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$4f \to 5d$ transition studies of Ho^{+3} in calcium fluoride*

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$4f \to 5d$ transitions of the Ho^{+3} ion in CaF_2 are investigated. Phonon structure on more than just one of the vacuum-ultraviolet-absorption peaks is observed. The structure on some peaks is interpreted in terms of delocalized CaF_2 frequencies. The results are in general agreement with our previous work on CaF_2:Ce^{+3}.

I. INTRODUCTION

The $4f^{n-1}$ $5d$ configuration of the trivalent rare-earth ions in solids like CaF_2 is essentially assumed[1,2] to be formed by weak interaction between the $5d$ orbitals and the $4f^{n-1}$ core. It should be remembered that the $5d$ orbitals themselves are strongly split in the crystal field. The detailed interpretation, however, of the vacuum-ultraviolet-absorption spectra of the different rare-earth ions with their complicated phonon structure is still not possible. An additional difficulty is the possible presence of more than just a single type of rare-earth-ion site in the crystal.

In the present work we present a relatively high-resolution (0.5 Å), liquid-helium-temperature absorption spectrum of the CaF_2:Ho^{+3} ($4f^{10}$) system in the 1280–1600-Å region. It will become evident that some conclusions can nevertheless be drawn from the presented curves. These conclusions will be related to our previous work[3] on the vibronic structure in the absorption spectrum of Ce^{+3} ($4f^1$) in CaF_2. Specifically, we establish the presence of many delocalized CaF_2 frequencies in the vibronic spectrum of Ho^{+3}. This suggests, as we have pointed out[3] in the cases of Dy^{+3} and Ce^{+3}, that despite the presence of a charge compensator, the lattice is not much distorted by the Ho^{+3} ion.

II. EXPERIMENTAL

Our crystals were supplied by Optovac Inc. or Harshaw Inc. They were cleaved into plates of varying thicknesses. Next the crystals were mounted in our "home-made" liquid-helium cryostat. This cryostat is properly fitted on the exit slit of the McPherson (Model No. 225) 1-m vacuum ultraviolet spectrograph. A double-beam adaptor, developed[4] in our laboratory, enables the recording of absorption spectra of the doped samples with reference to pure CaF_2. The spectrum presented here was obtained with the sample and reference CaF_2 at liquid-helium temperature. The light source in our measurements is a "home-made" noble-gas lamp excited by a 200-W microwave generator (Microtron Model No. 200).

III. RESULTS AND DISCUSSION

In Fig. 1 we present the absorption spectrum at liquid-helium temperature in the 1280–1600-Å region of a CaF_2:Ho^{+3} crystal supplied by Optovac Inc. with impurity concentration of 0.05 at.%. It

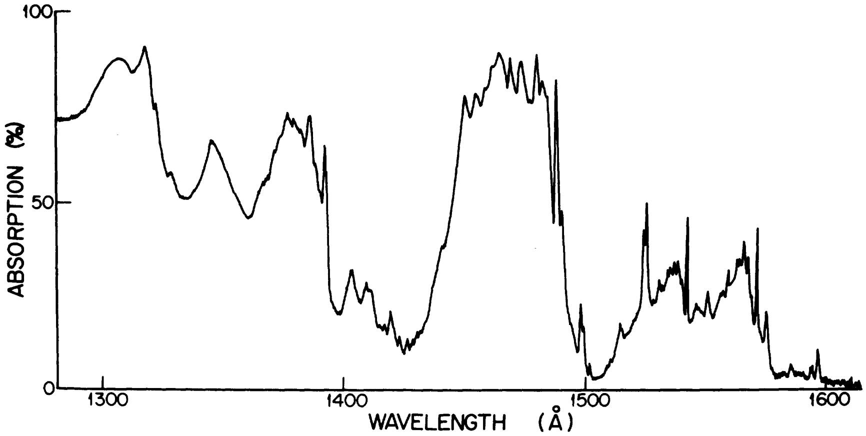

FIG. 1. Absorption spectrum at liquid-helium temperature of an Optovac CaF_2:Ho^{+3} crystal in the 1280–1600-Å region. Impurity concentration 0.05-at. %, sample thickness 0.65 mm.

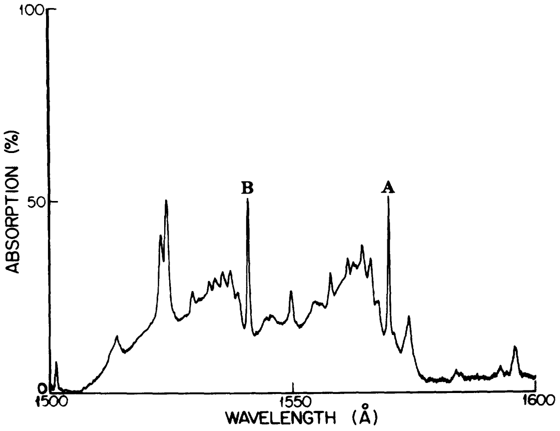

FIG. 2. Extended view of the 1500–1600-Å region of Fig. 1.

will be noticed that phonon structure is evident on more than just *one* absorption peak. This is somewhat surprising as one would expect[5] phonon structure on the lowest $4f \rightarrow 5d$ transition peak only, as is the case for Ce^{+3}. A possible explanation would be the simultaneous existence of more than one type of impurity-ion site in the crystal. If this is so, one would expect that their relative abundance would be sample dependent. We have, therefore, examined the absorption spectrum, in the same spectral region, of samples of different origins and different impurity concentrations. (See Table I.)

In all these, we have found the relative intensities and shapes of the various absorption peaks to be essentially sample independent. In contrast to this, in the case of Er^{+3}, for instance, we did find[6] marked changes in the relative intensities of various peaks as we examined different samples even from the same supplier. It is still possible, though not very likely, that the Ho^{+3} ions favor a certain relative distribution of ion sites in the lattice.

In Fig. 2 we present a more detailed picture of the absorption in the 1500–1600-Å region. Here, we identify tentatively two narrow absorption lines (*A* and *B* on Figs. 1 and 2) at 1571 and 1542 Å as no-phonon lines. To their respective lower-wavelength sides we identify the structure as vibronic in character. In Table II the no-phonon lines and their vibronics are given in terms of their wavelengths and frequencies.

TABLE I. Samples examined in the present work.

Supplier		Impurity concentration (at. %)	
Optovac Inc.		0.1	Value quoted by supplier
		0.05	
		0.01	
		0.005	
Harshaw Inc.	(No. 12)	0.05	≈ estimated
	(No. 13)	0.05	
	(No. 14)	0.05	
	(No. 15)	0.05	

TABLE II. Wavelengths and frequencies corresponding to Fig. 2.

Peak No.	λ(Å)	ν(cm^{-1})	$\Delta\nu$(cm^{-1})
A	1571	63 654	
A_1	1569	63 735	81
A_2	1567.5	63 796	142
A_3	1565.5	63 877	223
A_4	1564	63 939	285
A_5	1563	63 980	326
A_6	1560.5	64 082	428
A_7	1559	64 144	490
B	1542	64 850	
B_1	1540	64 935	85
B_2	1538.5	64 998	148
B_3	1537	65 062	212
B_4	1535.5	65 125	275
B_5	1534	65 189	339
B_6	1532	65 274	424
B_7	1530.5	65 338	488

In Table III we make a comparison between the energy differences inferred from Fig. 2 and those obtained for $CaF_2:Ce^{+3}$ in Ref. 3. One has to remember that the values in Table III are accurate to within 10 cm^{-1}. Under those circumstances the agreement between the two set of values inferred from Fig. 2 and the $CaF_2:Ce^{+3}$ values is rather good. This we feel lends further support to our identification of the ≈488-cm^{-1} mode as the one associated with the $\omega_{LO} = 463$-cm^{-1} frequency of the CaF_2 host lattice.

TABLE III. Comparison of energy differences (cm^{-1}).

Present work		$CaF_2:Ce^{+3}$ (Ref. 3)
A	B	
81	85	102
		159[a]
142	148	169
		195[a]
223	212	221
		236[a]
	275	267
285		288
		298[a]
326	337	334
		376
428	424	434
490	488	486

[a] Identified as local modes (see Ref. 3).

This last point is in some conflict with a recent paper by Hayes *et al.*[7] In that work, the side band at 490 cm^{-1} was proposed to be due to a local mode arising from the vibration of the eight nearest fluorine neighbors of the Ce^{+3} ion.

In general, phonon frequencies may correspond either to local modes of oscillation involving the impurity and its nearest neighbors and/or to delocalized modes of the CaF_2 lattice, depending on the amount of lattice distortion and electron-phonon coupling.

The observation of many delocalized CaF_2 frequencies, associated with these well isolated $4f \rightarrow 5d$ transitions, clearly suggests that despite the presence of a charge compensator, the lattice is not too much distorted by the Ho^{+3} ion. This is also in harmony with earlier conclusions[8] concerning Dy^{+3}.

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