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Covalent Effects in Rare-Earth Crystal-Field Splittings

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Covalent contributions to the optical splitting of rare-earth ions are discussed. Tm^{2+} in CaF_2, the system studied by Bleaney, Axe, and Burns, and others, was chosen because it is an outstanding example of the breakdown of the traditional electrostatic theory when applied to rare-earth ions in cubic environments. Upon separating out overlap from covalent contributions, overlap effects are found to dominate. The role of the closed $5p$ shell in covalent mixing is shown to be as important as, or more important than, that due to the $4f$ shell alone.

I. INTRODUCTION

IN recent years, developments in theory and experiment have revealed shortcomings inherent in the crystal-field-theory description of the magnetic and optical properties of ions in solids. For the $3d$ transition-metal complexes, the need to abandon the electrostatic crystal-field (ECF) model in favor of a more sophisticated molecular-orbital-cluster approach was recognized when the importance of change transfer, or covalency, effects was revealed in a number of experiments. The ECF theory as applied to the description of rare-earth ions has had a different historical development. The physical isolation of the open $4f$ shell, well inside the closed $5p$ and $5s$ shells, made it plausible to view the $4f$ shell as interacting only electrostatically with the environment external to the ion; until recently, covalency effects were thought to be unimportant.

In the last few years, the importance of electrostatic contributions arising from the closed $5s$ and $5p$ shells distorted by the ECF in both a linear[1–3] and nonlinear[2] way was demonstrated. For crystal fields of low symmetry, the inclusion of these $5s$ and $5p$ shielding terms appears to account satisfactorily for the dominant ($L=2$) contributions to the observed crystalline-field energy levels.[2–4] For the case of cubic symmetry, Jørgensen, Pappalardo, and Schmidtke[5] suggested that covalent effects dominate and offer a better semiempirical fitting scheme than does the traditional purely electrostatic approach. We must emphasize that covalent effects do not simply make contributions to ECF parameters, but add new terms to the description of crystalline effects. The significance of covalency has gained increasing acceptance lately,[6–10] despite the apparent success of ECF theory when employed semiempirically to fit experiment. A general description of the way covalency could be incorporated into a crystal-field theory including shielding effects has been discussed by us previously,[10] but no numerical calculations were reported. Recently, Axe and Burns[6] (AB) used their measured stress-induced changes in the spectrum of Tm^{2+} in CaF_2 (and in SrF_2) to calculate the radial dependence of the cubic splitting. To account for their results, $4f$-shell covalency effects were introduced. Their calculations, which, of necessity, were crude, suggested that "covalent" effects contributed a term somewhere between 10 and 100% of the entire observed crystal-field splitting energy.

Now, Tm^{2+} in CaF_2 is an outstanding example of the breakdown of the traditional purely electrostatic theory when applied to an ion in a cubic environment. The electrostatic crystal potential has the form

$$V_c(\mathbf{r})=\sum_{L,M} A_L{}^M r^L Y_L{}^M(\theta,\varphi) \qquad (1)$$

involving $L=4$ and 6 terms with the former making the dominant contribution to the energy. Bleaney[11] has performed the lattice sums necessary for evaluating the $A_L{}^M$. Utilizing Hartree-Fock $4f$-shell expectation

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[1] G. Burns, Phys. Rev. **128**, 2121 (1962); C. J. Lenander and E. Y. Wong, J. Chem. Phys. **38**, 2150 (1963); D. K. Ray, Proc. Phys. Soc. (London) **82**, 47 (1963); R. E. Watson and A. J. Freeman, Phys. Rev. **133**, A1571 (1964).

[2] A. J. Freeman and R. E. Watson, Phys. Rev. **139**, A1606 (1965).

[3] R. M. Sternheimer, Phys. Rev. **146**, 140 (1966).

[4] One source of satisfaction with the electrostatic model has been experiments [D. T. Edmonds, Phys. Rev. Letters **10**, 129 (1963); R. G. Barnes, E. Kankeleit, R. L. Mössbauer, and J. M. Poindexter, *ibid.* **11**, 253 (1963); Phys. Rev. **136**, A175 (1964); J. Blok and D. A. Shirley, J. Chem. Phys. **39**, 1128 (1963); Phys. Rev. **143**, 278 (1966); Q. H. F. Vrehen and J. Volger, Physica **31**, 845 (1965); H. H. Wickman and I. Nowik, Phys. Rev. **142**, 115 (1966)] which, assuming the electrostatic model, have yielded $(1-\gamma_\infty)/(1-\sigma_2)$, i.e., the ratios of the external field gradient Sternheimer shielding factor and the shielding of the $L=2$ component of the crystal potential as seen by the $4f$ shell. Computed values of (Refs. 2 and 3) these ratios agree qualitatively with experiment.

[5] C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, J. Chem. Phys. **39**, 1422 (1963).

[6] J. D. Axe and G. Burns, Phys. Rev. **152**, 331 (1966).

[7] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience Publishers, Inc., New York, 1964).

[8] J. H. M. Thornley, Proc. Phys. Soc. (London) **88**, 325 (1966).

[9] M. M. Ellis and D. J. Newman, Phys. Letters **21**, 508 (1966).

[10] R. E. Watson, in Fifth Rare-Earth Research Conference, Ames, Iowa, 1965 (unpublished).

[11] B. Bleaney, Proc. Roy. Soc. (London) **277**, 289 (1964).

values[12,13] for $\langle r^L\rangle$, he obtained an $L=4$ crystal-field term which was a factor of 4 (and the less important $L=6$ an order of magnitude) smaller than values obtained by fitting experiment, assuming the electrostatic model. A 10% enhancement of the $L=4$ interaction term from closed 5*s*- and 5*p*-shell antishielding seems[2] possible, but this cannot account for the discrepancy within the model between theory and experiment, not even when considered together with the uncertainties in the lattice sums[11] and the 4*f* wave functions.[12] This inability of ECF theory to predict what it had apparently satisfactorily accounted for semiempirically, led to the estimate of covalency by AB.

In this paper, we inspect in detail the AB results and extend these investigations in several ways. First, we sort out the two physically distinct effects, overlap and true covalent mixing, which contributed to the AB result. While for their purpose it was unnecessary to sort these effects out, the division becomes very important if one is interested in observables such as hyperfine interactions, electronic *g* shifts, neutron form factors, and Slater interelectronic F^k parameters. Overlap effects will be seen to dominate and, taken alone, this would suggest that the rare-earth cubic crystal-field energy problem would be very amenable to a broad semiempirical attack. Second, we follow our previous work[2,10] to inspect the role played by the 5*p* shell in the covalent mixing. Just as this shell contributes significantly to the purely electrostatic interaction of the ion with its environment,[1–4] we show that, in its contributions to the crystal-field energy, 5*p* covalent mixing is as important as, or more important than, that of the 4*f* shell alone. As with the electrostatic terms, the simplicities offered by having the open 4*f* shell relatively isolated from the external environment are destroyed by the higher-order, but quantitatively significant, participation of the closed outer shells of the rare-earth ion "core." Finally, we discuss the importance of various approximations to the final computational results, some of which have raised unnecessary doubts about the AB results.

In Sec. II, we review the definitions of overlap and covalent mixing effects and briefly inspect their implications for spin and charge densities, and, in turn, hyperfine interactions. In doing this, our reasons for wishing to sort out the two effects will become clear. In Sec. III, we consider the 4*f*-shell calculation and its breakup into overlap and covalent terms, and in Sec. IV the role of the 5*p* shell in covalent mixing is inspected. It must be emphasized that the breakdown of the electrostatic model has been shown for the cubic case and not for environments of lower symmetry, where a dominant $L=2$ term appears, for which the electrostatic model (with shielding) seems to be essentially correct. It is in cases of low symmetry, where there are strong V_2^0 fields, that we believe nonlinear shielding effects may contribute spuriously to the experimentally fit V_L^M parameters and hence affect any opinion one might have concerning the apparent role of overlap and covalency in these parameters. There is a strong suggestion of a breakdown in ECF theory for the $L\neq 2$ terms of noncubic systems; this matter, and the recent overlap estimate of Ellis and Newman[9] for such a case, will be discussed in Sec. V.

II. OVERLAP, COVALENCY, AND THEIR ASSOCIATED CHARGE AND SPIN DENSITIES

The concepts of overlap and covalency follow directly from the model[14] one uses to describe a transition-metal or rare-earth salt—namely, a Hartree-Fock description of the solid constructed from free-ion or *essentially*[15] free-ion wave functions. Given "free-ion" one-electron orbitals ψ_{n,i_n} (where n indicates ion site, i_n an orbital at that site), one constructs a familiar many-electron Slater determinant Ψ which gives the proper antisymmetry of the many-electron function.

Let us consider the implications[14] of such a construct for the simple case of a metal ion with a single open-shell orbital φ, occupied with, say, spin ↑, and from the neighboring closed-shell ions (for Tm in $\mathrm{CaF_2}$ this would be a cube of $\mathrm{F^-}$ ions), a pair of "molecular orbitals," $\chi_\uparrow$ and $\chi_\downarrow$, of the same spatial symmetry[16] as $\varphi_\uparrow$. In other words, one constructs a Ψ from $\varphi_\uparrow$, $\chi_\uparrow$, $\chi_\downarrow$. Insertion into Ψ has two effects. Firstly, any mixing of the two occupied orbitals, say, $\varphi_\uparrow$ and $\chi_\uparrow$, between themselves has no effect on the value of Ψ, hence on any observable. This follows, mathematically, for any pair of occupied orbitals from the properties of a determinant and, physically, from the antisymmetry. Secondly, the $\varphi_\uparrow$ and $\chi_\uparrow$, coming from the free ions, will, in general, not be orthogonal, having an overlap integral $S\neq 0$. One can Schmidt-orthogonalize these orbitals, obtaining the set

$$(1-S^2)^{-1/2}[\varphi_\uparrow - S\chi_\uparrow],\chi_\uparrow,\chi_\downarrow\,,$$

without affecting the value of Ψ. [The $(1-S^2)^{-1/2}$ is a normalization constant.] *Whether* one orthogonalizes them *or* simply constructs Ψ from $\varphi_\uparrow$, $\chi_\uparrow$, and $\chi_\downarrow$ and then accounts for nonorthogonality when evaluating Ψ, one obtains in the system's charge density $|\Psi|^2$, an "overlap" term *in addition* to a simple superposition of free-ion densities which, to second order in

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[12] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[13] Hartree-Fock values of rare-earth 4*f* shell $\langle r^L\rangle$ integrals appear in Appendix B of A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA.

[14] For a previous discussion of overlap and covalency see, for example, R. E. Watson and A. J. Freeman, Phys. Rev. **134**, A1526 (1964).

[15] By this we mean ion orbitals, which are still free ion in essential character, and which are perturbed, thus accounting for the environment in the salt (in turn providing a better basis for constructing the multicenter salt wave function). An expansion of the open metal shell, first suggested for iron series ions by L. Orgel [J. Chem. Phys. **23**, 1824 (1955)], is an example of this.

[16] The symmetries and symmetry combinations of the 4*f* and neighboring ligand ion orbitals of immediate concern here are given in Table I of Ref. 6.

S, is

$$\Delta\rho_{\mathrm{ov}\uparrow}(\mathbf{r})=S^2[|\varphi_\uparrow(\mathbf{r})|^2+|\chi_\uparrow(\mathbf{r})|^2]-S[\varphi_\uparrow{}^*(\mathbf{r})\chi_\uparrow(\mathbf{r})+\varphi_\uparrow(\mathbf{r})\chi_\uparrow{}^*(\mathbf{r})]. \quad (2)$$

Note that this density is associated with spin ↑ electrons. Spin orthogonality, of course, keeps $\chi_\downarrow$ from being involved in this.

While the mixing of occupied orbitals has no effect on Ψ and, in turn, on any observable, any mixing of *unoccupied* orbital character into an occupied orbital does. The obvious mixing is between the empty $\varphi_\downarrow$ and the occupied $\chi_\downarrow$, giving us the set

$$(1-S^2)^{-1/2}[\varphi_\uparrow-S\chi_\uparrow],\quad \chi_\uparrow,\quad \times(1+2S\gamma+\gamma^2)^{-1/2}[\chi_\downarrow+\gamma\varphi_\downarrow].$$

This corresponds to letting the neighboring, or ligand, ion spin ↓ electron spend time in the metal spin ↓ hole site; γ is the weighting or mixing factor. This "covalent" mixing will occur to the extent that it stabilizes the energy of the many-electron system. One can estimate the mixing and associated "bonding" energy in terms of the above occupied "bonding" orbital or, *equivalently*, in terms of the energy increase and mixing in the unitarily related *hole* state.[17] In the case of Tm^{2+}, with its single $4f$ hole, the latter procedure is more convenient. The covalent mixing also contributes to the charge density of the system, giving, to second order in γ and S,

$$\Delta\rho_{c\downarrow}(\mathbf{r})=\gamma^2[|\varphi_\downarrow(\mathbf{r})|^2-|\chi_\downarrow(\mathbf{r})|^2]-\gamma[\varphi_\downarrow{}^*(\mathbf{r})\chi_\downarrow(\mathbf{r})+\varphi_\downarrow(\mathbf{r})\chi_\downarrow{}^*(\mathbf{r})-2S|\chi_\downarrow(\mathbf{r})|^2], \quad (3)$$

the first line explicitly showing the shift of charge off the ligands onto the metal. One adds this to $\Delta\rho_{\mathrm{ov}}$ when obtaining the charge density, but *subtracts* it, because of its spin ↓ character, when estimating the system's spin density. The interplay of covalent and overlap effects is indicated in Fig. 1, where the spin and charge densities are plotted along a metal-ligand internuclear line (actually for a Ni^{2+} $3d$ orbital and a neighboring F^- $2p$ appropriate to KNiF_3) as a function of γ/S for a fixed spin-density distribution at the ligand site. Two facts are to be seen by inspecting either the figure or Eqs. (2) and (3). Firstly, overlap and covalent mixing act *cooperatively* in producing a spin density change at the ligand sites and a charge shift at the metal, but act *destructively* for the charge change at the ligand site and spin shift at the metal. Secondly, *overlap and covalent effects convey a spin density on to the ligand site whose spin direction is parallel to that of the local metal moment.* Weaker covalent effects, such as the promotion of local moment electrons out onto empty neighboring ion shells (e.g., the $3s$ of F^-), also preserve this sign sense.

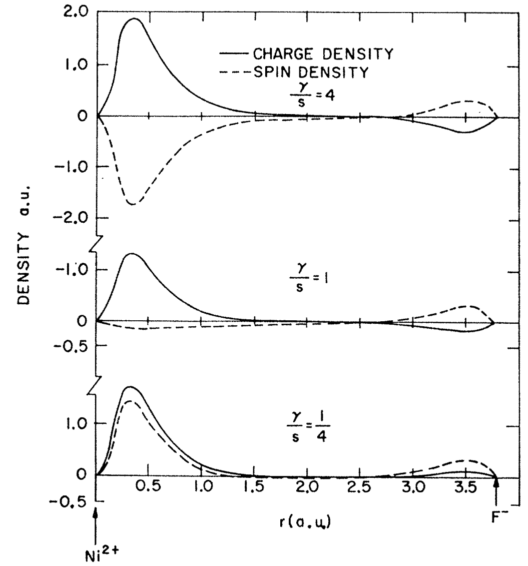

FIG. 1. Overlap plus covalent charge (solid curves) and spin (dashed) densities plotted along a metal-ligand nuclear line as a function of the ratio of the covalent mixing parameter to the overlap integral, S/γ. The sum $(S+\gamma)$ is held constant in the three plots, thus maintaining a fixed spin density [inspect the $|\chi|^2$ terms arising from the difference of Eqs. (2) and (3)] at the ligand site. This plot has been drawn for a Ni^{2+} $3d$ and F^- $2p$ appropriate to KNiF_3 [see also Fig. 2 of Watson and Freeman (Ref. 14)].

Shulman[18] and others have gained some of our best information concerning $3d$ transition-metal salt covalency by observing "transferred" hyperfine interactions at ligand sites, e.g., the F^{19} resonance in KNiF_3. The source of the interactions is the spin density produced in the otherwise closed-shell interior of the ligand ion. Some of the success in extracting covalency information from such experiments must be attributed to the fact that covalency and overlap contribute cooperatively to the spin density at the ligand site. Systematics are seen in neutron diffraction, hyperfine field, and other data which reflect the spin-density behavior at the metal site, but they have supplied little quantitative information concerning covalency. The failure to obtain information from this source reflects, in part, the fact that overlap and covalency oppose one another here, and, in turn, that we inadequately understand, and must learn more, concerning the relative roles of overlap and covalency and the model (and its basis set[15]) from which they arise. While interesting, space does not allow a detailed cataloguing of this failure here.

There is a considerable literature[19–21] of isotropic transferred hyperfine effects due to rare-earth ions.

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[17] At times, it is desirable to do both calculations simultaneously (see Ref. 14) as a check on internal consistency. This was done, for example (see Ref. 14), for KNiF_3 (where identical results were happily obtained).

[18] R. G. Shulman and V. Jaccarino, Phys. Rev. **103**, 1126 (1956); **108**, 1219 (1957); J. W. Stout and R. G. Shulman, *ibid.* **118**, 1136 (1960); R. G. Shulman and K. Knox, *ibid.* **119**, 94 (1960); Phys. Rev. Letters **4**, 603 (1960); R. G. Shulman, Phys. Rev. **121**, 125 (1961).

[19] R. G. Shulman and B. J. Wyluda, J. Chem. Phys. **30**, 335 (1959); W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, *ibid.* **36**, 694 (1962); R. G. Bessent and W. Hayes, Proc. Roy. Soc. (London) **A285**, 430 (1964) (the one case of uncertain sign); V. Saraswati and R. Vijayaraghavan, Phys. Letters **21**, 363 (1966).

[20] R. E. Watson and A. J. Freeman, Phys. Rev. Letters **6**, 277 (1961); **6**, 529E (1961).

[21] J. M. Baker and J. P. Hurrell, Proc. Phys. Soc. (London) **82**, 742 (1963).

TABLE I. The covalent-plus-overlap contributions $\Delta\epsilon$ to the crystal-field hole-state energies of Tm^{2+} in CaF_2, employing the compromise numerators of Axe and Burns. All values are in cm^{-1}.

	Mixing term			
$4f$ hole	$2s$	$2p\sigma$	$2p\pi$	Total energy
a_{2u}	250	381	···	631
t_{1u}	66	102	17	185
t_{2u}	···	···	154	154

These isotropic terms arise from spin induced in ligand s shells which then interact with the nucleus via the Fermi contact term. In every case where the sign has been determined, it has indicated a contact term *opposite in sign* and an order of magnitude greater than what would be produced by $4f$ covalent and overlap effects. While one can argue about magnitudes, a contact term associated with a spin direction antiparallel to that of the metal moment is impossible for $4f$-shell overlap and covalent terms. A quantitatively satisfactory explanation of the experimental results appears[20,21] to be the occurrence of a negative spin density induced[20] in the outer reaches of the $5s$ and $5p$ rare-earth shells by the $4f$. What is important to us here is that $4f$ covalent and overlap contributions to rare-earth transferred hyperfine interactions are small and experimentally in the noise. This denies us one of the best sources of information concerning covalency.

In this section, we have inspected overlap and covalent mixing. They arise, given a *model*, from different physical sources, and their effect is sometimes cooperative and sometimes mutually destructive. We have dwelt on this in some detail because while the model, with minor variations, is generally (too freely) accepted, its implications seem insufficiently digested in the literature. For our purposes, we are interested in knowing how appropriate the model is and, given the model, the relative roles of overlap and covalency. In the next section, we will proceed and inspect these roles for rare-earth cubic-crystal-field energies.

III. COVALENCY AND OVERLAP IN THE LIGAND FIELD ENERGIES OF Tm^{2+} IN CaF_2

The case of Tm^{2+} in CaF_2 may be treated[6] in terms of the single $4f$-shell hole in the strong-field limit, where it goes into the singly degenerate a_{2u} and the two triply degenerate t_{1u} and t_{2u} cubic representations.[16] The calculation of γ, for the mixing between a particular pair of orbital (hole) φ_{4f} and (occupied) χ, becomes the solution[22] of

$$(S+\gamma)=\frac{\langle\varphi|h|\chi\rangle-S\langle\varphi|h|\varphi\rangle}{\langle\chi|h|\chi\rangle-\langle\varphi|h|\varphi\rangle}, \qquad (4)$$

where h is the appropriate one-electron Hamiltonian for our system. Now equations such as (4) have yet to be solved with high accuracy for a transition-metal salt, and the computational problems are worse for the rare-earth case (some of the complications will be suggested by Sec. IV). This forced AB to two approximations when estimating matrix elements. First, they employed a Wolfsberg-Helmholz approximation[23] for the off-diagonal matrix element, namely,

$$\langle\varphi|h|\chi\rangle=S(\langle\varphi|h|\varphi\rangle+\langle\chi|h|\chi\rangle). \qquad (5)$$

Experience with the iron-series salt case indicates this approximation to be good or very bad, depending on one's point of view. Actually, *this assumption is not essential to the results*, contrary to what has been generally assumed. Having done this, values of the two diagonal matrix elements were still required. Energy denominators of 100 000 cm^{-1} for the $4f$-ligand $2p$ mixing and thrice this for the $2s$ were obtained from charge-transfer spectra. Their utilization involves arguments concerning correlation and polarization effects and is most justified in a Heitler-London treatment of covalency,[24] where such effects are most naturally incorporated. It is more difficult to argue, with rigor, their role in the molecular-orbital approach utilized here and, if anything, the above values are too small for the problem at hand. The implications of increasing them will be discussed toward the end of this section. Holding the denominators fixed, results were obtained as a function of varying one of the diagonal matrix elements (or rather the entire numerator). Considering all contributing uncertainties, it appears fair, although pessimistic, to say that the calculations[6] displayed a "covalent" contribution to the crystal-field energy which lies between 10 and 100% of the full experimental crystal-field splitting.

The $4f$ hole energy shift is given by[25]

$$\begin{aligned}\Delta\epsilon=&-2S\langle\varphi|h|\chi\rangle+S^2[\langle\varphi|h|\varphi\rangle+\langle\chi|h|\chi\rangle]\\&-2\gamma\langle\varphi|h|\chi\rangle+(2\gamma S+\gamma^2)\langle\chi|h|\chi\rangle-\gamma^2\langle\varphi|h|\varphi\rangle,\end{aligned} \qquad (6)$$

where the first line is associated purely with overlap effects, the remainder with covalent mixing. An alternative expression of identical accuracy is

$$\Delta\epsilon=(S+\gamma)^2[\langle\varphi|h|\varphi\rangle-\langle\chi|h|\chi\rangle], \qquad (7)$$

which is correct *only* when γ is the solution of Eq. (4). This form has the computational virtue that, given γ, one only requires the energy denominator already utilized in Eq. (4) in order to obtain $\Delta\epsilon$. Axe and Burns obtained $\Delta\epsilon$'s as a function of varying numerators in Eq. (4), and chose to report results for a compromise set of matrix elements; these results are reproduced in Table I. The holes in the table indicate mixing which is not allowed by symmetry.[16] The essential feature of the results is that the t_{2u} and t_{1u} levels are close together, with the a_{2u} hole state some 450 to 480 cm^{-1} lower. This

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[22] This equation is correct to second order in γ and S. For its derivation, see Sec. VI of Ref. 14.

[23] See for example, C. J. Ballhausen and H. Gray, *Molecular Orbital Theory* (W. A. Benjamin, Inc., New York, 1964).

[24] J. Hubbard, D. E. Rimmer, and F. R. A. Hopgood, Proc. Phys. Soc. (London) **88**, 13 (1966).

[25] See Eq. (38) of Ref. 14.

energy difference, to which one should add the purely electrostatic field contribution[11] of ~200 cm^{-1}, is to be compared with an experimental level splitting Ω_{exp} of ~960 cm^{-1}. When the numerators were varied, the covalent-plus-overlap contribution to the splitting varied from 200 to 650 cm^{-1}, a range which is less than the pessimistic uncertainty we have already attributed to the calculation.

As already indicated, we believe that the approximations employed by Axe and Burns are not essential to the main features of their results, that Table I is *characteristic* of what could be obtained in a more refined calculation, and that a realistic assessment of the uncertainty of the result would be of smaller range than the above-mentioned 10 to 100%. Several of the arguments supporting this view are given in the Appendix. If one accepts covalency and overlap as responsible for a large fraction of the observed crystal-field splitting Ω_{exp}, we can inspect the relative importance of overlap and covalency to this and other observables *without* assumptions concerning numerators (but instead as a function of the total contribution of overlap and covalency to the splitting).

The purely covalent contribution to the splitting may be obtained from the second and third lines of Eq. (6) or by[26]

$$\Delta\epsilon_{\text{cov}}=\gamma^2[\langle\varphi|h|\varphi\rangle-\langle\chi|h|\chi\rangle], \tag{8}$$

which, like Eq. (7), holds when γ is the solution of Eq. (4). The difference between Eqs. (7) and (8) is entirely associated with overlap, and is equivalent to the first line of Eq. (6), despite its odd appearance. The results of Table I when analyzed in terms of overlap and covalent contributions are given in Table II. We see that covalent mixing is responsible for less than 15% of either the level splittings or the important overlap and covalent contributions to the a_{2u}-level energy. If one acknowledges the uncertainty in the numerators (holding the denominators fixed), one discovers that as the combined overlap-plus-covalent contribution to the level splitting decreases, so does the relative role of covalency. Crudely speaking, as the covalent-plus-overlap contribution to Ω varies from 200 to 800 cm^{-1}, the covalent contribution varies from 5 to 20% of the total.

One can also inspect the relative roles of overlap and covalency in the spin and charge densities appropriate to the ground a_{2u} hole state. This is best done by inspecting the ratios γ/S. As the contributions to Ω again vary from 200 to 800 cm^{-1}, this ratio goes from 0.2 to 1.0 for the $2p_\sigma$ electrons and from 0.1 to 0.4 for the $2s$ electrons. Ratios of 0.72 and 0.24 are appropriate to the results of Tables I and II.

In the above, we have held the denominators of Eq. (4) fixed at 100 000 cm^{-1} for $2p$ and 300 000 for $2s$. As already discussed, we suspect that any error, if significant, is in the direction of these numbers being too small. Now, any increase in these denominators for a given level splitting causes the relative role of covalency to drop. This is readily seen by holding $\Delta\epsilon$ (and, by definition, S) of Eq. (7) constant and increasing $[\langle\varphi|h|\varphi\rangle-\langle\chi|h|\chi\rangle]$. The lesser role of covalency in the $2s$, as against the $2p_\sigma$, reflects mostly its larger denominator. The tendency for any correction to cause the denominators to increase implies that our summary of the relative role of covalency represents an upper estimate.

TABLE II. The relative contributions of overlap and covalent mixing to the crystal-field state energies $\Delta\epsilon$ of Table I. All values are in cm^{-1}.

$4f$ hole	Individual overlap contributions $2s$	$2p\sigma$	$2p\pi$	Total overlap energy	Total covalent energy
a_{2u}	241	315	···	556	75
t_{1u}	63	85	···	162	23
t_{2u}	···	···	128	128	26
$a_{2u}-t_{1u}$	splitting			394	

The lesser role of covalency, as evidenced by $\gamma/S<1$, has some severe implications for our understanding of the rare earths in crystalline environments. We are in the regime appropriate to the bottom plot in Fig. 1, where $|\varphi(r)|^2$ terms contribute an *increase in both spin and charge density* at the rare-earth site. Of course, the covalent density is associated with the a_{2u} hole, while overlap effects involve all 13 occupied orbitals. Since the spin is paired off for all but one $4f$ electron, the spin density receives overlap contributions from that one electron while the charge density is affected by all 13 (*plus* the ion's closed shells), causing the latter effect to be appreciably greater. Now, crystalline environments are observed to produce small reductions in the rare-earth spin-dependent hyperfine interactions—an effect opposite that produced above. This implies that a model of a salt, utilizing free-ion $4f$ orbitals, does not yield the sign of the observed change. It further suggests that distortions of the shape of the $4f$ shell due to environment and overlap charge (from *all* the rare-earth ion's shells) play an essential role in spin (and perhaps other) "reduction" effects. There exists, by the way, a growing body of evidence[27] that the same type of distortion plays a significant, though perhaps relatively less important, role in the case of $3d$ transition-metal salts.

IV. COVALENT EFFECTS AND THE 5*p* SHELL

The closed $5p$ shell of the rare earths appears[1–3] to strongly shield the $L=2$ electrostatic crystal-field component and to affect significantly, though less strongly, the other electrostatic terms of higher L, via linear and nonlinear shielding effects. The latter effect

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[26] This may be obtained from Eq. (3.19) of Hubbard *et al.* (Ref. 24).

[27] This was first inferred by inspection of experiment [e.g., see L. Orgel, J. Chem. Phys. **23**, 1824 (1955)], but is currently based on the inability of *a priori* calculations employing undistorted orbitals to reproduce experiment [e.g., see R. E. Watson and A. J. Freeman, Phys. Rev. **134**, A1526 (1964)].

TABLE III. The effect of the $5p$ shell on the covalent-plus-overlap contribution to the energy of the $4f^{13}t_{1u}$ hole state of Tm^{2+} (energies in cm^{-1}): (i) utilizing Bleaney's calculation of $V_4{}^0(r)$; (ii) utilizing the experimental $A_4{}^0$ [an upper estimate of the $V_4{}^0(r)$ field]; (iii) utilizing a characteristic potential matrix element from the $4f$ shell (this result is not appropriate to the $4f^{13}$ configuration).

Choice of $\langle 4f\|h\|5p\rangle$ matrix element (see text)	2s mixing energy	$2p\sigma$ mixing energy	Total mixing energy (including $2p\pi$)	$5p$ effect[a]
(i)	69	119	205	20
(ii)	88	139	244	59
(iii)	587	798	1402	1217

[a] That is, the difference with covalent-plus-overlap energy obtained omitting the $5p$ (as in Table I).

causes one $V_L(r)$ to affect $A_{L'}$ parameters, where $L \neq L'$. Experimentally, there is evidence that, together with the $5s$ shell, it plays a significant role in transferred hyperfine effects—a matter touched on in Sec. II. Given such observations, there arises the obvious question of what role, if any, the $5p$ shell plays in covalent mixing.

Covalent mixing would occur by having a $5p$ electron drop into the $4f$ shell with the $5p$ hole then being involved in covalent mixing with the ligands.[10] For our case of Tm^{2+} surrounded by a cube of F^- ions, we would have

$$4f^{13}5p^6(\mathrm{F}^-)_8{}^{-8} \rightarrow 4f^{14}5p^5(\mathrm{F}^-)_8{}^{-8} \rightarrow 4f^{14}5p^6(\mathrm{F}^-)_8{}^{-7}. \quad (9)$$

Similarly, direct $4f$ covalency involves the process

$$4f^{13}5p^6(\mathrm{F}^-)_8{}^{-8} \rightarrow 4f^{14}5p^6(\mathrm{F}^-)_8{}^{-7}, \quad (10)$$

and $5p$-shell electrostatic shielding arises from

$$4f^{13}5p^6(\mathrm{F}^-)_8{}^{-8} \rightarrow 4f^{13}5p^5\varphi_{nlm}(\mathrm{F}^-)_8{}^{-8} \quad (11)$$

terms, where φ_{nlm} is some excited unoccupied one-electron orbital. Linear shielding occurs when $V_c(\mathbf{r})$ appears linearly in the associated perturbation-energy expressions, and the shielding is, of course, nonlinear when $V_c(\mathbf{r})$ appears in higher order.[2] The $5p$ covalency enters in higher order in perturbation theory than the $4f$-ligand mixing we have been considering, but since it involves the outer $5p$ shell, we will shortly see that it is significant. A p-shell electron is of t_{1u} cubic symmetry, and therefore the mixing will enter only the t_{1u} covalent energies of Tables I and II.

It was decided to estimate the effect of $5p$ mixing by explicitly diagonalizing 3×3 matrices appropriate to the $4f$, $5p$, and ligand χ orbitals and monitoring the increase in energy of the hole of predominantly $4f$ character. Larger matrices, simultaneously involving the various ligand χ's of common cubic symmetry, were not dealt with, as this would have involved overlap and energy matrix elements between the different χ's—a quantitatively significant matter which must be accounted for in any ultimate treatment (with or without $5p$ effects) of the problem. Using the 3×3 results, the energy contributions associated with different χ's were added, as was done in Tables I and II. We will attribute the total additional energy to "$5p$ covalent mixing."

The new matrix elements necessary for the calculation were obtained in the following way. From previous crystal-field shielding experience,[2] we obtain a $\langle 5p|h|5p\rangle - \langle\varphi_{4f}|h|\varphi_{4f}\rangle$ energy difference of $-215(\pm50)\times10^3\ \mathrm{cm}^{-1}$. This was used with Eq. (5), the A B choice of φ and χ matrix elements, and the approximate t_{1u} overlap integrals[28]

$$S_{5p,2p\sigma} = -0.128\,,$$
$$S_{5p,2s} = -0.071\,,$$
$$S_{5p,2p\pi} = 0.028\,,$$

to obtain the $\langle 5p|h|\chi\rangle$ matrix elements. This is exceedingly crude, but adequate for our purposes. The above overlaps are to be compared with their $4f$ counterparts of -0.0188 -0.0120, and 0.0077, respectively. The increased size of the $5p$ integrals simply reflects the more diffuse character of the $5p$ shell. The resulting larger $\langle 5p|h|\chi\rangle$matrix elements contribute towards making the higher-order $5p$ effects significant, but more important, and of more interest, is the $\langle 5p|h|4f\rangle$ matrix element.

A $\langle 5p|h|4f\rangle$ matrix element may arise from two sources. Firstly, the electrostatic crystal potential components of $Y_2{}^0$ and $Y_4{}^0$ symmetry will connect orbitals of like t_{1u} symmetry. Secondly, the $4f^n$ shell may provide a potential connecting the $4f^n5p^6$ and $4f^{n+1}5p^5$ configurations. Such matrix elements tend to be significantly stronger than those arising from the crystal field. The free-ion Hamiltonian (without spin-orbit coupling) connects states of common L, S, M_L, and M_S (otherwise J and M_J) and, therefore, *cannot* produce $\langle 4f|h|5p\rangle$ matrix elements for crystal states arising from the ground multiplets of the $4f^7$, $4f^{12}$, and $4f^{13}$ configurations where there are no $4f^{n+1}5p^5$ states with common quantum numbers. This source of mixing is therefore not available to us for Tm^{2+}. It will tend to be most important for the less-than-half-filled f-shell ions where there are numerous intermediate states of appropriate symmetry (e.g., see Table I of Ref. 2). This mixing, incidentally, induces hole character in the $5p$ shell which is characteristic of the free ion.

Results are reported for three choices of $\langle 4f|h|5p\rangle$ in Table III, where attention was concentrated on the important $2s$ and $2p_\sigma$ terms. The choices are:

(i) a $\langle 5p|h|4f\rangle$ matrix element arising from the $V_4{}^0$ field computed by Bleaney[11]—this yields the value $283\ \mathrm{cm}^{-1}$;

(ii) an upper estimate of $V_4{}^0$ field mixing utilizing the experimental $\langle V_4{}^0\rangle_{4f4f}$ obtained by Bleaney, yielding a value of $1133\ \mathrm{cm}^{-1}$. Both this and (i) involve an off-diagonal $\langle r^4\rangle_{4f5p}$ integral ($=4.0$ a.u.).

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[28] Obtained employing our (Ref. 12) Hartree-Fock wave functions.

(iii) In this case, a matrix element equal to 10 000 cm^{-1}, characteristic of those arising from a $4f^n$-shell potential, V_{4f}, is employed. This is not appropriate to the case of Tm^{2+}, and is typical[2] of the lighter ions. This result was obtained to give some indication of what might be expected from this source for these lighter ions.

The results for cases (i) and (ii) indicate that $5p$ contributions to the t_{1u} energy level are as important as the direct $4f$ covalent term, or more so, when the external V_4^0 crystal field is the source of the $\langle 4f|h|5p\rangle$ matrix element. Moreover, the covalent energy contributions are of experimental significance although much smaller than the overlap terms.

The case (iii) result has violent implications, even if it represents an overestimate of the effect for the $4f^n$ configurations where $\langle 4f|V_{4f}|5p\rangle$ matrix elements occur. Even if reduced, the result suggests that $5p$ covalent terms may make crystal-field energy-level contributions which are of the order of characteristic level splittings.

The variation in results from (i) to (iii) reflects the varying weight of $5p$-shell hole character, where a $5p$ electron has fallen into the $4f$ shell. The resulting energy then, in turn, reflects both overlap and covalent effects of the opened $5p$ shell with the environment. Calling all this "5p covalency" is a somewhat loose but convenient title—overlap plus a small component of the previously discussed[2] $5p$ shielding being included.

V. DISCUSSION

In this paper, we have inspected in some detail Tm^{2+} in CaF^2, the system studied by Bleaney[11] and Axe and Burns.[6] Before making any concluding comments, we should also make note of the PrCl_3 system. Here, the Pr^{3+} is in a site of less than cubic symmetry involving V_2^0, V_4^0, V_6^0, and V_6^6 electrostatic terms. Hutchings and Ray have performed[29,30] lattice sums which converge particularly poorly for the V_2^0 potential. Their results, taken with Hartree-Fock $4f$ functions and ignoring shielding, overlap, and covalency, yield matrix elements which are an order of magnitude too large for $L=2$, in rough agreement for $L=4$, and an order of magnitude too small for $L=6$ when compared with experiment.[31] Computations[1–3] suggest a V_2^0 shielding of about 70%, leading to a theoretical electrostatic $L=2$ matrix element which appears too large, but which agrees with experiment within the uncertainties of the calculations. While the $L=4$ term agrees with experiment, the $L=6$ disagreement is reminiscent of what Bleaney obtained for Tm^{2+} in CaF_2.

Recently, Ellis and Newman[9] have reported results for PrCl_3 which give computed V_L^M parameters in extraordinary agreement with experiment. The agreement is better than anyone has yet achieved for the single parameter $10Dq$ entering the cubic iron-series crystal-field problem. Their treatment differs from the purely electrostatic field approach in two ways. Firstly, they omit all but near-neighbor contributions to the electrostatic potential, thus leaving out terms which were important in the calculation of Hutchings and Ray. Shielding arguments[32] can be made for a reduction in the omitted terms, but a complete, or almost complete, cancellation would be surprising. Secondly, they treated the effect of the near neighbors in detail, including overlap, but omitting covalent mixing. We are not in sympathy with this, because, while overlap may be more important, we expect the $4f$ covalent terms to be quantitatively significant. These terms will almost inevitably produce poorer agreement with experiment. We should note that an accurate estimate of the overlap terms involves matrix elements which can readily yield at least a poor estimate of the $4f$ covalent mixing and its associated energy.

Of course, we also wonder about the role of the $5p$ shell. In our view, PrCl_3 would be an excellent example of a case where nonlinear shielding effects[2] might contribute spuriously to the $L=6$ experimental parameters. We also expect $5p$ covalency to be far more important here than it was for Tm^{2+}. The key $\langle 5p|h|4f\rangle$ matrix element(s) will involve the potential arising from the $4f$ shell as well as the V_2^0 and V_4^0 electrostatic field contributions. The V_2^0 potential which enters this matrix element is expected to be far less strongly shielded than it is when viewed purely by the $4f$ shell, i.e., in $\langle 4f|V_2^0|4f\rangle$. The above observations make it difficult to take the numerical agreement between computation and experiment seriously, but this does not take away the real importance of the result of Ellis and Newman. Together with the results obtained for Tm^{2+} in CaF_2, it suggests quantitatively that overlap and covalency are of extreme experimental significance for the high L crystal-field parameters appropriate to both cubic- and lower-symmetry environments. The situation is less clear for the noncubic $L=2$ component. It is perhaps most realistic to say that overlap and covalency make an observable contribution here, but that the behavior of this term is almost completely determined by electrostatic effects (of course, with their associated shielding terms).

Since we have not taken one set of computed numbers seriously, we must not err by inspecting an even more crudely based set for quantitative detail. Such detail has not been our purpose. We have attempted to indi-

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[29] M. T. Hutchings and D. K. Ray, Proc. Phys. Soc. (London) **81**, 663 (1963).

[30] See also A. K. Raychaudhuri and D. K. Ray, Proc. Phys. Soc. (London) **86**, 891 (1965).

[31] J. S. Margolis, J. Chem. Phys. **35**, 1367 (1961).

[32] A number of recent iron-series crystal-field studies have also concentrated on the metal ion and its nearest neighbors, but for a very different reason which does not involve shielding arguments. They have dealt with KNiF_3 and KMnF_3 for which, by accident of the crystal structure, more distant neighbors contribute an almost constant potential throughout the whole region of a *3d* metal ion and its near-neighbor F^- ions [e.g., see S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963)].

cate why overlap and covalent mixing are separately of interest, and then have inspected their relative roles. We believe the dominance of overlap is not simply characteristic of the calculated results, but will be seen in the more refined work of the future. We have also been interested in the role of the $5p$ shell, and, in our opinion, the results of Sec. IV strongly indicate that this shell must be included in any full treatment of rare-earth overlap and covalency. Finally, it was seen that the experimentally observed spin effects at metal and ligand sites are of opposite sign to the spin terms arising directly from $4f$-shell covalency and overlap. The outer $5s$ and $5p$ shells appear [20,21] to play a dominant role in ligand spin behavior, while distortions of $4f$ orbital shape appear essential to an understanding of the magnetic behavior at the metal site. These (small) distortions are due, in large part, to environmental and overlap charge effects.

Our traditional understanding of the rare earths is based on the isolation of the open $4f$ shell in the interior of the ion. This is true not because the $4f$ shell is small (its radial extent is roughly that of an iron-series 3d shell), but because the rare earths are large ions owing to their outer diffuse $5s$ and $5p$ shells. Overlap and covalent effects are small because the $4f$ electrons are isolated by these outer shells, but the sheer size of the ions keeps neighbors relatively far away, thereby making electrostatic potential terms *also* small.[33] Overlap and covalency then become *relatively* significant. Once dealing with small effects, one must worry about others, in particular those arising from the intervening $5s$ and $5p$ shells. We have attempted to document evidence to the effect that these shells introduce essential quantitatively significant complications to the problem of the rare earths.

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APPENDIX

The set of $\Delta\epsilon$'s of Table I allows us to make some observations concerning the accuracy and importance of the approximations employed. As we have already implied, the essential features of the results are largely independent of the Wolfsberg-Helmholz approximation. The calculation can be viewed as taking place in three stages. First, the energy denominators are determined, as was discussed in Sec. III. Second, results are obtained, by varying the numerator, for one of the important covalent terms, e.g., the $2p_\sigma$ mixing in the a_{2u} ground state. This is obtained *independently* of the Wolfsberg-Helmholz approximation, and its success and significance rest, in the absence of detailed calculation, on our judgment of the appropriateness of the chosen numerator—a judgment which will shortly be made. Third, having determined one mixing term, the version of the Wolfsberg-Helmholz approximation given in Eq. (5) is then employed to obtain the others. Table I suggests that overlap plus mixing energy for the a_{2u} level is far more important than for the t_{1u} and t_{2u}; to this extent, we believe the Wolfsberg-Helmholz approximation. This observation lets us concentrate on the a_{2u} level when determining the essentials of the role played by covalency and overlap. This is a convenient choice, since the a_{2u} level is the ground state, and these a_{2u} terms thus affect other spin- and charge-dependent observables. (We also inspect the t_{1u} and t_{2u} contributions, but a greater uncertainty must be attached to their results.) While experience with iron-series complexes suggests that one can go via Eq. (5) from $2p_\sigma$ to the $2s\langle\varphi|h|\chi\rangle$ matrix element with some certainty,[34] one best judges the results by inspecting the matrix elements employed. Now, it is the numerator of Eq. (4), rather[35] than the $\langle\varphi|h|\chi\rangle$, which particularly interests us here. For lack of knowledge of the rare earths, we employ the bad approximation of multiplying the $2s$ and $2p_\sigma$ numerators, as obtained in various[14,23] $KNiF_3$ calculations, by the overlap integral ratio $S_{4f,a_{2u}}/S_{sd}$. This predicts $2s(a_{2u})$ and $2p_\sigma(a_{2u})$ numerators equal to 4.7–10 and $5.3\text{–}9.9\times10^3$ cm^{-1}, respectively. These values are to be compared with the values 8.7 and 6.2×10^3 cm^{-1} actually employed when obtaining the a_{2u} results of Table I. In other words, the present results rely on numerators which appear to be of reasonable magnitude with respect to one another and with the naive extrapolation of our $KNiF_3$ experience.

Given the above observations, we believe that the AB results of Table I provide strong evidence of the important role of covalent and overlap effects in the rare-earth crystal-field level scheme. It is this view, rather than any detailed correctness of the numerators in Eq. (4), which is essential to the observations made in Secs. III and IV. We might note that in the process of obtaining their results, AB did employ the Wolfsberg-Helmholz approximation, and the adequacy of their results reflects the fact that the Wolfsberg-Helmholz approximation can be useful when cleverly applied. From our experience above, we would suggest an extension of the approximation to a treatment of the whole numerator of an equation such as (4) rather than just $\langle\varphi|h|\chi\rangle$.

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[33] G. Burns, J. Chem. Phys. **42**, 377 (1965).

[34] Obtaining the $2p\pi$, in turn, seems less reliable, and we suspect that the two close-lying t_{1u} and t_{2u} levels (which rely entirely on π mixing) may be moved significantly (as compared with their computed splitting) closer *or* farther apart with a more refined treatment of the numerators.

[35] Actually, the $\langle\varphi|h|\chi\rangle$ matrix elements are in as good agreement, as are the numerators, with what might be anticipated from $KNiF_3$ experience.