Impact of ion-host interactions on the $5d$-to-$4f$ spectra of lanthanide rare-earth-metal ions. I. A phenomenological crystal-field model

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Dielectric crystals doped with Ce^{3+}, Eu^{2+}, Sm^{2+}, and Yb^{2+} display broadband $5d$-to-$4f$ emission, and are candidate solid-state tunable laser materials. The absorption and emission wavelengths, however, are very host sensitive, and a better understanding of $5d$ crystal-field interactions is needed in order to design lasing materials. This paper focuses on the $5d$ energy levels of Ce^{3+} in an octahedral complex. A phenomenological model is proposed for the bond-distance dependence of these levels based on first-principles expressions derived by others for contributions to the crystal-field energies. The magnitudes of these contributions are estimated for the CeF_6 complex.

I. INTRODUCTION

In recent years there has been a growing interest in solid-state tunable lasers based on impurity-doped dielectric crystals. For example, crystals doped with transition-metal ions such as chrysoberyl doped with Cr^{3+},[1] MgF_2 with Ni^{2+},[2] and with Co^{2+} (Ref. 3) have been lased. The iron-group transition-metal ions display vibrationally assisted optical transitions within the $3d$ shell and generally lase in the red or near-ir region.

The lack of tunable solid-state lasers at shorter visible wavelengths has motivated investigation of the $5d$-to-$4f$ optical transitions of lanthanide rare earths, particularly Ce^{3+}, Eu^{2+}, Sm^{2+}, and Yb^{2+}. Optical transitions between the $4f^N$ ground state and the first excited configuration $4f^{N-1}5d$ are parity allowed, and because of the large spatial extent of the $5d$ wave function, they are vibrationally broadened much more than the forced electric-dipole transitions which occur within the $4f$ shell. $5d$-to-$4f$ emission bands in crystals are typically several tens of nanometers in width. By the same token, the peak wavelength of the emission band varies greatly from host to host, and the choice of host is a critical design parameter. For example, Ce^{3+}:$LiYF_4$ and Ce^{3+}:LaF_3 have been lased,[4,5] but the lasing wavelengths are in the near uv near 300 nm. Ce^{3+}:YAG emits in the visible, but laser action seems to be frustrated by excited-state absorption losses.[6,7] The lowest $5d$ level of Eu^{2+} and of Sm^{2+} often lies close to excited $4f$ levels ($^6P_{7/2}$ in Eu^{2+}, and $^5D_0$ in Sm^{2+}). Unless the crystal field lowers this $5d$ level to below these excited $4f$ levels, it will be completely depopulated by rapid relaxation, and there will be no broadband emission. Even if broadband emission occurs, there may be excited $4f$ levels at twice the energy of this emission, leading to allowed excited-state absorption transitions. Thus a 1000 wave number change in the $5d$ crystal-field splitting, the $5d$ centroid, or the Stokes shift could "make or break" tunable laser action. Thus, in order to "design" good tunable lasers, we must be able to predict the spectroscopic effects of parameters such as site size, site symmetry, and coordination number. This requires that we study trends that occur when the host is varied in systematic ways.

In this paper, the crystal-field effects which determine the $5d$ levels of the Ce^{3+} ion are surveyed, and their magnitudes are estimated. A phenomenological model is synthesized which describes the dependence of the $5d$ levels on bond distance in an octahedral complex. It will be assumed that the ligands are very electronegative donor ions (e.g., F^- or O^{2-}). A key issue is the adequacy of a purely electrostatic description of the crystal field. In a following paper, this is tested by application of the model to Ce^{3+}-doped fluoride elpasolites.

The Ce^{3+} ion is singled out for consideration because its single-electron configuration yields a simple energy spectrum. Figure 1 shows a typical energy-level diagram for the Ce^{3+} ion in a fluoride host with cubal coordination.[8] The $5d$ splitting is proportional to the fourth-rank crystal-field parameter and can be deduced from inspec-

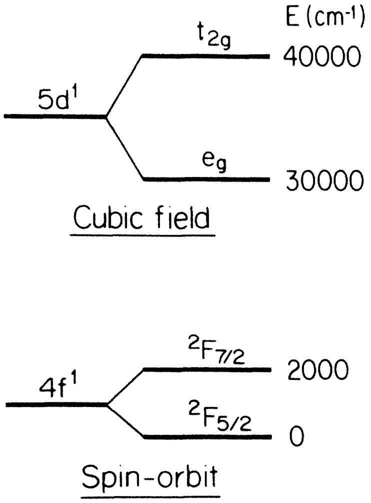

FIG. 1. Ce^{3+} energy levels.

tion of the absorption spectrum. Eu^{2+} and Sm^{2+}, on the other hand, have very complex energy spectra arising from Coulombic and exchange splittings of the free ions, which in turn are effectively modified by the host. This makes it difficult to extract crystal-field parameters from an examination of optical spectra. Ce^{3+} is also attractive as a lasing ion because its photoionization threshold is higher than in the divalent rare earths.

For Ce^{3+} in an octahedral complex, two parameters are of interest for prediction of absorption spectra. First, the center of gravity of the $5d$ configuration is lower in a polarizable matrix than in the free ion (using the $4f$ centroid as the zero of energy) by an amount which we label Δ. Second, the $5d$ level is split by a cubic crystal field into two levels separated by a gap $10Dq$.

II. THE ELECTROSTATIC CRYSTAL-FIELD MODEL AND ITS LIMITATIONS

The crystal-field interaction for a localized state of an impurity atom is generally expanded in spherical harmonics. For the ith electron at position $\mathbf{r}_i$,

$$V(\mathbf{r}_i)=\sum_{k,q} B_{kq}C_{kq}(\hat{\mathbf{r}}_i)\ , \tag{1}$$

where $\hat{\mathbf{r}}_i$ denotes the angular part of $\mathbf{r}_i$ and the radial dependence is in the crystal-field parameter B_{kq}. The C_{kq} are the spherical harmonics. If the crystal field arises from *fixed* classical electrostatic charge distributions in the lattice, it must obey Poisson's equation. If the charge distributions do not overlap the $4f$ or $5d$ wave function in question, the field must obey Laplace's equation. The solution to Laplace's equation in spherical coordinates is (1), provided that

$$B_{kq}=A_{kq}r^k\ , \tag{2}$$

where A_{kq} is a constant, and the subscript i is dropped. If the lattice charge distributions are expanded in multipoles, it is found that a 2^p-pole moment located a distance R away contributes a term proportional to $R^{-(k+p+1)}$ to the A_{kq} parameter.

In O_h site symmetry, (1) becomes

$$V(\mathbf{r})=A_{00}+A_{40}r^4\{C_{40}(\hat{\mathbf{r}})+5[C_{44}(\hat{\mathbf{r}})+C_{4\bar{4}}(\hat{\mathbf{r}})]/\sqrt{70}\}\ . \tag{3}$$

For d electrons the matrix elements vanish for $k>4$. The A_{00} term is the Madelung potential, and for negatively charged ligands this quantity is positive, raising the $4f$ and $5d$ energies by the same amount. The A_{40} term splits the d level into e_g and t_{2g} levels with energies

$$\begin{aligned} E(e_g)&=E_{\text{centroid}}+6Dq\ ,\\ E(t_{2g})&=E_{\text{centroid}}-4Dq\ . \end{aligned} \tag{4}$$

The point-charge contribution to Dq for an octahedral $(CeF_6)^{3-}$ complex is positive because the lobes of the e_g wave function point toward the repulsive F^- ligands, and the lobes of the t_{2g} wave functions avoid them. (Note: The parameter $10Dq$ is often used as a purely experimental parameter quantifying a splitting. In this work, it is also strictly identified with the parameter B_{40}. For the d electron, $B_{40}=21Dq$.)

The ligands also possess permanent multipole moments induced by the crystal field. This "lattice-induced" multipole field must be self-consistently solved; that is, the point-charge field induces multipole moments on all the atoms, and the field due to these moments induce more moments, and so on.[9] For a highly charged cation like Ce^{3+} in an isovalent site, lattice-induced multipole moments would tend to make the ligands more repulsive to the $5d$ electron. Another effect which contributes to the multipole moments of the ligands is the field due to the instantaneous displacement of the $5d$ electron. This gives rise to a correlation crystal field, to be discussed in Sec. III, but also causes the ligands to look more attractive on the average. The latter effect is called the "self-induced" multipole field.[10] As long as the ligands are modeled as *point multipoles,* both lattice-induced and self-induced fields obey (1) and (2).

So far we have insisted on a crystal field that obeys Laplace's equation. Such a model predicts that the $5d$-$4f$ centroid difference should be unchanged from the free ion value (neglecting configuration mixing by the crystal field). It further predicts a cubic $5d$ splitting whose leading contribution goes as $1/R^5$, where R is the metal-to-ligand distance.

The model can be refined by solving Poisson's equation, that is, by regarding the ligands as delocalized charge clouds obtained by summing the squared magnitudes of ligand orbitals, and then calculating the crystal field classically. We will refer to the resulting correction as "classical overlap," although in the absence of actual metal-ligand overlap, it is equivalent to including all terms in a ligand multipole expansion.

Experimentally, there are deficiencies in the electrostatic crystal-field model, even for $4f$ electrons. Morrison[9] points out that corrections must be introduced for screening and covalency. Furthermore, the $5d$-$4f$ centroid difference decreases quite significantly for rare earths in crystals. In Ce:YLF, for example, the shift is 6000 cm^{-1} with respect to the free-ion value.[4]

The inclusion of classical overlap in the calculation of splittings does not lead to a better model. Such calculations were done by Kleiner[11] on $3d$ electrons and by Garcia and Faucher[12] on $4f$ electrons; the delocalization of the ligand electron clouds in this model causes the positive ligand cores to become more "visible." As a result, F^-, Cl^-, or O^{2-} ligands are predicted to be more "attractive" than they are experimentally. The magnitude of the error is greater for the higher-rank crystal-field components because of the r^k weighting, and in many cases the calculated splitting is of the wrong sign.

In order to clarify and classify what is missing from electrostatic crystal-field theory, consider a simple quantum-mechanical model. Let $\mathbf{r}_1$ be the coordinate of a $5d$ electron on a Ce^{3+} ion and $\mathbf{r}_2$ the coordinate of a ligand electron. Let both electrons be moving in a common background potential $V(\mathbf{r})$. Let us write the wave function as a Slater determinant.

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=[\phi_M(\mathbf{r}_1)\phi_L(\mathbf{r}_2)-\phi_L(\mathbf{r}_1)\phi_M(\mathbf{r}_2)]/\sqrt{2}\ . \tag{5}$$

The first-order energy of the system is

$$E = E_M + E_L + \langle \phi_M \phi_L \,|\, e^2/r_{12} \,|\, \phi_M \phi_L \rangle - \delta(m_{sL}, m_{sM}) \langle \phi_M \phi_L \,|\, (e^2/r_{12}) \,|\, \phi_L \phi_M \rangle \ . \qquad (6)$$

The first two terms are the eigenvalues for the metal and ligand orbitals, respectively, in the absence of the Coulomb repulsion. The third term is the Coulomb repulsion and the last term is the exchange. In the product bras and kets, the first orbital is a function of the coordinate of electron 1, and the second orbital, electron 2. m_{sL} and m_{sM} are the spin projection quantum numbers for the ligand and metal eigenstates, respectively.

If we assume that $|\phi_M\rangle$ and $|\phi_L\rangle$ are nonoverlapping atomic orbitals, then $|\phi_M\rangle$ diagonalizes the one-body Hamiltonian,

$$H = p^2/2m + V + \int d^3 r_2 \, |\phi_L(\mathbf{r}_2)|^2 e^2/r_{12} \ . \qquad (7)$$

The effective ligand field obeys Laplace's equation, and (2) is valid. If there is overlap, but the exchange term in (6) is ignored, the third term in (7) obeys Poisson's equation. In either case, (7) is a quantum-mechanical equivalent of classical crystal-field theory which includes the classical overlap field due to one ligand electron.

To go beyond electrostatic crystal-field theory, several of the following refinements in the model are possible.

(1) The improvement of $|\phi_M\rangle$ and/or $|\phi_L\rangle$ by allowing configuration mixing by the crystal field.

(2) The inclusion of the exchange term of (6) in the Hamiltonian.

(3) The improvement of $|\phi_M\rangle$ and $|\phi_L\rangle$ by allowing for covalency. That is, admix $|\phi_L\rangle$ and $|\phi_M\rangle$ to form bonding and antibonding orbitals.

(4) The inclusion of correlations between the orbital motions of the ligand and metal electrons.

Most crystal-field calculations start by using the best available free-ion wave functions and neglecting additional configuration mixing entirely. Sugano and Shulman[13] have done covalency calculations on Ni^{2+} in $KNiF_3$, incorporating improvements 2 and 3 above. They obtained $3d$ splittings that are close to experimental values. We will discuss this approach to ligand field theory in detail, but first let us examine correlation crystal fields.

III. CORRELATION CRYSTAL FIELDS

Regardless of how much we embellish the functions ϕ_M and ϕ_L in (5), our quantum-mechanical model still cannot incorporate explicitly coupled orbital motions of the metal and ligand electrons. The original motive for investigating correlation crystal fields was the observation of host-induced shifts in the Coulombic repulsion parameters of rare earths. Morrison[9] gives a semiclassical analysis of this mechanism, which we summarize here. The term "correlation crystal field" is used here in a different way than it is by Newman,[14] who uses the term to denote any interaction which can be parametrized by two-electron crystal-field parameters.

The instantaneous displacement of a $4f$ (or $5d$) electron induces multipole moments on the ligands, and the field due to these moments reacts back on the electron or on other electrons. In the case of Ce^{3+}, the self-interaction is most important because it explains the $4f$-$5d$ centroid shift. In the case of many-electron configurations, as in the divalent rare earths, the two-electron crystal field is also important.

Referring to Fig. 2, let there be a ligand at $\mathbf{R}$ and two electrons at $\mathbf{r}_1$ and $\mathbf{r}_2$ with respect to the metal ion. $\mathbf{R}_1$ and $\mathbf{R}_2$ are the vectors from electrons 1 and 2, respectively, to the ligand. The electrostatic potential at the ligand due to the field of electron 1 is expanded in spherical harmonics.

$$\phi(R_1 + x) = -\sum_{n,m} E^*_{nm}(\mathbf{R}_1) x^n C_{nm}(\hat{\mathbf{x}}) \ , \qquad (8)$$

where

$$E_{nm} = e(-1)^n C_{nm}(\hat{\mathbf{R}}_1)/R_1^{n+1} \ .$$

Each term in the above sum induces a multipole moment Q_{nm} on the ligand given by

$$Q_{nm} = \alpha_n E_{nm} \ . \qquad (9)$$

The potential of electron 2 in the field of the nth rank multipole is

$$U^{(n)} = -e \sum_m Q_{nm}(-1)^n C_{nm}(\hat{\mathbf{R}}_2)/R_2^{\,n+1} \ . \qquad (10)$$

Substitution yields

$$U^{(n)}(\mathbf{r}_1, \mathbf{r}_2) = -e^2 \alpha_n \sum_m C_{nm}(\hat{\mathbf{R}}_1) C_{nm}(\hat{\mathbf{R}}_2)/R_1^{n+1} R_2^{n+1} \ . \qquad (11)$$

The self-interaction is obtained by setting $\mathbf{R}_1 = \mathbf{R}_2$ and introducing a factor of $\frac{1}{2}$ to account for the disappearance of the second electron.

$$U^{(n)}(\mathbf{r}_1) = -e^2 \alpha_n / 2R_1^{2n+2} \ . \qquad (12)$$

Next, (12) must be expanded in $\mathbf{r}_1$. The leading two spherically symmetric terms turn out to be

$$U^{(n)}(r_1) = -e^2 \alpha_n [\, 1/R^{2n+2} + (n+1)(n+2) r_1^2 / 3R^{2n+4}]/2 \ . \qquad (13)$$

In the special case of dipoles ($n = 1$) this is

$$U^{(1)}(r_1) = -e^2 \alpha (1/R^4 + 2r_1^2/R^6)/2 \ . \qquad (14)$$

The first term is a "self-induced" contribution to the Madelung potential which is not really correlation. It could have been incorporated into our quantum-

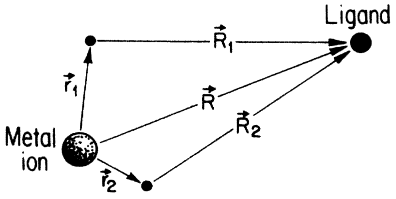

FIG. 2. Notation for the analysis of correlation crystal field.

mechanical model (5) by admixing excited ligand orbitals into ϕ_L.

The second term of (14) is an isotropic parabolic potential with a maximum at $r=0$, a violation of Laplace's equation. This term arises purely from correlation. It causes the effective one-electron potential of the metal ion to be "less steep," which decreases energy differences between configurations. In particular, the $5d$-$4f$ centroid difference changes by the amount

$$\Delta = -\alpha e^2(\langle r^2\rangle_{5d} - \langle r^2\rangle_{4f})/R^6 , \tag{15}$$

where $\langle\ \rangle$ denotes the expectation value with respect to the subscript eigenstate. If there are many ligands with different values of R and α, we sum them.

Similarly we can treat the fourfold field, obtaining a self-induced B_{4q} proportional to $\langle r^4\rangle/R^8$,[10] and a correlation B_{4q} proportional to $\langle r^6\rangle/R^{10}$.

This semiclassical approach yields the same results as a more rigorous quantum-mechanical analysis,[15] as long as it is understood that the polarizability used is the in-crystal value rather than the free-ion value.

IV. COVALENCY

So far we have considered a strictly ionic model, that is, one not allowing for any electronic excitations which involve transfer of charge between the ligand and metal ions. There is good evidence that such effects have important spectroscopic consequences for $3d$ electrons. Sugano and Shulman[13] performed NMR and optical measurements on $\mathrm{KNiF_3}$, and showed that their results fit a covalent model in which the $\mathrm{F^-}$ $2s$, $2p\sigma$, and $2p\pi$ orbitals display different amounts of mixing with $\mathrm{Ni^{2+}}$ $3d$ orbitals. We will review their method and results in detail in order to guide us in the formulation of a model for $\mathrm{Ce^{3+}}$ $5d$ orbitals. They performed a calculation of the $3d$ cubic splitting using a Hartree-Fock potential which was the superposition of free-ion Hartree-Fock potentials. Their trial wave functions were

$$\begin{aligned}\Psi_{ai} &= (\phi_i - \lambda_i\chi_i)/(N_i)^{1/2} ,\\ \Psi_{bi} &= (\chi_i + \gamma_i\phi_i)/(N_i')^{1/2} ,\end{aligned} \tag{16}$$

where ϕ_i is a metal orbital, and χ_i a ligand-complex orbital. N_i and N_i' are normalization constants. Orthogonality of the antibonding and bonding wave functions imposes the constraint $\lambda_i = \gamma_i + S_i$, where S_i is the group overlap, $\langle\phi\,|\,\chi\rangle$. The i subscript in (16) includes an O_h symmetry group representation and partner index. So χ_i is a linear combination of ligand s or p orbitals which transforms like ϕ_i.

The phase factors of the orbitals ϕ and χ are such that they constructively interfere in the bonding region. Thus the parameters S, γ, and λ are positive, and the algebraic signs in (16) are physically significant, indicating charge buildup in the bond region for the bonding orbital, and a node in the bond region for the antibonding orbital.

The calculation of Sugano and Shulman is equivalent to a variational approach, minimizing the energy of the system with respect to the parameter γ. The Hamiltonian of the system is written with a one-body potential which has the full symmetry of the complex.

$$H = \sum T + V_M + V_L . \tag{17}$$

The summation is over the electrons, T is the kinetic energy operator, V_M is the metal-ion potential, and V_L is the ligand-complex potential.

For each value of the label i, which we drop, the bonding and antibonding orbital energies are

$$\begin{aligned}E_a &= E_M' + |S\langle\phi\,|\,V_L\,|\,\phi\rangle - \langle\phi\,|\,V_L\,|\,\chi\rangle|^2/(E_M' - E_L') ,\\ E_b &= E_L' - |S\langle\chi\,|\,V_M\,|\,\chi\rangle - \langle\phi\,|\,V_M\,|\,\chi\rangle|^2/(E_M' - E_L') ,\end{aligned} \tag{18}$$

where

$$\begin{aligned}E_M' &= E_M + \langle\phi\,|\,V_L\,|\,\phi\rangle ,\\ E_L' &= E_L + \langle\chi\,|\,V_M\,|\,\chi\rangle ,\end{aligned}$$

and

$$\begin{aligned}(T + V_M)\phi &= E_M\phi ,\\ (T + V_L)\chi &= E_L\chi .\end{aligned}$$

Sugano and Shulman measure the "amount of covalency" by the parameter γ, not λ or S. This is physically reasonable because $\gamma > 0$ indicates bonding. If $\gamma = 0$, however, there is still "antibonding" needed to ensure orthogonality. That is, we have

$$\begin{aligned}\Psi_a &= (\phi - S\chi)/(1 - S^2)^{1/2} ,\\ \Psi_b &= \chi .\end{aligned} \tag{19}$$

Thus $\langle\Psi_a\,|\,H\,|\,\Psi_a\rangle$ contains a term of the form $-S\langle\chi\,|\,H\,|\,\phi\rangle$ which is ascribed to "nonorthogonality" rather than to "covalency." The normalization coefficient in (16) introduces a term of the form $(2\lambda S - S^2)\langle\phi\,|\,H\,|\,\phi\rangle$ which is termed "renormalization." Sugano and Shulman reserve the term "covalency" exclusively for contributions arising from nonzero γ.

Sugano and Shulman determine an experimental value for $10Dq$ by measuring the absorption from the $(t^6e^2)\ ^3A_2$ ground state to the $(t^5e^3)\ ^3T_2$ excited state of $\mathrm{Ni^{2+}}$. This experimental value was $7250\ \mathrm{cm^{-1}}$. The calculated value was $6350\ \mathrm{cm^{-1}}$, and the breakdown of the contributions to this are shown in Table I. This calculation does not include lattice-induced and self-induced dipolar contributions. The former is zero because the fluoride ion site has inversion symmetry. For $\alpha = 1\ \mathrm{\AA}^3$, the self-induced dipolar contribution to the splitting is $-759\ \mathrm{cm^{-1}}$.[10]

TABLE I. Calculated contributions to $10Dq$ of $\mathrm{Ni^{2+}}$ in $\mathrm{KNiF_3}$ ($\mathrm{cm^{-1}}$) (Ref. 13).

Point charge	1390
Classical overlap	−2080
Exchange	−2880
Renormalization	900
Nonorthogonality	3730
Covalency	5290
Total	6350
Experimental	7250

Neglect of metal-ligand wave-function mixing ($S=\gamma=\lambda=0$) leads to a crystal-field splitting of the wrong sign because of the attractive exchange and classical overlap interactions. The other terms are all repulsive. The covalency contributes over 80% of the total splitting. The calculated mixing is also quite large. λ for $p\sigma$ is 0.396, for example. The mixing coefficients agree quite well with those deduced from Sugano and Shulman's NMR measurements.

Several methods of approximation have been applied to (18). The extended Huckel method[16] yields for the antibonding orbital energy:

$$E_a=E_M'+S^2E_L'^2/(E_M'-E_L') . \tag{20}$$

The antibonding energy is proportional to the square of the group overlap integral, and therefore should show a roughly exponential dependence on the metal-ligand distance. For an octahedral CeF_6 complex in a fluoride crystal, S is on the order of 0.1, E_L' $(2p)$ is about $-150\,000$ cm^{-1}, and $E_M'(5d)$ is about $-50\,000$ cm^{-1}.[17] These values in (20) yield an antibonding energy of 2250 cm^{-1}. Therefore, significant covalent contributions to the $5d$ splitting and centroid should be expected. Equation (20) includes the last three terms of Table I, which we will refer to as "antibonding" contributions. The classical overlap and exchange will be referred to as "overlap" contributions.

The $5d$ splitting of Ce^{3+} in an octahedral field would have a covalent contribution equal to the difference between the e_g σ and s antibonding energy and the t_{2g} π antibonding energy. This contribution should have the same sign as the point-charge contribution. A degeneracy-weighted average of these antibonding energies gives the centroid shift.

V. CONFIGURATION MIXING

In this work the term "configuration interaction" will be used to denote admixture of atomic configurations by the Coulombic repulsion interaction of the free ion. "Configuration mixing" will denote an additional admixture introduced by the crystal field.

Configuration interaction is a spherically symmetric interaction in the product space of all the electrons, mixing states with the same values of L, S, and other quantum numbers indicating Lie group representations. The quantum number l is not valid, but for a lone $4f$ or $5d$ electron plus closed shells, l mixing is negligible. The principal effect is n mixing, which arises from the spherically symmetric interaction with the closed shells and leads to wave-function expansion with respect to hydrogenic wave functions. In multielectron configurations (like Pr^{3+} $4f^2$) l mixing is significant and leads to an L and S dependence of the phenomenological crystal-field parameters. This effect has been parametrized by Newman[14] as a two-electron crystal field ("correlation crystal field" in his terminology).

Configuration mixing, on the other hand, is a departure from spherical symmetry which has several potentially important consequences for Ce^{3+}. First, the crystal field acting on the (Xe) core mixes excited configurations into the $5s^2$-$5p^6$ state, which in turn alters the effective crystal field on the $4f$ or $5d$ electron. For $4f$ electrons in the rare earths, this effect shields the crystal field. Sternheimer[18] calculated reduction factors for $4f^n$ crystal-field parameters, and found that A_{2q} is reduced by about 65%, A_{4q} by 9%, and A_{6q} by 4%. For $5d$ electrons this effect will lead to less shielding because the $5d$ wave function extends further outside the (Xe) core, but quantitative values for the shielding parameters are not known. This effect does not alter the range dependence of the crystal field, that is, a shielded point charge B_{40} still has a $1/R^5$ dependence. Experimentally, however, this effect would manifest itself in a difference between the phenomenological A_{kq} obtained for $4f$ electrons and those obtained for $5d$ electrons (assuming the $\langle r^k\rangle$ values used are valid).

The second consequence of configuration mixing is that it acts on the $4f$ or $5d$ state directly. A cubic field will mix $6d$, $7d$, and $5g$ (e_g, t_{2g}) states into the $5d$ states. This gives a second-order downward shift of the $5d$ levels. For $6d$ mixing, for example,

$$\Delta E(t_{2g})=-\,|\langle 5d(t_{2g})\,|\,V\,|\,6d(t_{2g})\rangle|^2/(E_{6d}-E_{5d}) . \tag{21}$$

This shift, however, should only be a few tens of wave numbers because the energy denominator is on the order of 100000 wave numbers, and the matrix element in the numerator is no more than 2000 or 3000 wave numbers. The isotropic overlap and correlation crystal-field terms will also mix the $5d$ with $6d$ and $7d$ states, again leading to a slight second-order downward shift of the $5d$ energy levels.

A measure of the importance of configuration mixing is the degree to which ion polarizabilities are altered by the crystalline environment. Mahan[19] studied this effect. For anions, the spherically averaged crystal field rises sharply beyond the nearest-neighbor distance. This compresses the potential, which increases the energies of excited anion configurations and reduces the amount of admixing between configurations. For cations, the overlap with negative ligands expands rather than contracts the potential, which lowers the energies of excited configurations and admixes them more. Mahan calculated cation and anion polarizabilities in alkali halides, and compared the results to experimental values. He found that while the polarizabilities of anions decrease significantly from free-ion values, the cations show no significant increase.

VI. MODEL FOR AN OCTAHEDRAL COMPLEX

We now construct a phenomenological model for the $5d$ energies in an octahedral complex. The splitting, $10Dq$, will include contributions from the point-charge, lattice-induced dipole, and self-induced dipole terms plus a contribution from overlap and antibonding effects. The centroid shift, Δ, will include the correlation term (15) and again an antibonding-overlap contribution.

The antibonding-overlap contribution to the $5d$ energies consists of antibonding, exchange, and classical overlap; the latter two make the ligands look "attractive," and therefore give negative contributions to both $10Dq$ and Δ. In predicting the qualitative behavior of the system we assume that the net antibonding-overlap contributions to both $10Dq$ and Δ are positive. The justification for this is provided by Phillips,[20] who pointed out that even without covalency [$\gamma=0$ in Eq. (16)], metal-ligand overlap gives rise to the "nonorthogonality" and "renormalization" terms shown in Table I. Using the wave function of Eq. (19), Phillips argues on general grounds that these terms give rise to an effective repulsion which approximately cancels the classical overlap and exchange. Physically, this is Pauli repulsion, since the necessity of orthogonalizing Ψ_b and Ψ_a is a reflection of the Pauli principle. Indeed, in Table I, the sum of the classical overlap, exchange, renormalization, and nonorthogonality terms is $-330\ \mathrm{cm}^{-1}$, or 5% of the splitting. Although Phillips applied this argument to the splitting, the cancellation of terms affects the energy eigenvalues of the individual levels, and therefore applies to the centroid as well.

For an octahedral complex we write

$$\begin{aligned} 10Dq &= 5e^2\langle r^4\rangle/3R^5 + 25e\alpha E\langle r^4\rangle/3R^6 \\ &\quad - 145e^2\alpha\langle r^4\rangle/21R^8 + Ae^{-R/b}\,, \\ \Delta &= -6e^2\alpha(\langle r^2\rangle_{5d} - \langle r^2\rangle_{4f})/R^6 + Be^{-R/b}\,, \end{aligned} \tag{22}$$

where it is assumed that the π antibonding energy for the t_{2g} level and the σ antibonding energy for the e_g level both vary exponentially on the nearest-neighbor distance R with the same decay distance b. In the above expressions, α is the ligand polarizability, E is the axial, outward-directed electric field at the ligand, and $\langle r^n\rangle$ denotes the expectation value of r^n with respect to the $5d$ state, or the state indicated by subscript. The electric field E is given by e^2/R times a constant on the order of unity which is computed by lattice sum.

Experimentally the t_{2g} and e_g energies can be taken to be the energies corresponding to the centroids of the absorption bands to the respective levels. This strategy relies on a semiclassical model of vibrationally broadened optical spectra: The lattice tends to remain stationary during the electronic transition, and therefore the absorption band arises primarily from vertical transitions in configurational coordinate space. The energies of these vertical transitions are the energies which would be observed if the lattice could be fixed in its equilibrium position. These are the energies that crystal-field theory attempts to predict.

A first-principles calculation of the antibonding-overlap terms in (22) is very difficult, requiring a detailed knowledge of wave functions both on the metal ion and the ligands. Even for calculating the other terms, however, the correct values for α and $\langle r^n\rangle$ are not clearly established. Morrison[9] shows, for example, that the use of Hartree-Fock wave functions for the $4f$ electron underestimates $\langle r^4\rangle$ by a factor of 3.

Polarizability estimates for F^- in NaF vary from Mahan's[19] value of 0.69 Å^3 to Fowler and Madden's[21] value of 1.12 Å^3. Wilson and Curtis[22] obtain a value of either 1.56 or 1.83 Å^3 for alkali fluorides, depending on the model used. These estimates are based on isotropic or spherically averaged crystal fields, and their correctness is tested by examining refractive index data for cubic crystals. The polarizabilities appearing in (22), however, are dominated by the axial polarizability in the octahedral complex, whereas the crystal refractive index reflects an average of the axial polarizability and two transverse polarizabilities. Thus, in addition to the great uncertainty in the isotropic value for α, anisotropic components of the crystal field at the ligand may enhance the axial polarizability at the expense of transverse polarizability, or vice versa.

Therefore, it is best to express (22) in phenomenological form

$$\begin{aligned} 10Dq &= C_1/R^5 + C_2/R^8 + Ae^{-R/b}\,, \\ \Delta &= -C_3/R^6 + Be^{-R/b}\,. \end{aligned} \tag{23}$$

In effect, $\langle r^4\rangle$, $\langle r^2\rangle_{5d}-\langle r^2\rangle_{4f}$, α, A, B, and b are phenomenological parameters adjusted to fit (23) to the measured dependence of $10Dq$ and Δ on R in a series of isostructural hosts. At least three hosts are required to determine the parameters, and more are desirable.

This quantitative approach can be supplemented by a purely qualitative approach. Figure 3 shows the dependence of the $5d$ levels and their centroid on bond distance for an octahedral CeF_6 complex as given by (22) for plausible values of the unknown parameters. The range of bond distances shown in Fig. 3 is divided into three regimes, which are distinguishable in terms of qualitative dependence of the levels on the lattice constant.

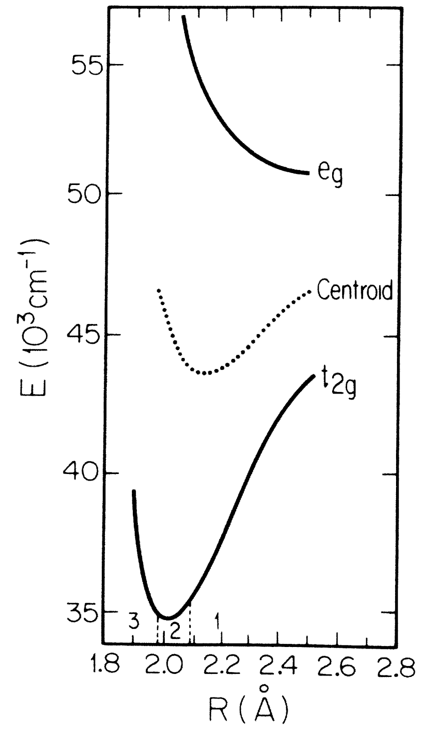

FIG. 3. $5d$ energy levels in a CeF_6 complex using Eq. (22) with $\langle r^4\rangle = 3.7904$ Å^4, $\langle r^2\rangle_{5d}-\langle r^2\rangle_{4f}=1.2439$ Å^2 (Ref. 23), $\alpha=1$ Å^3, $b=0.1$ Å, $A=5B/7=3.58\times10^{12}\ \mathrm{cm}^{-1}$. The sum of the lattice-induced and self-induced dipolar contributions to $10Dq$ are neglected.

(1) Covalency negligible: In this regime the t_{2g} level and the $5d$ centroid are both decreasing as the lattice constant decreases.

(2) Covalency intermediate: The $5d$ centroid has begun to rise with decreasing lattice constant, and the t_{2g} level is near the minimum of the curve in Fig. 3, and is therefore insensitive to the lattice constant.

(3) Covalency dominant: The t_{2g} level rises with decreasing lattice constant due to overwhelming antibonding and exclusion effects.

Thus even if data can only be obtained for two or three isostructural hosts, the movement of the $5d$ levels with changes in nearest-neighbor distance or lattice constant can be used to classify the system into one of these categories with respect to covalent effects.

If we constructed a table of contributions to the $10Dq$ of Ce^{3+} in a fluoride host (e.g., Rb_2NaYF_6) analogous to Table I, the entries would differ as follows. The point-charge term would be an order of magnitude greater than for Ni^{2+} because the $\langle r^4 \rangle$ value is 15 times as large, whereas the R^5 value is only 35 percent larger. A similar argument applies to lattice-induced or self-induced dipolar contributions; however, where these are both important they tend to offset each other. The classical overlap, exchange, renormalization, and nonorthogonality terms are difficult to calculate, and we will assume the validity of Phillips's claim that their sum is a negligible contribution. The covalency term is also difficult to calculate because we do not know the overlap as a function of nearest-neighbor distance. However, for both Ce^{3+} $5d$ and Ni^{2+} $3d$ orbitals, the square root of $\langle r^2 \rangle$ is roughly equal to the ionic radius of the ion. This indicates that the two ions should have roughly equal overlaps with a given ligand. Ce^{3+} is much more electropositive, that is, the energy denominators used in (20) are two to three times larger than for Ni^{2+}.[13,17] Thus for $S = 0.1$, which is close to the value calculated by Sugano and Shulman, the covalency entry for Ce^{3+} would be 2000–3000 cm^{-1}.

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