$  of pure  $\text{CaF}_2$ . The only "candidates" for local-vibrational modes are those frequencies which do not appear in the Raman or ir spectrum of pure  $\text{CaF}_2$ . These frequencies are 159, 195, 236, and  $298\text{ cm}^{-1}$ . The lowest local-mode frequency  $159\text{ cm}^{-1}$  is not far from the value  $135\text{ cm}^{-1}$  inferred by Nara and Schlesinger<sup>10</sup> from the thermoluminescence spectrum of  $\text{CaF}_2:\text{Dy}^{+3}$ .

The presence of many delocalized  $\text{CaF}_2$  frequencies in the vibronic spectrum of  $\text{Ce}^{+3}$  suggests that, despite the presence of a charge compensator, the lattice is not much distorted by the  $\text{Ce}^{+3}$  ion. This conclusion is in harmony with the findings of Nara and Schlesinger<sup>11</sup> in their analysis of the  $\text{CaF}_2:\text{Dy}^{+3}$  spectrum.

TABLE II. Comparison of energy differences ( $\text{cm}^{-1}$ ).

Peak No.	$\text{CaF}_2:\text{Ce}^{+3}$ <sup>a</sup>	$\text{CaF}_2:\text{Sm}^{+2}$ <sup>b</sup>	$\text{CaF}_2:\text{Tm}^{+2}$ <sup>c</sup>	$\text{CaF}_2(\text{Raman})$ <sup>d</sup>	$\text{CaF}_2(\text{ir})$ <sup>e</sup>
1	102		96		71 ( $\nu_{\text{ac}}$ )
2	159				
3	169		173	157	
		184	180		
4	195	199			
5	221	228	221	218	
6	236	239			
7	267	259	255	254	257 $\nu_1(\text{TO})$
8	288	289		275	
9	298				
10	334	339	339	322	
			348	337	
		379			
11	376	389	391	386	
12	434			408	
13	486			467	463 $\nu_{\text{LO}}$

<sup>a</sup>Vibronic spectrum, present work.

<sup>b</sup>Vibronic spectrum, Ref. 1.

<sup>c</sup>Vibronic spectrum, Ref. 2.

<sup>d</sup>Raman spectrum, Ref. 5.

<sup>e</sup>Infrared spectrum, Ref. 8.

*Note added in proof.* Similar vibrational structure to ours has been reported by Jacobs *et al.*<sup>12</sup> and more recently by Hayes *et al.*<sup>13</sup> The former observe a sharp line separated by  $404\text{ cm}^{-1}$  from the zero phonon line not observed by the latter. Concentration-dependent studies carried out in our

laboratory indicate that the  $404\text{-cm}^{-1}$  line results from Ce-Ce interactions and disappears at low impurity concentrations. Our interpretation is similar to that of Hayes *et al.*<sup>13</sup> except that in our work the strong line at  $486\text{ cm}^{-1}$  is associated with the pure-CaF<sub>2</sub> Raman<sup>5</sup> and ir<sup>8</sup> modes (see Table II).

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