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$4f^{n}\rightarrow 4f^{n-1}5d$ Spectra of Rare-Earth Ions in Crystals

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The $4f^n\rightarrow 4f^{n-1}5d$ absorption spectra of rare-earth ions, RE^{2+} or RE^{3+}, in crystals can be fitted with energy gaps in the ground multiplets of the $4f^{n-1}$ core. Unlike the shielded $4f^n$ configuration, the $4f^{n-1}5d$ levels of RE in crystals are therefore very different from those of free ions, and are formed through the interaction between the electron in $5d$ orbitals with the $4f^{n-1}$ core.

THE absorption spectra of rare-earth ions, RE^{2+} or RE^{3+}, in crystals arise mainly from two types of electronic transitions: weak $4f\rightarrow 4f$ at low energies, and strong $4f\rightarrow 5d$ at higher energies. The former are analogous to free-ion levels due to the shielded character of the $4_f{}^n$ configuration. The $4f^n\rightarrow 4f^{n-1}5d$ transitions in crystals are not well understood because of uncertainties[1] in the relative magnitude of the crystal field, electrostatic interaction, and spin-orbit coupling in the $4f^{n-1}5d$ configuration.

In this work we show that the complex patterns in the $4f^n\rightarrow 4f^{n-1}5d$ absorption spectra of most RE^{2+} or RE^{3+} ions in solids can be fitted to energy gaps in the ground multiplets of the $4f^{n-1}$ core. The $4f^{n-1}5d$ levels may therefore be understood as formed[2–4] by the electron in the $5d$ orbitals e_g or t_{2g} interacting with the $4f^{n-1}$ core. As a consequence of this strong crystal-field effect[5] on the $5d$ electron, the $4f^{n-1}5d$ configurations of RE in solids are very different from those of free ions.

The $4f^n\rightarrow 4f^{n-1}5d$ absorption spectra of most RE^{2+} or RE^{3+} in crystals exhibit two features. First, they consist of strong bands corresponding to components of $5d$ orbitals split in the crystal field. Consequently, their spectra are similar [among RE^{2+} ions,[2,6–8] e.g., Eu^{2+} (Ref. 6) and Yb^{2+} (Ref. 6); or RE^{3+} ions,[9–12] e.g., Ce^{3+} (Ref. 10), Pr^{3+} (Ref. 11), and Nd^{3+} (Ref. 12)] when the ions are embedded in the same type of hosts. Second, the structures of the $5d$ bands can be fitted to energy differences in the ground multiplets of the $4f^{n-1}$ core.[13] It is this second feature we wish to demonstrate in the absorption spectra of most RE^{2+} or RE^{3+} ions in alkaline-earth fluorides.

Five common RE^{2+} ions, Sm^{2+}, Eu^{2+}, Dy^{2+}, Tm^{2+}, and Yb^{2+}, are shown in Fig. 1. The gross feature in the spectra of some ions has been characterized[6] as the e_g and t_{2g} components of the $5d$ electron in the cubic crystal field. We shall now consider the structure, i.e., strong lines, broad peaks, and shoulders, within each component. We assign most of the strong lines as pure electronic transitions to $4f^{n-1}5d$ levels and other structures as their vibronics, which are not yet resolved. We assume further that the $4f^{n-1}5d$ levels are formed through interaction between the $5d$ (e_g or t_{2g}) electron and the $4f^{n-1}$ core, and are spaced with the energy gaps in the $4f^{n-1}$ ground multiplets. In Fig. 1 these levels are marked by bars, which precede most of the structure due to vibronics. For convenience we discuss the spectra of RE^{2+} in the following order: (1) Tm^{2+} and Dy^{2+}, (2) Eu^{2+} and Yb^{2+}, and (3) Sm^{2+}.

(1) In the $4f^{13}\rightarrow 4f^{12}5d$ spectra of Tm^{2+}, a set of three bars corresponding to the $^3H_6$, $^3H_4$, and $^3H_5$ levels of the ground multiplet of the $4f^{12}$ core precedes peaks or humps in both the e_g, 14 000 cm^{-1} to 28 000 cm^{-1}, and t_{2g}, 28 000 cm^{-1} to 43 000 cm^{-1} regions. In the $4f^{10}\rightarrow 4f^{9}5d$ absorption spectra of $CaF_2:Dy^{2+}$, a set of nine bars corresponding to ^6H_j and ^6F_j levels of the $4f^9$ core again precedes structures in both the e_g, 10 000 cm^{-1} to 27 000 cm^{-1}, and t_{2g}, 27 000 cm^{-1} to 44 000 cm^{-1} regions.

(2) The e_g band of Eu^{2+} in CaF_2 and SrF_2 has been resolved directly by Kaplyanskii *et al.*[4] into the pure electronic transitions, shown by bars in Fig. 1, and their associated vibronics at liquid-helium temperature. By analogy, we analyze the t_{2g} band of Eu^{2+} in these two hosts by translating the same set of bars from e_g band to precede the unresolved vibronics in the t_{2g} band at liquid-nitrogen temperature, Fig. 1. The energy gaps in the ground multiplet of $4f^6$, or Eu^{3+}, are among the

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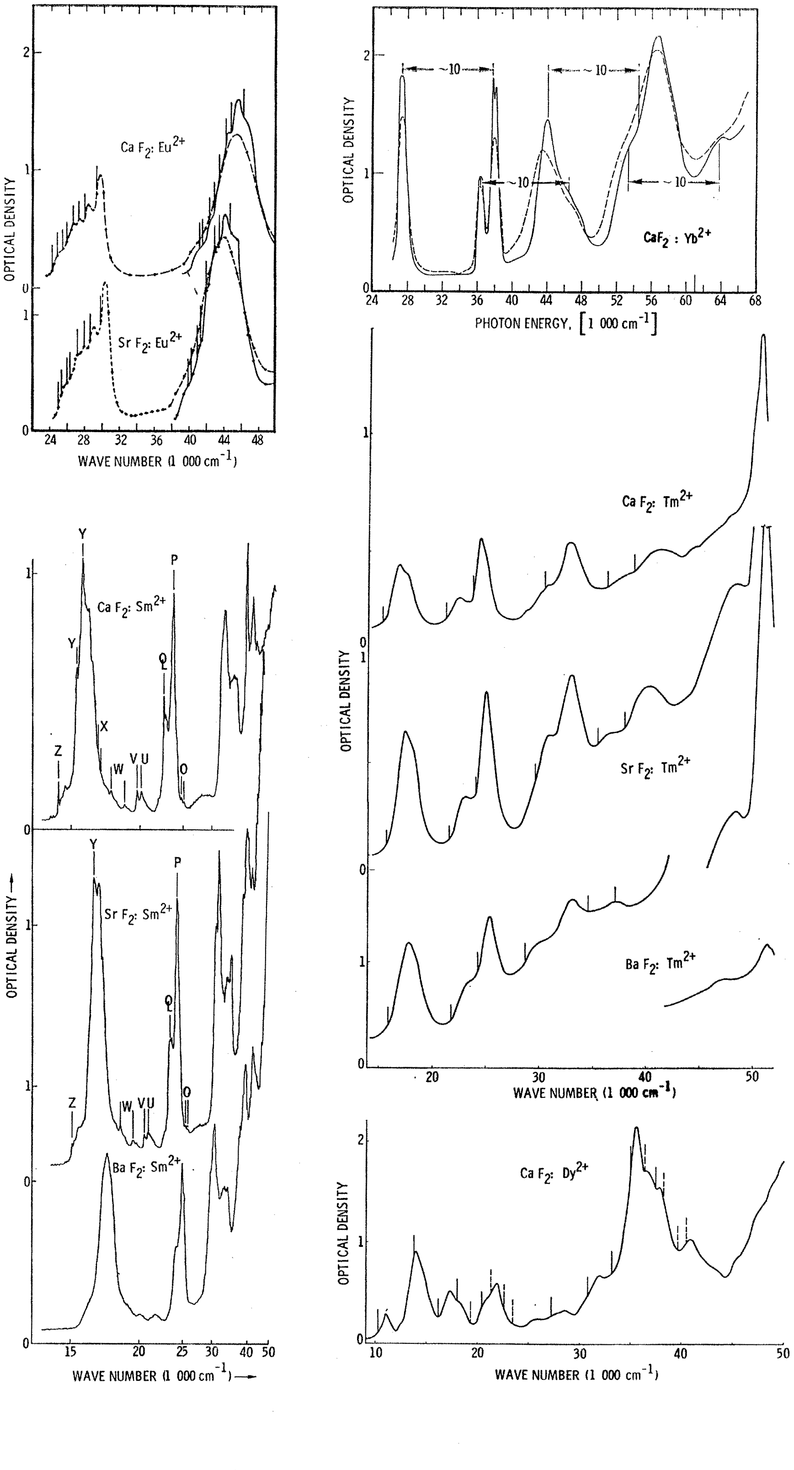

FIG. 1. $4f^n \rightarrow 4f^{n-1}5d$ absorption spectra of some divalent rare-earth ions Sm^{2+}, Eu^{2+}, Dy^{2+}, Tm^{2+}, and Yb^{2+} in alkaline-earth fluorides. (Sm^{2+} and solid curves of Eu^{2+} and Yb^{2+} at liquid-nitrogen temperature, Dy^{2+} and Tm^{2+} at room temperature.)

narrowest of all RE, while that of $4f^{13}$, or Yb^{3+}, is the largest. The Yb^{2+} spectrum in Fig. 1 clearly demonstrates this contrast by showing the huge $Yb^{3+}(^2F_{5/2}) - Yb^{3+}(^2F_{7/2}) \approx 10\,000$ cm^{-1} separation between e_g bands[12] 37 800 cm^{-1} − 27 400 cm^{-1} = 10 400 cm^{-1}, and 46 800 cm^{-1} − 36 400 cm^{-1} = 10 400 cm^{-1}, and t_{2g} bands[12] 54 500 cm^{-1} − 44 100 cm^{-1} = 10 400 cm^{-1}, and 63 500 cm^{-1} − 53 100 cm^{-1} = 10 400 cm^{-1}.

(3) We assign most of the strong lines in the e_g, ~14 000 cm^{-1} to ~30 000 cm^{-1} region of the Sm^{2+} spectra in CaF_2 and SrF_2, Fig. 1, as pure electronic transitions and mark them with vertical bars. Following

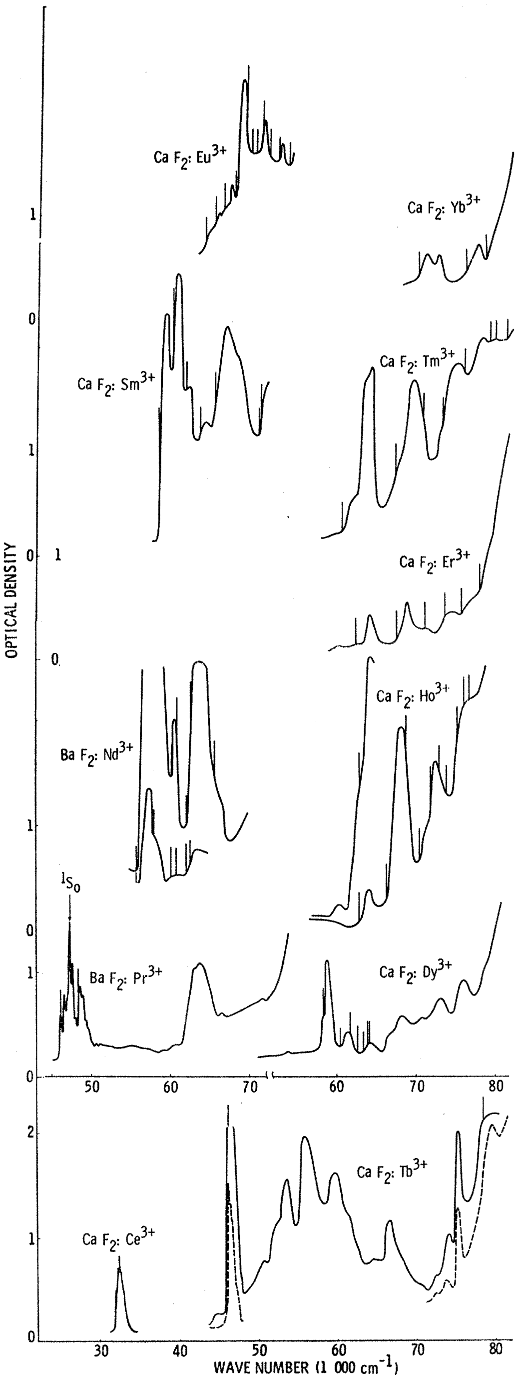

FIG. 2. $4f^n \rightarrow 4f^{n-1}5d$ absorption spectra of trivalent rare-earth ions Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+} in alkaline-earth fluorides. (All RE^{3+} are in CaF_2 except Pr^{3+} and Nd^{3+} in BaF_2. All are measured at liquid-nitrogen temperature, except Ho^{3+} and Er^{3+} at room temperature. Concentration and sample thickness are 0.15% $Ce^{3+} \times 0.29$ mm, 0.005% $Pr^{3+} \times 0.95$ mm, 0.005% $Nd^{3+} \times 1$ mm and 0.01% $Nd^{3+} \times$ 13 mm, 0.005% $Sm^{3+} \times 10$ mm, >0.006% $Eu^{3+} \times 10$ mm, 0.2% $Tb^{3+} \times \sim 1$ mm and 0.02% $Tb^{3+} \times \sim 1$ mm, 0.01% $Dy^{3+} \times \sim 1$ mm, 1% $Ho^{3+} \times \sim 1$ mm and 0.1% $Ho^{3+} \times \sim 1$ mm, 0.01% $Er^{3+} \times \sim 1$ mm, 0.1% $Tm^{3+} \times \sim 1$ mm and >0.005% $Yb \times \sim 10$ mm.)

the work[4] on the e_g band of Eu^{2+}, we compare our assignment in the spectra[14] of Sm^{2+} with the ground multiplets[13] of $4f^5$ or Sm^{3+} in Table I. The agreement in corresponding energy gaps is satisfactory. We do not venture to make similar comparison in the t_{2g} region of Sm^{2+} from $\sim$30 000 cm^{-1} to $\sim$40 000 cm^{-1} because of the presence of strong defect absorption,[7,15] e.g., at $\sim$33 000 cm^{-1} in the Tm^{3+} spectra and probably at $\sim$36 000 cm^{-1} in the Dy^{2+} spectrum of Fig. 1.

Based on the above assignment of $4f^{n-1}5d$ levels of RE^{2+} and other considerations, such as the dependence of the absorption spectra on lattice parameters, we are able to assign the regions of e_g, t_{2g}, and their separation, i.e., the crystal-field strength $10Dq$, more reliably. The data due to gross crystal-field effects on $5d$ electrons of some RE^{2+} will be summarized in a separate publication.

All available RE^{3+} ions are shown in Fig. 2. Only Gd^{3+} and Lu^{3+} are absent because of their excessive $4f \rightarrow 5d$ energies. The $4f^{n-1}5d$ levels are again marked by vertical bars. Following this procedure used for RE^{2+}, these bars are placed in the spectra to precede most structures due to vibronics. For Pr^{3+} the $^1S_0$ level[16,11] at $\sim$47 200 cm^{-1} accidentally coincides with the $4f(^2F_{7/2})5d(e_g)$ level in CaF_2. We use the spectrum of BaF_2:Pr^{3+} to avoid this overlap and hence unambiguously demonstrate the $4f(^2F_{5/2})5d(e_g)$ and $4f(^2F_{7/2})5d(e_g)$ levels as indicated by bars. For Tb^{3+} a huge separation between $4f^7(^8S)5d(e_g)$ and $4f^7(^6P_{7/2})5d(e_g)$ corresponding to the energy gap of $\sim$32 000 cm^{-1} between ^8S and $^6P_{7/2}$ levels[13] of Gd^{3+} is expected. Accordingly, we assign some of the structures between 72 000 and 80 000 cm^{-1} in the Tb^{3+} spectra of Fig. 2 as unresolved vibronics of the $4f^7(^6P_{7/2})5d(e_g)$ level as suggested by the bar at 78 400 cm^{-1}. We abandon our previous[9] speculation on the strong absorption peak at 75 200 cm^{-1} as due to $4f \rightarrow 5d$ absorption of Tb^{4+}, since the energy of Tb^{4+} absorption should be higher than that of the isoelectronic Gd^{3+} because of higher effective nuclear charge in Tb^{4+} ion.

The $4f \rightarrow 5d$ absorption spectra of RE^{3+} in alkaline-earth fluorides are more complicated than that of RE^{2+} because of the presence of charge compensators[10,11] accompanying trivalent ions. The charge compensators, e.g., interstitial fluorine ion, may lower the symmetry at RE^{3+} sites and can introduce cluster absorptions[10,11] due to clusters of RE^{3+}–charge-compensator complexes. The deduction of data on e_g, t_{2g}, and $10Dq$ of single-ion RE^{3+} in alkaline-earth fluorides from their spectra is therefore not as reliable as for RE^{2+} in the divalent host.

In conclusion, the $4f^n \rightarrow 4f^{n-1}5d$ absorption spectra of RE^{2+} and RE^{3+} in crystals can be fitted to energy gaps in the ground multiplets of the $4f^{n-1}$ core. The $4f^{n-1}5d$

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TABLE I. Pure electronic transitions in e_g component of $4f^6 \rightarrow 4f^5 5d$ absorption of Sm^{2+} in CaF_2 and SrF_2 (wave number ν in 1000 cm^{-1}).

$CaF_2:Sm^{2+}$			$SrF_2:Sm^{2+}$			Sm^{3+} ground multiplets	
ν	$\Delta\nu$		ν	$\Delta\nu$		$\Delta\nu$	
14.5	0		15.2	0		0	Z or $^6H_{5/2}$
15.47	0.97	1.15	16.45	1.25		1.1	Y or $^6H_{7/2}$
15.8	1.3						
16.76	2.26	2.36				2.3	X or $^6H_{9/2}$
16.96	2.46						
17.68	3.18	3.68	18.3	3.1	3.6	3.6	W or $^6H_{11/2}$
18.68	4.18		19.32	4.12			
19.7	5.2		20.39	5.19		5	V or $^6H_{13/2}$
20.12	5.62		20.77	5.57		5.75	U or $^6F_{1/2}$
21.85	7.35		22.55	7.35		7	R or $^6F_{5/2}$
22.47	7.97		23.15	7.95		7.9	Q or $^6F_{7/2}$
23.64	9.14		24.12	8.92		9.05	P or $^6F_{9/2}$
24.7	10.2	10.4	25.33	10.13	10.28	10.4	O or $^6F_{11/2}$
25.1	10.6		25.62	10.42			

configurations of RE in crystals are therefore understood as formed through interaction of the 5*d* orbital with the $4f^{n-1}$ core.

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