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$4f \rightarrow 5d$ Transition Studies of Some Rare-Earth Ions in CaF_2†

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High-resolution absorption spectra due to the lowest $4f \rightarrow 5d$ transitions for some rare-earth ions in CaF_2 are presented. It is shown that these absorption peaks are complex and include two or more components.

I. INTRODUCTION

The $4f^{n-1}5d$ configuration of the divalent and trivalent rare-earth ions in solids such as CaF_2 is fairly well understood.[1] It is essentially assumed to be formed by weak interaction between the $5d$ orbitals, which themselves are strongly split in the crystal field, with the $4f^{n-1}$ core.

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.

In his paper[2] concerning the lowest $4f \rightarrow 5d$ transitions of trivalent rare-earth ions in CaF_2 crystals, Loh points out the existence of twin peaks in the absorption spectra of Sm^{+3} $(4f^5)$, Eu^{+3} $(4f^6)$, and Yb^{+3} $(4f^{13})$. As a source of these he mentions two possibilities: (a) the presence of the corresponding doubly ionized rare-earth ion and (b) the structure of $4f^{n-1}$ electrons in the $4f^{n-1}5d$ configuration.

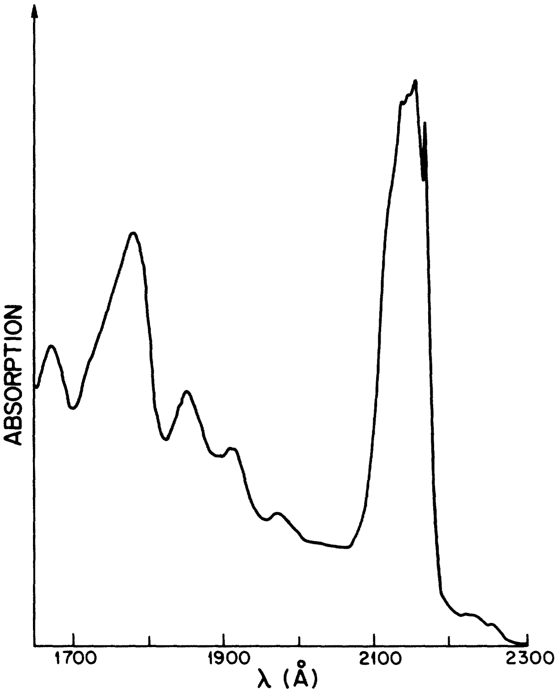

FIG. 1. Absorption spectrum of CaF_2: Tb^{+3} in the range 1650–2200 Å. Sample thickness 0.42 mm and Tb^{+3} concentration of 0.05 at.%.

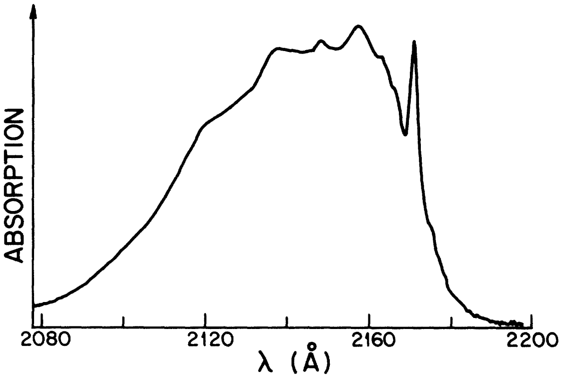

FIG. 2. High-resolution absorption spectrum of the lowest $4f \rightarrow 5d$ transition of Tb^{+3} in CaF_2 (same sample as in Fig. 1).

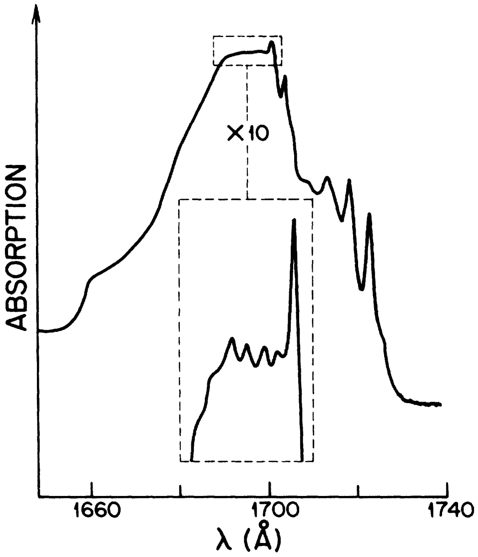

FIG. 3. High-resolution absorption spectrum of the lowest $4f \rightarrow 5d$ transition of Dy^{+3} in CaF_2. Sample thickness 0.49 mm and impurity concentration of 0.05 at.%. An expanded ×10 in intensity and ×2 in wavelength view of the top portion is given in the bottom.

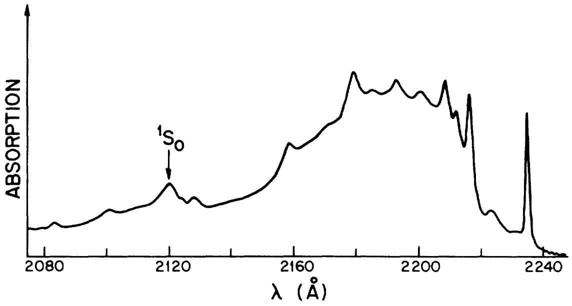

FIG. 4. High-resolution absorption spectrum of the lowest $4f \rightarrow 5d$ transition of Pr^{+3} in CaF_2. Sample thickness 0.38 mm and impurity concentration of 0.05 at.%.

In the present work, we present relatively high-resolution (0.5-Å) absorption spectra of the lowest $4f \rightarrow 5d$ transitions of $Pr^{+3}(4f^2)$, $Nd^{+3}(4f^3)$, $Tb^{+3}(4f^8)$, and $Dy^{+3}(4f^9)$ ions in the CaF_2 matrix.

It will become evident that in these ions, as well, the lowest $4f \rightarrow 5d$ band is complex and most probably contains at least two components.

This, we feel, lends support to possibility (b) above.

II. EXPERIMENTAL

Our crystals were supplied by Optovac or Harshaw. They were cleaved into plates of varying thicknesses as indicated on the figures, and mounted in the "home made"[3] cryostat. This cryostat was properly fitted on the exit slit of the McPherson (model No. 225) vacuum-uv spectrograph. A double-beam adaptor, developed in our laboratory,[3] enabled the recording of the absorption spectra of the doped samples with reference to pure CaF_2. All spectra presented in the present work were recorded with the samples and reference CaF_2 at liquid-nitrogen temperature.

III. RESULTS AND DISCUSSION

Figure 1 is the absorption spectrum of a $CaF_2:Tb^{+3}$ crystal (0.05 at.%) at liquid-nitrogen temperature in the wavelength range of 1650–2200 Å. Figure 2 is the detailed spectrum of the absorption peak at ≈ 2150 Å, for the same crystal. The existence of at least two band components in this lowest $4f \rightarrow 5d$ transition is quite evident from these figures.

In Fig. 3 the absorption due to the lowest $4f \rightarrow 5d$ transition in $CaF_2:Dy^{+3}$ (0.05 at.%) is presented. Here, too, the existence of at least two (probably even more) components is evident. An extended (×10) view of the top of the curve is presented also in Fig. 3. Figures 4 and 5 are the absorption spectra of $CaF_2:Pr^{+3}$ (0.05 at.%) and $CaF_2:Nd^{+3}$ (0.05 at.%), respectively. Here the complexity of the bands and their phonon structure is also evident.

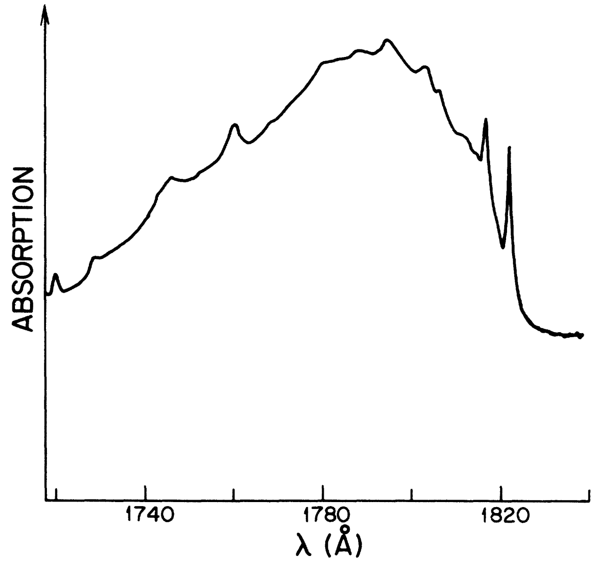

FIG. 5. High-resolution absorption spectrum of the lowest $4f \rightarrow 5d$ transition of Nd^{+3} in CaF_2. Sample thickness 0.33 mm and impurity concentration of 0.05 at.%.

It is not impossible that our experimental spectra are due to more than just a single type of ion site in the lattice. Indeed it should be emphasized that before any detailed theoretical study of these and similar spectra can be undertaken, it is important to determine whether they are due to a single or many types of ion sites in the solid. At the same time, however, one should remember that two different site symmetries could well be expected to manifest themselves by, "two" lowest $4f \rightarrow 5d$ absorption peaks separated by more than just a few hundred wave numbers. This can be seen,[4] for instance, in the case of $CaF_2:Ce^{+3}$. Introduction of another site symmetry resulted in bands $(4f^1 \rightarrow 4f^0 5d)$ shifted by more than 2000 cm^{-1}. The above line of consideration then brings us back to possibility (b) above, i.e., the structure of $4f^{n-1}$ electrons in the $4f^{n-1}5d$ configuration needs further study.

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[1] E. Loh, Phys. Rev. B **7**, 1846 (1973), and references cited therein.

[2] E. Loh, Phys. Rev. **147**, 332 (1966).

[3] M. Schlesinger and T. Szczurek (unpublished).

[4] M. Schlesinger and P. W. Whippey, Phys. Rev. **171**, 361 (1968).