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Ab initio calculation on crystal fields of Sm^{2+} in solids with Cl and F ligands

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The linear combination of atomic orbitals (-molecular orbitals) crystal-field theory in the context of the superposition model was used to calculate the intrinsic crystal-field parameters for Sm^{2+} ions in solids with Cl and F ligands at different interionic distances. The five main contributions: point charge, charge penetration, exchange, overlap, and covalency considered in the present work can reasonably describe the experimental results. A direct comparison between divalent and trivalent lanthanide ions leads to the conclusion that the initial intrinsic crystal-field parameters and the power-law exponents corresponding to the distance dependence for divalent lanthanide ions are larger than those for trivalent lanthanide ions. [S0163-1829(98)03434-1]

I. INTRODUCTION

The crystal-field (CF) properties of luminescent rare-earth (RE) and transition-metal ions have been extensively studied over the past three decades and continue to attract attention because of the practical applications of optical materials activated by these ions.[1–5] Experimental methods for obtaining CF energy levels through optical spectroscopy are well developed and a variety of systems have been thoroughly analyzed.[2,5–8]

The typical experimental objective is the determination of a phenomenological set of CF parameters (usually B_q^k) that is consistent with measured CF energies and that can be used to predict the energies of states not directly measured. Current experimental directions include an extension of optical techniques into the ultraviolet to probe higher lying states[9,10] and the characterization of long-wavelength transitions in low phonon energy systems.[11]

Theoretical methods seek to predict, from first principles or in a semiempirical manner, the effect of a crystal lattice on the energies of valence electron states of RE and transition-metal ions through calculations of the experimentally derived phenomenological CF parameters. Theoretical models range from simple, nearest-neighbor electrostatic approaches[12] to more complicated ligand field[4,8] and extended lattice[13] approaches that seek to include covalency and long-range effects. For simplicity, most of these models assume that the CF experienced by a RE or transition-metal ion in a solid arises from simple additivity of contributions from individual lattice ions. Depending on the model and the degree of approximation, the number of contributing lattice ions varies from only nearest-neighbor ligands to the entire lattice.

The most commonly used ligand additivity models include the simple point-charge model,[14] the superposition model (SM),[15] and the angular overlap model (AOM).[16,17] The point-charge model is most effective in the limit of pure ionic bonding while the angular overlap model is normally used for systems with significant covalency contributions (normally transition-metal ions in organometallic complexes). The SM is formally related to the AOM (Ref. 8) and can be viewed as an extension of the point-charge model in which small covalency contributions can be incorporated. The primary applications to date of the SM have focused on trivalent RE^{3+} dopants in oxide and halide host lattices.[8,18,19]

In the SM, phenomenological CF parameters are resolved into distinct physical (radial) and geometric (angular) contributions. An important potential advantage of the SM formulation is the transferability of radial parameter values. Once radial CF parameters are obtained in one system for a given central metal ion-ligand pair, the theory predicts that within a simple rescaling to account for differences in nearest-neighbor bond lengths, the values are valid for the central metal ion in all systems involving the same ligand. In principle, the transferability extends even further because the CF effects are strictly properties only of the ligands, which means that radial parameter values obtained for a given central metal ion-ligand pair should also be valid for other metal ions coordinated to the same ligand when allowance is made for differences in bond length.

The purpose of this paper is to explore the application of the SM to CF effects in divalent RE^{2+} ions. Divalent RE^{2+} ions are currently of interest as activators in scintillation materials, optical recording materials, and solid-state tunable laser materials.[20–23] A number of luminescence studies of divalent RE^{2+} ions have been reported and phenomenological CF parameters are available for several systems.[19,24–26] From a theoretical point of view, however, CF effects in divalent rare earths have been much less studied. We expect that overlap and covalency effects in divalent RE^{2+} systems will be intermediate between those of trivalent RE^{3+} and transition-metal systems. The divalent rare earths therefore provide a fruitful test for the extent of applicability of the SM and provide a useful experimental and theoretical bridge between the more ionic trivalent RE dopants and the more covalent transition-metal dopants.

We will present theoretical predictions of CF parameters based on the SM for Sm^{2+} in MFCl ($M = Ba^{2+}$, Sr^{2+}, and Ca^{2+}) host lattices. The predictions will consider contributions from point-charge, charge penetration, exchange, overlap, and covalency effects. The analysis will also include a discussion of the effect of $Sm^{2+}-F^-$ and $Sm^{2+}-Cl^-$ bond lengths on the magnitude of the CF parameters. The distance-dependent theoretical predictions will be compared to recent high-pressure studies of the Sm^{2+}:MFCl systems.[26,27] In these studies, high pressure was used to sys-

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tematically vary the CF strength and Sm^{2+}-ligand bond lengths. As a result, it was possible to experimentally characterize the effect of bond length on CF parameters. These results will be used to test the predictions of the SM.

II. THEORETICAL

In the SM, the CF experienced by a central metal ion is given by a sum of contributions from ligands in the nearest-neighbor coordination shell. Each nearest-neighbor ligand is presumed to perturb the free ion valence orbital energies independently with the combined effect of all ligands constituting the overall crystal field. The contributions from individual ligands are further resolved into distinct physical and geometric factors and these are related to the phenomenological CF parameters through

$$B_q^k=\sum_L \overline{B}_k(R_L)K_{kq}(L), \tag{1}$$

where $\overline{B}_k(R_L)$ and $K_{kq}(L)$ are referred to as the intrinsic CF parameters and geometric coordination factors, respectively. The coordination factors depend only on the angular positions of the nearest-neighbor ligands L and can be determined experimentally through x-ray or neutron diffraction. The intrinsic parameters $\overline{B}_k(R_L)$ depend only on the ligand type and the interionic distance R_L between the ligand and the central metal ion. The intrinsic parameters account for all physical interactions present at the central metal ion due to the individual nearest-neighbor ligands. Depending on the system, these interactions can include both electrostatic (point-charge and charge penetration) and contact (exchange, ligand overlap, and covalency) contributions. Assuming that the coordination factors are known, Eq. (1) can be fit to the experimentally derived B_q^k to obtain values for the intrinsic parameters.

Theoretical calculation of the intrinsic parameters can be accomplished through[18]

$$\overline{B}_k=(2k+1)\left[(2l+1)\begin{pmatrix} l & l & k \\ 0 & 0 & 0 \end{pmatrix}\right]^{-1} \times\sum_{m=-l}^{l}(-1)^m\begin{pmatrix} l & l & k \\ -m & m & 0 \end{pmatrix}\overline{\mathcal{E}}_m, \tag{2}$$

where l and m are the orbital and azimuthal angular momentum quantum numbers of the $4f$ electrons and $\overline{\mathcal{E}}_m$ are the one-electron $4f$ orbital energies upon combination of free ion $4f$ wave functions φ_m with ligand orbital wave functions χ_τ $(s,\ \sigma,\ p_{\pi x},\ p_{\pi y})$ to form molecular orbitals. For Sm^{2+}, the energies $\overline{\mathcal{E}}_m$ contain both electrostatic and contact contributions and can be written

$$\overline{\mathcal{E}}_m=\mathcal{E}_m^{\mathrm{pc}}+\mathcal{E}_m^{\mathrm{cp}}+\mathcal{E}_m^{\mathrm{ex}}+\mathcal{E}_m^{\mathrm{ov}}+\mathcal{E}_m^{\mathrm{co}}, \tag{3}$$

where $\mathcal{E}_m^{\mathrm{pc}}$, $\mathcal{E}_m^{\mathrm{cp}}$, $\mathcal{E}_m^{\mathrm{ex}}$, $\mathcal{E}_m^{\mathrm{ov}}$, and $\mathcal{E}_m^{\mathrm{co}}$ denote the point-charge, charge penetration, exchange, overlap, and covalency contributions, respectively. The eigenvalue problem for the metal-ligand system can be solved by a diagrammatic method[28] and the contributions to the overall eigenvalues $\overline{\mathcal{E}}_m$ can be expressed in the following forms:[18]

$$\begin{aligned}
\mathcal{E}_m^{\mathrm{pc}}&=\langle\varphi_m|r_L^{-1}|\varphi_m\rangle,\\
\mathcal{E}_m^{\mathrm{cp}}&=2\left(\sum_\tau \langle\varphi_m\chi_\tau|r_{12}^{-1}|\varphi_m\chi_\tau\rangle-4\langle\varphi_m|r_L^{-1}|\varphi_m\rangle\right),\\
\mathcal{E}_m^{\mathrm{ex}}&=-\sum_\tau \langle\varphi_m\chi_\tau|r_{12}^{-1}|\chi_\tau\varphi_m\rangle,\\
\mathcal{E}_m^{\mathrm{ov}}&=-\sum_\tau \langle\varphi_m|\chi_\tau\rangle(N_{m\tau1}+2N_{m\tau2}),\\
\mathcal{E}_m^{\mathrm{co}}&=\sum_\tau \frac{\left(\sum_i N_{m\tau i}\right)^2}{D_\tau},
\end{aligned} \tag{4}$$

with

$$\begin{aligned}
N_{m\tau1}&=\langle\varphi_m|\chi_\tau\rangle(\epsilon_{4f}-\epsilon_\tau+U^++U^-+R^{-1}),\\
N_{m\tau2}&=2\left(\sum_{\tau'} \langle\varphi_m\chi_{\tau'}|r_{12}^{-1}|\chi_\tau\chi_{\tau'}\rangle-4\langle\varphi_m|r_L^{-1}|\chi_\tau\rangle\right)\\
&\quad-\langle\varphi_m\chi_\tau|r_{12}^{-1}|\chi_\tau\chi_\tau\rangle,\\
N_{m\tau3}&=\langle\varphi_m\overline{\varphi}|r_{12}^{-1}|\chi_\tau\overline{\varphi}\rangle-\langle\varphi_m|\chi_\tau\rangle\langle\overline{\varphi}\chi_\tau|r_{12}^{-1}|\overline{\varphi}\chi_\tau\rangle,\\
D_\tau&=\epsilon_{4f}-\epsilon_\tau+U^++U^-+\langle\overline{\varphi\varphi}|r_{12}^{-1}|\overline{\varphi\varphi}\rangle-\langle\overline{\varphi}\chi_\tau|r_{12}^{-1}|\chi_\tau\overline{\varphi}\rangle.
\end{aligned} \tag{5}$$

In Eq. (5), ϵ_{4f} is the free ion $4f$ orbital energy and ϵ_τ are the free ligand ion s and p orbital energies. U^+ and U^- are the Madelung potential energies of electrons on the positive and negative ions, respectively, and therefore U^++U^- represents the interaction of the rest of the host lattice with the formed ion pair. R is the interionic distance between the central RE ion and the ligand ions and r_L is the ligand electron position referred to the ligand center. $\overline{\varphi}$ is used to represent the radial $4f$ wave function.

Each of the contributions $\mathcal{E}_m^{\mathrm{pc}}$, $\mathcal{E}_m^{\mathrm{cp}}$, $\mathcal{E}_m^{\mathrm{ex}}$, $\mathcal{E}_m^{\mathrm{ov}}$, and $\mathcal{E}_m^{\mathrm{co}}$ can be substituted directly into Eq. (2) to obtain the contribution of each of the five physical interactions under consideration to the intrinsic CF parameters. The electrostatic contributions $\mathcal{E}_m^{\mathrm{pc}}$ and $\mathcal{E}_m^{\mathrm{cp}}$ are easily formulated in terms of the radial integrals T_k for the matrix elements $\langle\varphi_m|r_L^{-1}|\varphi_m\rangle$ and $T_k(\tau)$ for $\langle\varphi_m\chi_\tau|r_{12}^{-1}|\varphi_m\chi_\tau\rangle$:[18]

$$\langle\varphi_m|r_L^{-1}|\varphi_m\rangle=7\sum_k\begin{pmatrix} 3 & 3 & k \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 3 & 3 & k \\ -m & m & 0 \end{pmatrix}T_k$$

and

$$\langle\varphi_m\chi_\tau|r_{12}^{-1}|\varphi_m\chi_\tau\rangle=7\sum_k\begin{pmatrix} 3 & 3 & k \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 3 & 3 & k \\ -m & m & 0 \end{pmatrix}T_k(\tau).$$

These results and Eq. (2) can then be used to obtain a simple expression for the electrostatic contributions to the intrinsic CF parameters: $\overline{B}_k=T_k$ (assuming that the ligand electrons locate far from the $4f$ orbital we have $T_k=\langle r^k\rangle$) for the point-charge contribution and $\overline{B}_k=2T_k(s)+6T_k(p)$

TABLE I. Overlap integrals ($\times 10^2$) and matrix elements (cm^{-1}) at different distances R (a.u.) between Sm^{2+} central ion and Cl$^-$ or F$^-$ ligands.

	R(Sm-Cl)			R(Sm-F)		
	6.206	5.606	5.006	5.004	4.404	3.804
$\langle 4f\|s\rangle$	0.3981	0.7531	1.3565	0.8420	1.7752	3.4439
$\langle 4f\|\sigma\rangle$	0.8132	1.2342	1.8098	1.5178	2.2796	3.1737
$\langle 4f\|\pi\rangle$	0.4339	0.7455	1.2779	0.8635	1.6096	2.9150
$\langle 4f_0\|r_L^{-1}\|s\rangle$	363.8	795.4	1673.9	1219.7	2857.3	6234.8
$\langle 4f_0\|r_L^{-1}\|\sigma\rangle$	697.0	1241.4	2160.3	1820.3	3341.6	5814.8
$\langle 4f_1\|r_L^{-1}\|\pi\rangle$	283.7	561.7	1117.2	795.5	1742.9	3751.4
$\langle 4f_0 s\|\|ss\rangle$	338.6	721.8	1469.0	1109.9	2558.8	5473.1
$\langle 4f_0 s\|\|\sigma s\rangle$	675.4	1180.8	2000.0	1720.4	3080.1	5172.6
$\langle 4f_1 s\|\|\pi s\rangle$	279.0	546.5	1070.0	766.8	1654.0	3483.8
$\langle 4f_0 p\|\|sp\rangle$	318.5	669.1	1338.7	1059.4	2430.8	5173.4
$\langle 4f_0 p\|\|\sigma p\rangle$	646.6	1111.8	1845.0	1666.4	2952.2	4896.9
$\langle 4f_1 p\|\|\pi p\rangle$	271.8	526.4	1016.1	750.7	1606.8	3354.3
$\langle 4f_0 4\overline{f}\|\|s 4\overline{f}\rangle$	264.6	529.7	1020.2	546.8	1290.5	2840.5
$\langle 4f_0 4\overline{f}\|\|\sigma 4\overline{f}\rangle$	624.5	992.7	1555.8	1263.4	2063.4	3219.4
$\langle 4f_1 4\overline{f}\|\|\pi 4\overline{f}\rangle$	317.8	560.2	996.0	653.9	1289.2	2500.4
$\Sigma_\tau\langle 4f_0\tau\|\|\tau 4f_0\rangle$	11.9	29.7	71.6	57.5	151.2	375.7
$\Sigma_\tau\langle 4f_1\tau\|\|\tau 4f_1\rangle$	2.0	6.1	18.2	9.7	34.3	115.7
T_2	861.4	1168.7	1641.2	1643.2	2409.8	3734.3
T_4	54.2	90.1	158.6	158.9	299.8	614.5
T_6	7.2	14.7	32.3	32.4	77.6	203.0
$T_2(s)$	860.9	1166.3	1629.9	1637.1	2395.8	3682.5
$T_4(s)$	53.8	88.0	148.9	156.9	289.3	557.3
$T_6(s)$	6.9	13.2	25.3	30.6	66.8	144.8
$T_2(p)$	844.7	1126.3	1531.8	1625.2	2346.4	3509.8
$T_4(p)$	49.3	76.6	120.6	148.5	261.7	476.8
$T_6(p)$	5.6	9.8	17.0	26.5	55.0	116.7

$-8T_k$ for the charge penetration contribution. Equation (2) can similarly be used to evaluate the contact contributions to the intrinsic CF parameters once $\mathcal{E}_m^{\rm ex}$, $\mathcal{E}_m^{\rm ov}$, and $\mathcal{E}_m^{\rm co}$ are calculated.

In the SM, the distance dependence of the intrinsic parameters is expressed in terms of an empirical power-law rescaling $\overline{B}_k(R)=\overline{B}_k(R_0)(R_0/R)^{t_k}$, where $\overline{B}_k(R_0)$ is the value of the intrinsic parameter in a reference system. Knowledge of $\overline{B}_k(R_0)$ and the power-law exponent t_k permits a prediction of intrinsic CF parameters for other host crystals of the same ligand.

III. NUMERICAL EVALUATION

All of the two-center integrals in Eqs. (4) and (5), except the exchange integrals, were evaluated analytically using the ζ-function method.[29] The exchange integrals were evaluated in terms of the classic Mulliken approximation[30] that provides an effective and reasonable evaluation of many-center integrals:

$$\langle \varphi_m\chi_\tau|r_{12}^{-1}|\chi_\tau\varphi_m\rangle$$
$$=\tfrac{1}{4}\langle\varphi_m|\chi_\tau\rangle^2[\langle\varphi_m\varphi_m|r_{12}^{-1}|\varphi_m\varphi_m\rangle$$
$$+2\langle\varphi_m\chi_\tau|r_{12}^{-1}|\varphi_m\chi_\tau\rangle+\langle\chi_\tau\chi_\tau|r_{12}^{-1}|\chi_\tau\chi_\tau\rangle].$$

Slater-type radial wave functions were used for Sm^{2+} $(4f)$,[31] F$^-$ $(2s$ and $2p)$,[32] and Cl$^-$ $(3s$ and $3p)$ (Ref. 33) to calculate the integrals. The *ab initio* calculation was performed at seven different interionic distances $(R_n=R_0-0.2n$ with $n=0\cdots 6)$, where $R_0=5.004$ a.u. for F ligands and $R_0=6.206$ a.u. for Cl ligands. The present computation was carried out on a PC with a specially developed Turbo Pascal Program. The necessary two-center integrals for Sm$^{2+}-$F$^-$ and Sm$^{2+}-$Cl$^-$ ion pairs at three different interionic distances are collected in Table I.

It is noticed from Eqs. (2) and (3) that the free ion $4f$ and ligand orbital energies as well as the Madelung potentials are needed to calculate the overlap and covalency contributions to the intrinsic CF parameters. The free ion orbital energies in atomic units (Hartree) are taken to be $\epsilon_{2s}=-1.074$ and $\epsilon_{2p}=-0.181$ for F$^-$ (Ref. 32), $\epsilon_{3s}=-0.733$ and $\epsilon_{3p}=-0.150$ for Cl$^-$ (Ref. 34), and $\epsilon_{4f}=-0.890$ for Sm^{2+} (Ref. 35). The Madelung potentials $U^+ + U^-$ can be reasonably

TABLE II. Calculated intrinsic CF parameters $\overline{B}_k$ (cm^{-1}) at three different distances R (a.u.) for $\mathrm{Sm}^{2+}-\mathrm{Cl}^-$ and $\mathrm{Sm}^{2+}-\mathrm{F}^-$ ion pairs.

		R(Sm-Cl)			R(Sm-F)		
		6.206	5.606	5.006	5.004	4.404	3.804
$\overline{B}_2$	Point charge	861.4	1168.7	1641.2	1643.2	2409.8	3734.3
	Charge penetration	−101.4	−259.2	−678.8	−119.9	−408.2	−1450.8
	Exchange	−9.0	−24.2	−63.8	−40.6	−121.9	−352.2
	s overlap	3.0	14.2	62.7	21.1	113.3	525.0
	σ overlap	14.2	40.4	112.2	71.7	209.9	558.4
	π overlap	4.4	15.0	52.5	25.4	105.2	427.8
	s covalence	0.2	1.8	13.7	2.8	20.7	132.0
	σ covalence	8.9	29.4	99.2	99.7	365.7	1301.2
	π covalence	1.9	6.7	25.5	26.3	122.4	580.2
	Total	783.6	992.8	1264.4	1729.7	2816.9	5455.9
$\overline{B}_4$	Point charge	54.2	90.1	158.6	158.9	299.8	614.5
	Charge penetration	−30.7	−85.5	−247.0	−66.3	−249.6	−940.4
	Exchange	−13.1	−34.3	−87.0	−58.4	−167.0	−457.3
	s overlap	5.3	25.5	112.8	37.9	204.0	944.9
	σ overlap	25.6	72.7	202.0	129.0	377.9	1005.2
	π overlap	1.8	6.0	21.0	10.1	42.1	171.1
	s covalence	0.4	3.2	24.7	5.0	37.2	237.7
	σ covalence	16.0	52.9	178.5	179.5	658.3	2342.1
	π covalence	0.8	2.7	10.2	10.5	49.0	232.1
	Total	60.2	133.3	373.7	406.4	1251.7	4149.9
$\overline{B}_6$	Point charge	7.2	14.7	32.3	32.4	77.6	203.0
	Charge penetration	−10.4	−32.4	−105.6	−38.9	−156.9	−634.3
	Exchange	−11.9	−28.4	−62.4	−50.8	−122.3	−259.7
	s overlap	7.7	36.8	163.0	54.8	294.6	1364.9
	σ overlap	37.0	105.0	291.7	186.3	545.8	1452.0
	π overlap	−11.5	−39.0	−136.5	−65.9	−273.5	−1112.4
	s covalence	0.5	4.7	35.6	7.3	53.8	343.3
	σ covalence	23.2	76.3	257.8	259.3	950.9	3383.0
	π covalence	−4.9	−17.4	−66.3	−68.5	−318.3	−1508.6
	Total	36.9	120.3	409.7	316.0	1051.7	3231.1

assumed to be inversely proportional to the metal-ligand distance (α/R). We used the values for the Madelung potentials of cations and anions in BaFCl and SrFCl crystals[36] to obtain $U^+ + U^- = 2.042/R$ for $M^{2+}-\mathrm{Cl}^-$ and $U^+ + U^- = 1.049/R$ for $M^{2+}-\mathrm{F}^-$.

The calculated results for the contributions of the five mechanisms to the intrinsic CF parameters are presented in Table II. Figures 1 and 2 also demonstrate the dependence of the intrinsic CF parameters $\overline{B}_4$ and $\overline{B}_6$ on interionic distance for both $\mathrm{Sm}^{2+}-\mathrm{Cl}^-$ and $\mathrm{Sm}^{2+}-\mathrm{F}^-$ ion pairs.

It is evident from Figs. 1 and 2 that (i) the $\overline{B}_4$ and $\overline{B}_6$ parameters are dominated by overlap and covalency and the electrostatic point-charge contribution is insignificant especially in the case of $\overline{B}_6$, and that (ii) negative π overlap and covalency contributions appear in the case of $\overline{B}_6$ and vary strongly with distance. This leads to a cancellation in the contribution to $\overline{B}_6$ between the σ and π orbitals. As a consequence, this cancellation largely reduces the total p contribution and results in the small value for the t_6 parameters and even the negative value for the $\overline{B}_6$ parameter when the charge penetration contributions are also considered. This effect has been also observed theoretically in trivalent RE^{3+} ions[18,34,37] and experimentally in strong covalency-bonded systems and RE metals.[8,38]

In the present *ab initio* calculation, the Mulliken approximation was used to evaluate the electron exchange contributions to the intrinsic CF parameters. An obvious weakness of the Mulliken approximation in this case is that the $m=2$ and $m=3$ exchange contributions are neglected due to the zero overlap integrals ($\langle\varphi_m|\chi_\tau\rangle$). Newman and Ahmad[39] completed an exact exchange integral calculation in the $\mathrm{Pr}^{3+}-\mathrm{Cl}^-$ ion pair system to estimate the accuracy of the Mulliken approximation and found that the $m=0$ and $m=1$ exchange contributions are dominant and account for about 70% of the total amount of the exchange contributions. The

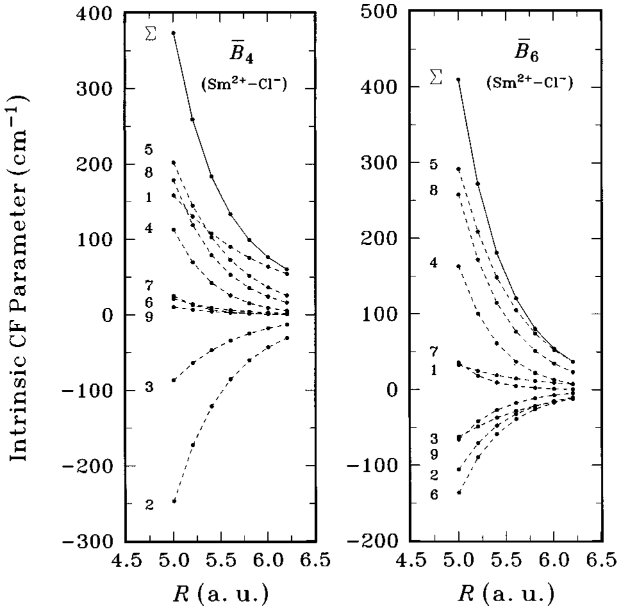

FIG. 1. Distance dependence of $\bar{B}_4$ and $\bar{B}_6$ for the $Sm^{2+}-Cl^-$ ion pair. 1: point charge, 2: charge penetration, 3: exchange, 4: s overlap, 5: σ overlap, 6: π overlap, 7: s covalency, 8: σ covalency, 9: π covalency, and Σ: total.

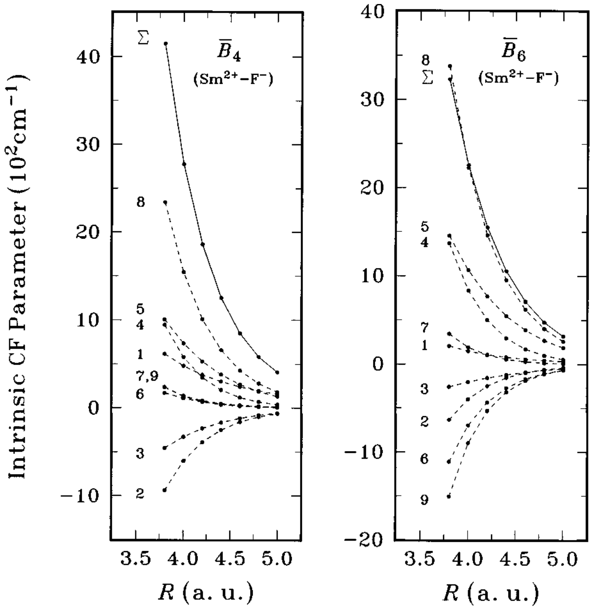

FIG. 2. Distance dependence of $\bar{B}_4$ and $\bar{B}_6$ for the $Sm^{2+}-F^-$ ion pair. 1: point charge, 2: charge penetration, 3: exchange, 4: s overlap, 5: σ overlap, 6: π overlap, 7: s covalency, 8: σ covalency, 9: π covalency, and Σ: total.

Mulliken approximation used in the exchange integral evaluation leads to a maximum uncertainty of 6% in the intrinsic CF parameters and is sufficiently accurate for *ab initio* crystal-field calculations.

IV. DISCUSSION

A. Comparison with experimental results

Sm^{2+} ions occupy sites of C_{4v} symmetry in MFCl host crystals and are surrounded by nine nearest-neighbor ligands: four symmetry equivalent F (R^F,Θ^F,Φ^F), four symmetry equivalent Cl ions ($R^{Cl},\Theta^{Cl},\Phi^{Cl}$), and one additional Cl ion ($R^{Cl'}$,0,0) located on the fourfold symmetry axis of the central Sm^{2+} ion. The ambient pressure bond lengths for SrFCl are $R^F=249.4$ pm, $R^{Cl}=311.2$ pm, and $R^{Cl'}=307.2$ pm.[40] In Sm^{2+}:SrFCl, the local site distortions around Sm^{2+} ions at substituted Sr^{2+} sites can be safely neglected because of the almost identical ionic size of Sm^{2+} and Sr^{2+}.

The ambient pressure experimental values of $\bar{B}_k$ ($k=4,6$) obtained previously[26] are $\bar{B}_4=124(14)$ cm^{-1} and $\bar{B}_6=152(16)$ cm^{-1} for the $Sm^{2+}-Cl^-$ ion pair and $\bar{B}_4=245(25)$ cm^{-1} and $\bar{B}_6=172(18)$ cm^{-1} for the $Sm^{2+}-F^-$ ion pair in Sm^{2+}:SrFCl. The corresponding calculated values are $\bar{B}_4=93$ cm^{-1} and $\bar{B}_6=66$ cm^{-1} for $Sm^{2+}-Cl^-$ and $\bar{B}_4=685$ cm^{-1} and $\bar{B}_6=556$ cm^{-1} for $Sm^{2+}-F^-$. A comparison of the values shows that the experimental values are larger than the theoretical ones for Cl ligands and conversely, are smaller than the theoretical ones for F ligands.

Full utilization of the SM requires knowledge of the t_k exponent in the empirical power-law rescaling equation $\bar{B}_k=\bar{B}_k(R_0)(R_0/R)^{t_k}$ used to predict the distance dependence of the intrinsic parameters. In principle, t_k can be obtained by determining $\bar{B}_k$ for a metal ion in a series of different host crystals, based on a given ligand, in which x-ray-diffraction data are available for determining R. In practice, this approach is oftentimes not straightforward because the metal ion is normally introduced as a low concentration dopant into a series of host crystals. As a result, a complication arises because the size mismatch associated with the dopant leads to local distortions of a host crystal in the vicinity of the dopant. This implies that nearest-neighbor bond lengths in the vicinity of the dopant will differ from the x-ray values. The magnitude of local distortions can be difficult to quantify and can vary significantly over a series of host crystals since the series will likely vary with respect to coordination environment and defects.

Recently, a new approach for determining t_k based on the application of high pressure has been proposed. In this approach, high pressure is used to continuously vary metal ion nearest-neighbor distances. Recent studies of some trivalent RE^{3+} ions in anhydrous chlorides[41] and Sm^{2+} in ternary compounds with the PbFCl structure type[26,27] have demonstrated the ability of pressure to provide crystal-field information as a function of metal ion-ligand distance. Although it is still necessary to correct for local distortion at ambient pressure, data obtained to date indicate that the local distortion is essentially constant over a wide range of pressure. As a result, trends obtained with bond length are expected to be more accurate in one composition over a range of pressure than in a series of different chemical compositions, each of which requires its own correction for local distortions. In addition to local distortions, different compositions may also vary with respect to defects, impurities, and dopant aggregation. These potentially complicating effects are avoided in the high-pressure approach.

The high-pressure results for $\bar{B}_k$ up to about 80 kbar[26] are illustrated together with the present calculated results in Figs. 3 and 4. It can clearly be seen from Figs. 3 and 4 that the

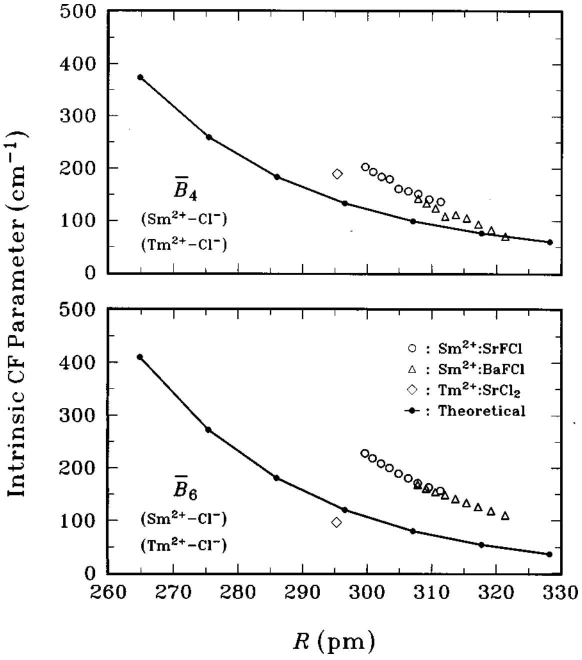

FIG. 3. Experimental and calculated values of $\bar{B}_4$ and $\bar{B}_6$ for $\mathrm{Sm}^{2+}-\mathrm{Cl}^{-}$ in SrFCl and BaFCl at different bond lengths. Ambient pressure values of $\bar{B}_4$ and $\bar{B}_6$ for $\mathrm{Tm}^{2+}-\mathrm{Cl}^{-}$ in SrCl_2 are also shown.

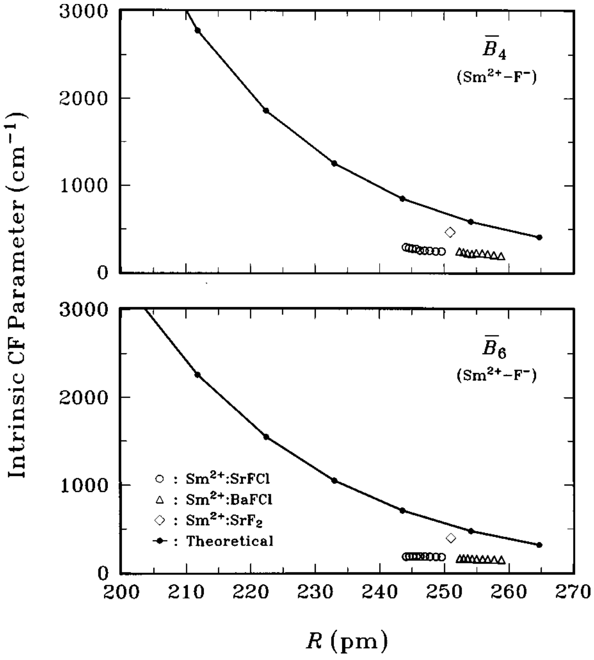

FIG. 4. Experimental and calculated values of $\bar{B}_4$ and $\bar{B}_6$ for $\mathrm{Sm}^{2+}-\mathrm{F}^{-}$ in SrFCl and BaFCl at different bond lengths. Ambient pressure values of $\bar{B}_4$ and $\bar{B}_6$ for $\mathrm{Sm}^{2+}-\mathrm{F}^{-}$ in SrF_2 are also shown.

theoretical intrinsic parameters vary more weakly with pressure than the experimental for Cl ligands and more strongly for F ligands.

For Sm^{2+}:BaFCl, the ambient and high-pressure results for $\bar{B}_k$ were also obtained in the previous work.[26] By taking into account the site local distortions around Sm^{2+} ions in BaFCl due to the larger ionic size of Ba^{2+} than Sm^{2+}, the intrinsic CF parameters were obtained for $\mathrm{Sm}^{2+}-\mathrm{Cl}^{-}$ and $\mathrm{Sm}^{2+}-\mathrm{F}^{-}$ ion pairs in Sm^{2+}:BaFCl. The values obtained at ambient pressure and high pressure for Sm^{2+}:BaFCl are also included in Figs. 3 and 4.

A possible source of the difference between the theoretical and experimental intrinsic CF parameters in $\mathrm{Sm}^{2+}:M\mathrm{FCl}$ systems is ligand-ligand interaction. Since the SM accounts only for two-body interactions, significant ligand-ligand interactions (that are formally three body in nature: ligand-metal-ligand) would lead to a breakdown of the theory. Ligand-ligand interactions are likely to be important in mixed ligand systems such as MFCl. One way to qualitatively assess the importance of ligand-ligand (F-Cl) interactions in MFCl is to consider CF effects in the corresponding single ligand-type $M\mathrm{F}_2$ and MCl_2 systems. The intrinsic CF parameters of Sm^{2+}:SrF_2 have been previously derived[26] from ambient pressure luminescence data[42] and are included in Table III and presented in Fig. 4. CF energy levels of Sm^{2+}:SrCl_2 are not available in the literature, but the Tm^{2+}:SrCl_2 system has been studied at ambient pressure.[43] The intrinsic CF parameters derived[26] for Tm^{2+}:SrCl_2, after correction for a relative local radial distortion due to a larger size mismatch between Tm^{2+} and Sr^{2+} compared to Sm^{2+} and Sr^{2+}, are also included in Table III and Fig. 3. The intrinsic CF parameters obtained from experiment for SrF_2 and SrCl_2 are much closer to the theoretical values than those for SrFCl. A consideration of the experimental values for SrFCl shows that the experimental intrinsic CF parameters for the Cl ligands are significantly higher than the theoretical values, while the experimental values for the F ligands are significantly lower. This suggests the existence of a ligand-ligand (F-Cl) interation in which the CF contribution of the F ligands is partially transferred to the Cl ligands.

In the case of the $k=2$ parameters, as seen from Table II, the present *ab initio* results for both $\mathrm{Sm}^{2+}-\mathrm{Cl}^{-}$ and $\mathrm{Sm}^{2+}-\mathrm{F}^{-}$ ion pairs show that the contact contributions to the $k=2$ parameters are negligibly small with respect to the electrostatic contributions, especially the point-charge contribution. This is due to neglecting the shielding of the electrostatic field by the filled outer $5s^25p^6$ shell of the lanthanide ion, an effect that considerably reduces the electrostatic field experienced by the $4f$ electrons. Based on the shielding factors given by Senguta and Artman[44] (0.792 for $k=2$, 0.139 for $k=4$, and 0.109 for $k=6$), it is clear that neglect of the shielding effect has a much more pronounced effect for the $k=2$ parameters than for the $k=4$ and $k=6$ parameters. If we include the shielding factor of 0.792 for the point-charge electrostatic contributions in the calculation of the intrinsic CF parameter $\bar{B}_2$, we obtain values of 432 cm^{-1} at R = 5.004 a.u., 913 cm^{-1} at R = 4.404 a.u., and 2506 cm^{-1} at R =3.804 a.u. for F ligands. We also obtain $t_2\approx 6.3$ for the $\mathrm{Sm}^{2+}-\mathrm{F}^{-}$ ion pair, which is reasonably close to the experimental value of $t_2=5.5$ obtained from the uniaxial stress experiment on $\mathrm{Tm}^{2+}:M\mathrm{F}_2$ (Ref. 45). However, a negative value of $t_2\approx -4$ is obtained in the same way for the $\mathrm{Sm}^{2+}-\mathrm{Cl}^{-}$ ion pair. Any further attempts to improve the presently available *ab initio* calculations for the $k=2$ parameters must clearly take full account of the properties of the electrostatic field in ionic crystals as well as configuration interaction processes.

TABLE III. Comparison of experimental and theoretical values of intrinsic CF parameters $\overline{B}_k$ (cm^{-1}) and power-law exponents t_k for $Sm^{2+}-Cl^-$ and for $Sm^{2+}-F^-$ ion pairs. The experimental values for Sm^{2+}:*M*FCl, Sm^{2+}:SrF_2, and Tm^{2+}:$SrCl_2$ are taken from Table III of Ref. 26.

	Cl ligand (R_0=5.575 a.u.)				F ligand (R_0=4.745 a.u.)				
	$\overline{B}_4$	t_4	$\overline{B}_6$	t_6	$\overline{B}_4$	t_4	$\overline{B}_6$	t_6	
Expt.	258(29)	14(4)	261(28)	10(3)	237(25)	5.8(1.5)	167(18)	4.6(1.1)	Sm^{2+}:*M*FCl
					470(40)		393(50)		Sm^{2+}:SrF_2
	190		≈97						Tm^{2+}:$SrCl_2$
Theory	148	8.5	121	11.2	651	8.5	529	8.5	

B. Comparison with trivalent lanthanide ions

Table IV presents the theoretical and experimental results for $Pr^{3+}-Cl^-$ and $Pr^{3+}-F^-$ ion pairs. Reasonable agreement between the theoretical and experimental values was observed. A comparison of the theoretical results for the trivalent Pr^{3+} ion with those for the divalent Sm^{2+} ion (Tables III and IV) shows that the exponents t_k for Sm^{2+} are larger than those for Pr^{3+}. It seems reasonable to expect that both the $\overline{B}_k(R_0)$ and t_k parameters for divalent RE^{2+} ions would be larger than those for trivalent RE^{3+} ions due to the more expanded $4f$ electron orbital of RE^{2+} with respect to RE^{3+}.

In order to test this expectation and to begin to generalize the present theoretical results, additional *ab initio* calculations on $Nd^{3+}-Cl^-$, $Sm^{3+}-Cl^-$, $Gd^{3+}-Cl^-$, $Dy^{3+}-Cl^-$, and $Er^{3+}-Cl^-$ ion pairs were carried out using the same calculation approach. The calculated results are illustrated in Fig. 5 and show that the exponent t_4 remains almost constant while t_6 increases very slightly from Pr^{3+} to Er^{3+} (on average, $t_4=6.1$ and $t_6=8.1$). Furthermore, we see that the intrinsic CF parameter $\overline{B}_k$ at a given interionic distance shows a strong decrease from Pr^{3+} to Er^{3+} due to the smooth decrease in ionic radius in the lanthanide series with increasing atomic number. From a direct comparison of Sm^{3+} with Sm^{2+}, it can furthermore be seen that the values of $\overline{B}_k$ for Sm^{2+} are larger than those for Sm^{3+}. For example, the calculated results for $Sm^{3+}-Cl^-$ are $\overline{B}_4(R_0)=81$ cm^{-1} and $\overline{B}_6(R_0)=74$ cm^{-1} at $R_0=5.575$ a.u. The responding calculated values of $Sm^{2+}-Cl^-$ are $\overline{B}_4(R_0)=148$ cm^{-1} and $\overline{B}_6(R_0)=121$ cm^{-1}.

Based on the present theoretical calculation, we expect that both the power-law exponents t_k and the initial intrinsic CF parameters $\overline{B}_k$ for divalent RE^{2+} ions will, in general, be larger than those for trivalent RE^{3+} ions.

C. Further considerations in *ab initio* MO calculations

In the present calculation, we used free ion $4f$ wave functions. In actuality, nephelauxetic effect considerations require that the actual $4f$ wave functions of RE ions in solids be spatially expanded relative to the free ion wave functions. A precise theoretical formulation of $4f$ wave functions in solids is currently not available, but we do expect radial expansion effects to have a significant effect on calculated CF parameters. If we assume, for example, a simple isotropic radial expansion of the Sm^{2+} free ion wave function by 1%, we find an increase of about 12% in the $\overline{B}_k(R_0)$ parameters and no significant change in the t_k parameters for both the $Sm^{2+}-Cl^-$ and $Sm^{2+}-F^-$ ion pairs. The radial expansion effect is clearly important and requires further attention concerning the extent and directionality of expansion.

$4f^n$-$4f^{n-1}5d^1$ configuration interaction (CI) is another potentially important effect in divalent RE^{2+} ions. The effect has recently been considered for the $Pr^{3+}-Cl^-$ ion pair by Ng and Newman.[47] Their results indicated that for trivalent RE^{3+} ions, the CI contributions are much less significant than the five contributions considered in the present theory. In RE^{2+} ions, however, the excited configurations are much closer to the ground $4f^n$ configuration than in RE^{3+} ions and the CI contributions to the lanthanide CF effects is correspondingly more significant for RE^{2+} ions than for RE^{3+} ions. Although the $4f^{n-1}5d^1$ configuration cannot directly contribute to the k=even crystal fields which govern the energy level positions and the CF energy level splittings, it may act as an intermediary between the $4f$ electrons of the central RE ion and the ligand electrons via the more expanded RE $5d$ electron orbitals. As a result, the $4f^55d^1$ configuration may influence the strength of interaction between metal valence and ligand orbitals. Also, as mentioned previously, the CI involving the filled outer $5s^25p^6$ shell of the RE ions clearly contributes to a shielding effect of the elec-

TABLE IV. Comparison of experimental and theoretical values of intrinsic CF parameters $\overline{B}_k$ (cm^{-1}) and power-law exponents t_k for Pr^{3+}:$LaCl_3$ (Refs. 37,41) and Pr^{3+}:LaF_3 (Refs. 46,48).

	Cl ligand (R_0=5.575 a.u.)				F ligand (R_0=4.745 a.u.)			
	$\overline{B}_4$	t_4	$\overline{B}_6$	t_6	$\overline{B}_4$	t_4	$\overline{B}_6$	t_6
Expt.	256(89)	4(4)	268(31)	6(3)	533(15)	6.1(1.3)	388(31)	8.7(1.1)
Theory	172	6.0	193	6.9	658	5.7	416	5.6

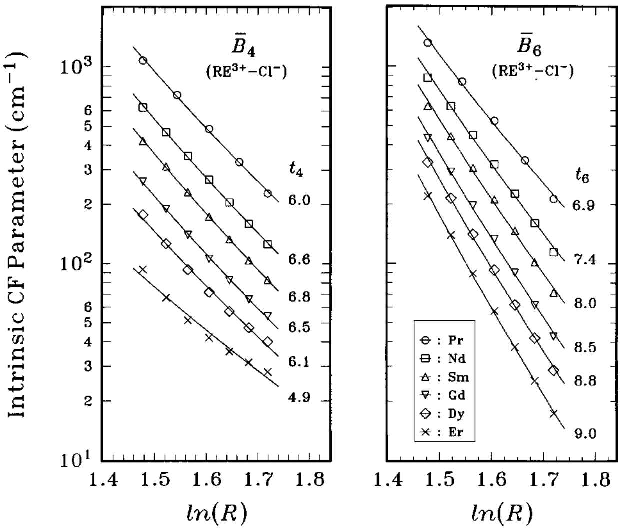

FIG. 5. Distance dependence of $\overline{B}_4$ and $\overline{B}_6$ for some RE^{3+} $-$Cl$^-$ ion pairs (RE = Pr, Nd, Sm, Gd, Dy, and Er). The data for Pr^{3+} are taken from Ref. 37. The radial $4f$ wave functions and the $4f$ orbital energies are taken from Refs. 31 and 35, respectively.

trostatic field on the $k=2$ CF parameters. These CI effects need to be considered more fully and it is believed that a more complete description of CF effects on divalent lanthanides will require a more complete basis set of wave functions $(\varphi_{4f},\varphi_{5s},\varphi_{5p},\varphi_{5d})$.

V. CONCLUSIONS

We have completed systematic linear combination of atomic orbitals (-molecular orbitals) *ab initio* calculations of crystal-field interactions in a divalent RE^{2+} system. Sm^{2+} ions in MFCl mixed ligand solids were specifically considered in the context of the superposition model. Variations in CF parameters with nearest-neighbor bond length were calculated and compared to experimental values obtained from recent high-pressure experiments. The calculated results indicate that five mechanisms—point charge, charge penetration, exchange, overlap, and covalency—are primarily responsible for the CF effects in Sm^{2+}. Difference observed between theoretical and experimental CF parameters are believed to be due to the use of free ion $4f$ wave functions and neglect of ligand-ligand and $4f^5 5d^1$ configuration interactions in the present model. Inner shell shielding effects are also shown to be important when considering second-order parameters.

The present calculation also shows that the CF parameters for Sm^{2+} are higher, and also more sensitive to the nearest-neighbor bond length, than those for Sm^{3+}. We expect this result to hold generally for divalent RE^{2+} ions relative to trivalent RE^{3+} ions.

Further work will focus on extending the theory to include ligand-ligand interactions, configuration interactions, and radially expanded $4f$ wave functions. Further high-pressure experiments on divalent rare earths in single ligand-type hosts MF$_2$ and MCl$_2$ will also be completed in an attempt to better understand these effects.

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[1] R. Reisfeld and C. K. Jørgensen, *Lasers and Excited States of Rare Earths* (Springer-Verlag, Berlin, 1977).

[2] S. Hüfner, *Optical Spectra of Transparent Rare Earth Compounds* (Academic, New York, 1978).

[3] C. A. Morrison and R. P. Leavitt, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, New York, 1982), p. 461.

[4] A. B. P. Lever, in *Studies in Physical and Theoretical Chemistry 33: Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1984).

[5] B. Henderson and G. F. Imbusch, *Optical Spectroscopy of Inorganic Solids* (Oxford Science, New York, 1989).

[6] W. T. Carnall, H. Crosswhite, and H. M. Crosswhite (unpublished).

[7] B. Di Bartolo, in *Disordered Solids: Structures and Processes*, edited by B. Di Bartolo (Plenum, New York, 1989).

[8] D. J. Newman and Betty Ng, Rep. Prog. Phys. **52**, 699 (1989).

[9] M. C. Downer, in *Laser Spectroscopy of Solids II*, edited by W. M. Yen (Springer-Verlag, Berlin, 1989), pp. 29–75.

[10] C. Campochiaro, D. S. McClure, P. Rabinowitz, and S. Dougal, Phys. Rev. B **43**, 14 (1991).

[11] J. Ganem, S. R. Bowman, and B. J. Feldman, J. Lumin. **58**, 298 (1994).

[12] M. Faucher and D. Garcia, Phys. Rev. B **26**, 5451 (1982).

[13] R. Saito and T. Kimura, Phys. Rev. B **46**, 1423 (1992).

[14] C. A. Morrison, *Crystal Fields for Transition-Metal Ions in Laser Host Materials* (Springer-Verlag, Berlin, 1992).

[15] M. I. Bradbury and D. J. Newman, Chem. Phys. Lett. **1**, 44 (1967).

[16] C. E. Schäffer and C. K. Jørgensen, Mol. Phys. **4**, 401 (1967).

[17] M. Gerloch and R. G. Woolley, Prog. Inorg. Chem. **31**, 371 (1984).

[18] D. J. Newman, Adv. Phys. **20**, 197 (1971).

[19] D. J. Newman, Aust. J. Phys. **31**, 79 (1978).

[20] A. L. N. Stevels and F. Pingault, Philips Res. Rep. **30**, 277 (1975).

[21] M. Sonoda, M. Takano, J. Miyahara, and H. Kato, Radiology **148**, 833 (1983).

[22] R. Jaaniso and H. Bill, Europhys. Lett. **16**, 569 (1991).

[23] O. J. Rubio, J. Phys. Chem. Solids **52**, 101 (1991).

[24] J. C. Gâcon, G. Grenet, J. C. Souillat, and M. Kibler, J. Chem. Phys. **69**, 868 (1978).

[25] G. Grenet, M. Kibler, A. Gross, J. C. Souillat, and J. C. Gâcon, Phys. Rev. B **22**, 5052 (1980).

[26] Y. R. Shen and W. B. Holzapfel, Phys. Rev. B **51**, 15 752 (1995).

[27] Y. R. Shen and W. B. Holzapfel, J. Phys.: Condens. Matter **7**, 6241 (1995).

[28] S. S. Bishton and D. J. Newman, J. Phys. Chem. Solids **29**, 1245 (1967).

[29] M. P. Barnett, in *Methods in Computational Physics—Advances in Research and Applications,* edited by B. Alder, S. Ferbach, and M. Rotenberg (Academic, New York, 1963), Vol. 2, p. 95.

[30] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

[31] The radial $4f$ wave function of Eu^{2+} given in A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962) can be used for Sm^{2+} due to the very slight difference in ionic size for both divalent ions.

[32] S. Sugano and R. G. Shulman, Adv. Phys. **120**, 517 (1963).

[33] M. M. Ellis and D. J. Newman, J. Chem. Phys. **49**, 4037 (1968).

[34] D. J. Newman and Betty Ng, J. Phys. C **19**, 389 (1986).

[35] A. J. Freeman and J. P. Desclaux, J. Magn. Magn. Mater. **12**, 11 (1979). The values for ϵ_{4f} are determined by averaging the values of $\epsilon_{4f}(j=\frac{5}{2})$ and $\epsilon_{4f}(j=\frac{7}{2})$.

[36] D. Garcia and M. Faucher, J. Chem. Phys. **82**, 5554 (1985).

[37] Y. R. Shen and W. B. Holzapfel, J. Phys.: Condens. Matter **6**, 2367 (1994).

[38] D. J. Newman, J. Phys. F **13**, 1983 (1511).

[39] D. J. Newman and S. Ahmed, Phys. Lett. **85A**, 51 (1981).

[40] M. Sauvage, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **30**, 2786 (1974).

[41] Th. Tröster, T. Gregorian, and W. B. Holzapfel, Phys. Rev. B **48**, 2960 (1993).

[42] D. L. Wood and W. Kaiser, Phys. Rev. **126**, 2079 (1962).

[43] G. Burns and J. D. Axe, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1967), p. 53.

[44] D. Sengupta and J. O. Artman, Phys. Rev. B **1**, 2986 (1970).

[45] D. J. Newman, Aust. J. Phys. **31**, 79 (1978).

[46] Y. Y. Yeung and M. F. Reid, J. Less-Common Met. **148**, 213 (1989).

[47] B. Ng and D. J. Newman, J. Chem. Phys. **87**, 7110 (1987).

[48] D. J. Newman and M. M. Curtis, J. Phys. Chem. Solids **30**, 2731 (1969).