[28] For an excellent review of the various approaches to the crystal-field formalism and the point-charge model see M. T. Hutchings, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 227.

[29] R. J. Birgeneau, J. Als-Nielsen, and E. Bucher (private communication).

[30] The discussion of these points, and a number of others in this paper, has benefited from extensive discussions with R. J. Birgeneau before, during, and after the neutron experiments of Refs. 14 and 15.

[31] A letter by S. R. P. Smith (to appear in J. Phys. C.) was received subsequent to submission of the present paper. This letter reports calculations giving a temperature dependence of the mode energies in the singlet-triplet case that is fundamentally different from the behavior for the singlet-singlet case. In particular, there is no soft-mode behavior. It is not obvious that even such singlet-triplet behavior would explain the experimental lack of temperature dependence for the exciton dispersion. Calculations along similar lines by Y. Y. Hsieh [(unpublished), also received subsequent to submission of the present paper] should help in verifying the correctness of Smith's results, and in judging the relevance to the experimental situation.

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Electronic Interactions in the $4f^6\,5d$ Configuration of Eu^{2+} in Crystals

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The electronic coupling in the $4f^6 5d$ configuration of Eu^{2+} in crystals has been studied. The complete f-d Coulomb matrix within $f^6\,({}^7F_J)\,{}^2e_g$ has been obtained and the Hamiltonian diagonalized for various values of the spin-orbit and Coulomb parameters. The magneto-optical spectra in the first band and the g values of the 4130-Å resonance line of $CaF_2:Eu^{2+}$ are quite well explained by using f-d Coulomb interaction about one-half that of the free ion. Even this reduced interaction is by no means negligible and it is shown qualitatively that the same Coulomb f-d parameters are appropriate for EuF_2 as well as $CaF_2:Eu^{2+}$. It is argued that the reduction from the free-ion case is a physically significant result caused by the crystal environment of the ion, and is not merely the result of some neglected configuration interactions.

I. INTRODUCTION

The optical-absorption, emission, and magneto-optical spectra of $CaF_2:Eu^{2+}$ and EuF_2 are rich in detail and have been the subject of numerous studies.[1-8] The absorption spectra contain two bands in the uv, and at low temperatures the lower energy band has considerable structure and strong magneto-optic dichroism.[4-6] The bands are due to allowed electric dipole transitions from the ground state of Eu^{2+}, $4f^7\,({}^8S_{7/2})$, to states of the $4f^6 5d$ configuration. A narrow intense resonance line at 4130 Å is observed in both emission and absorption[1] at 4 °K in $CaF_2:Eu^{2+}$. The excited state of this line is a fourfold degenerate level and is the lowest-energy component state of the $4f^6 5d$ configuration.[3]

The two bands have been attributed to the cubic crystal field splitting of the $5d$ electron; however, the Coulomb interaction between $5d$ and the $4f^n$ core is not small and this complicates the interpretation of the $4f^n 5d$ band states. The $4f^n 5d$ configurations have not been extensively studied, particularly in crystals. Several approximate calculations on $4f^6 5d$ have been made for Eu^{2+} in order to explain variously the structure in the first band,[8-10] the Faraday effect[4] and magnetic circular dichroism (MCD), and the Zeeman effect of the resonance line.[7] The coupling schemes used have ranged all the way from pure Russell-Saunders zero $5d$ crystal field splitting to strong $5d$ crystal field weak f-d Coulomb interaction. In fact, intermediate coupling is indicated by consideration of various typical energy splittings of the lanthanides: (a) $5d$ crystal fields of 10 000–15 000 cm^{-1}, (b) $4f\,5d$ term splittings of 2000–5000 cm^{-1}, (c) spin-orbit splittings of 2000–5000 cm^{-1}.

We shall show that the spectra and the g values of the excited state of the resonance line are well accounted for by intermediate coupling within $5d$ crystal field configurations. The configurations are formed by coupling the crystal field ${}^2e_g$ and ${}^2t_{2g}$ orbitals of $5d$ to the ${}^7F$ ground term of the f^6 core. The full matrix of $f^6\,({}^7F_J)\,{}^2e_g$, including spin-orbit and f-d Coulomb interaction, was diagonalized for various values of the parameters. The effect of configuration interaction with $f^6\,({}^7F)^2t_{2g}$ was adequately treated by perturbation theory. We find that the experimental $CaF_2:Eu^{2+}$ data are best explained by using the Coulomb f-d parameters $F_2 = 65$ cm^{-1} and $G_1 = 110$ cm^{-1}, which are approximately one-half of the free-ion values. This finding agrees with the conclusion of Yanase and Kasuya,[9] who interpreted the EuF_2 spectra by the application of perturbation theory to several different coupling schemes.

The *f-d* Coulomb interaction is not as small as we claimed earlier[6] on the basis of a preliminary analysis of the calculations. There is a significant reduction from the free-ion values, however, and we think that this is not merely the result of neglecting other Eu^{2+} electronic configurations, but results from an additional screening of the 5*d* charge distribution by the crystal environment.

II. ELECTRONIC STRUCTURE AND CALCULATIONS

The ground state of Eu^{2+} is $4f^7\,({}^8S_{7/2})$ and allowed electric dipole transitions to states of $4f^6 5d$ result in the strong band system beginning near 34 500 cm^{-1} in the free ion and near 24 000 cm^{-1} in crystals. CaF_2 and EuF_2 both have the fluorite structure and Eu^{2+} in either crystal is at a site having cubic O_h symmetry and is surrounded by a cube outlined by eight F^- ions. The 5*d* orbital is split by the crystal field into t_{2g} and e_g orbitals, with the latter lying lower in this case. The lowest energy band is assumed to be due to states resulting from the coupling of ${}^2e_g$ to the lowest term of the $4f^6$ core, ${}^7F$. The next band is composed primarily of $4f^6\,({}^7F){}^2t_{2g}$ and the band separation gives the not unreasonable estimate of $Dq \sim 1500$ cm^{-1} for the crystal field parameter of 5*d*. The excited configuration could be appreciably overlapped by $4f^6\,({}^5D){}^2e_g$ since the ${}^5D$-${}^7F$ term splitting is about 18 000 cm^{-1} in Eu^{3+}.[11]

The complete *f-d* Coulomb and spin-orbit Hamiltonian matrices were constructed for the $4f^6\,({}^7F){}^2e_g$ configuration. The crystal field effects within the ${}^7F$ core term were neglected; they are certainly quite small compared with the *f-d* Coulomb and core spin-orbit interactions. The Coulomb matrix elements were calculated in a basis consisting of products of $|\,f^6SLM_SM_L)$ and $|\,dm_sm_l)$, where $S = L = 3$. The core ${}^7F$ term is equivalent to one hole in a half-filled shell; therefore, the problem may be handled in many respects like a two-particle system. The calculations were done by the methods of Condon and Shortley,[12] with the added complication of having to perform spin integrations for $|\,3M_S)\,|\,\frac{1}{2}m_s)$ for the G_k exchange matrix elements. The only nonzero spin-orbit matrix elements are within the core ${}^7F$ term and these may easily be written down in the Russell-Saunders basis $|\,SLJM)$. Standard vector coupling[13] and symmetry coupling[14] coefficients for the O_h group were used to transform the matrices into a symmetry species basis. The principal genealogical character of the final symmetry basis is the core-term $J\Gamma$ quantum numbers. The original 196×196 matrix factors into three matrices which are to be diagonalized: a 16×16 $E_{1/2}$, a 16×16 $E_{5/2}$, and a 33×33 G matrix. Both E species are doubly degenerate and G is fourfold degenerate.

The matrix transformations and the eigenvalue calculations were carried out on an RCA Spectra 70 computer. A FORTRAN program was written in order to calculate the relative circular and π polarization intensities of transitions from the lowest-energy Zeeman component of the ${}^8S_{7/2}$ ground state, $M_J = -\frac{7}{2}$, to each calculated eigenstate. The diagonal g values of each eigenstate were also calculated.

The energy levels were calculated for a range of parameters F_2, G_1, and λ. We expect that λ lies in the range 220–250 cm^{-1}, typical of the ${}^7F$ term of europium.[11] In fact, we found that the results were not strongly dependent on λ in this range, but we did find that the best fit to the spectrum was obtained by use of the empirical non-Russell-Saunders J spacing of ${}^7F$ (*vide infra*). Although F_2 and G_1 were varied, we fixed F_4/F_2, G_3/G_1, and G_5/G_1 at the free-ion ratios. We really have insufficient data to allow all five Coulomb parameters to freely vary, and no especially strong dependence was found when the ratios were varied by about 10%. In any event, the low-order multipole terms F_2 and G_1 are the predominant ones. The direct (F_k) and exchange (G_k) parameters have not been determined from the free-ion spectrum; therefore, we estimated them by smooth interpolation between the well-determined values[15] of Ce^{2+}, Pr^{2+}, Tm^{2+}, and Yb^{2+}. We found $F_2 = 185$, $F_4 = 15$, $G_1 = 200$, $G_3 = 25$, and $G_5 = 4.5$, all in cm^{-1}.

The level scheme for the G states as a function of G_1 (using the free-ion ratios for the other parameters and $\lambda = 250$ cm^{-1}) is shown in Fig. 1. For the sake of clarity, the E states are not included in the figure, but they cluster within the groups of G states. A fourfold degenerate G state is lowest throughout the entire range of parameters used, $0 < F_2,\ G_1 < 250$ cm^{-1}. It is clear from Fig. 1 that the energy levels split into two groups, the upper group having a flat slope and the lower group having a large negative slope. These two groups may be classified by the total spin, obtained by coupling the spin of the d electron to the $S = 3$ spin of the F core term. The upper group has $S = \frac{5}{2}$ and the lower group has $S = \frac{7}{2}$. The classification becomes more exact the greater the *f-d* Coulomb interaction; however, the states very quickly develop the total spin character. Transitions from the ground state are spin allowed to $S = \frac{7}{2}$ states, and as a result a lower-energy group of states about 6000 cm^{-1} wide contains practically all the intensity throughout the entire range of parameters studied. We consider a detailed comparison of the calculated resonance-state g values and polarized spectra with the experimental data in Sec. III.

III. COMPARISON OF CALCULATIONS WITH EXPERIMENTAL DATA

A. Zeeman Splitting of Resonance Line

The excited state of the 4130-Å resonance line has been assigned as a G representation of O_h, and the g values were determined from Zeeman spectra by two different groups.[3,5] The g values were also determined recently by an optical-microwave double-resonance technique[7] and there are differences of several percent between the reported values. We have measured Zeeman spectra in absorption by using flash spectroscopy and pulsed magnetic fields up to 200 kOe. The g values obtained from these data are in good agreement with those obtained by using only the strongest lines of the data published by Kisliuk *et al.*,[5] and the averaged results are $g_a = 2.21 \pm 0.02$ and $g_b = 1.52 \pm 0.02$. These g values are defined as the roots of the Zeeman energy equation, $E/(\mu_B H) = \pm g_a$ and $\pm g_b$, for the G state in O_h with the magnetic field along a fourfold axis. Expressed in terms of the parameters δ and γ,[5,7] we find $\delta^2 = 4.59$ and $\gamma^2 = 0.118$.

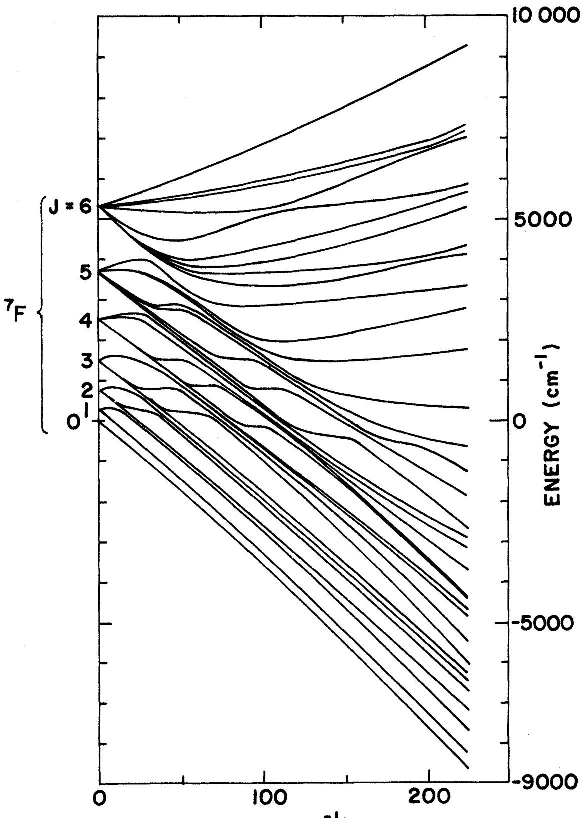

FIG. 1. Energies of the G states of $4f^6\,(^7F_J)^2e_g$ as a function of the exchange parameter G_1. The other Coulomb parameters are held fixed at the free-ion ratios to G_1 (see text) and $\lambda(^7F) = 250$ cm^{-1}.

Plots of the lowest two Zeeman energy levels for the magnetic field along a fourfold axis as functions of the Coulomb parameters F_2 and G_1 are shown in Fig. 2. The pair of Zeeman energies is shown for three different ratios $F_2/G_1 = \rho$ as functions of $(F_2^2 + G_1^2)^{1/2}$. The curves for different values of ρ represent cuts in the two-dimensional energy surface of F_2 and G_1. The higher moments were held fixed at the free-ion ratios of F_4/F_2, G_3/G_1, and G_5/G_1 and the plots in Fig. 2 are for $\lambda = 250$ cm^{-1}.

The ordering of the calculated Zeeman levels is in agreement with observations[3,5]; the magnetic quantum numbers in order of increasing energy are $\frac{3}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, $-\frac{3}{2}$. The quantum numbers are the values of the operator S_z for an effective spin $S = \frac{3}{2}$ representation of the cubic G state. The experimental g values are shown as horizontal lines on Fig. 2, and it is clear that a good fit between calculated and observed values cannot be obtained anywhere in the neighborhood of the free-ion values, $\rho = 0.93$ and $G_1 = 200$ cm^{-1}. A number of possible solutions exist for very small Coulomb parameters (F_2 and $G_1 \leqslant 50$ cm^{-1}), which represent a small perturbation on the spin-orbit J levels of the core term. The calculated spectra do not closely resemble the observed ones, so we reject these parameters as solutions.

A reasonable fit to both the g values and the observed spectra is obtained for $F_2 \sim 60$ cm^{-1} and $G_1 \sim 100$ cm^{-1}. The effects of configuration interaction were estimated by using perturbation-theory approximations. We assume that the second band in the uv is made up primarily of the states of $f^6\,(^7F_J)^2t_{2g}$. A few of the f-d Coulomb matrix elements were calculated for the $J = 0$, 1 states and they were found to be less than $0.3G_1$. This interaction gives very small corrections to the energies and the g values. The spin-orbit interaction between ^2e_g and $^2t_{2g}$ is larger, and in first-order perturbation gives a correction to the Zeeman energy of the $\mu = \pm\frac{3}{2}$ components of the G states. We have not diagonalized the matrix of $^7F_J^2t_{2g}$ so we can only roughly estimate the correction. The matrix elements of $(l_z + 2s_z)$ are diagonal with respect to J and the correction to the g factor of $\mu = \pm\frac{3}{2}$ is $\pm 4\zeta/(10Dq)$. Taking the excited configuration as completely degenerate with $10\,Dq = 15\,000$ cm^{-1} and using $\zeta_{5d} = 1000$ cm^{-1},[16] we obtain an upper estimate to the correction of 0.25, and the sign is such as to reduce the magnitude of g_a.

B. Magnetic Circular and Linear Dichroism (MCD and MLD)

The low-temperature MCD and MLD are rich in structure and prompted some of the earliest speculations[4,5] on the nature of the coupling in the f^6d

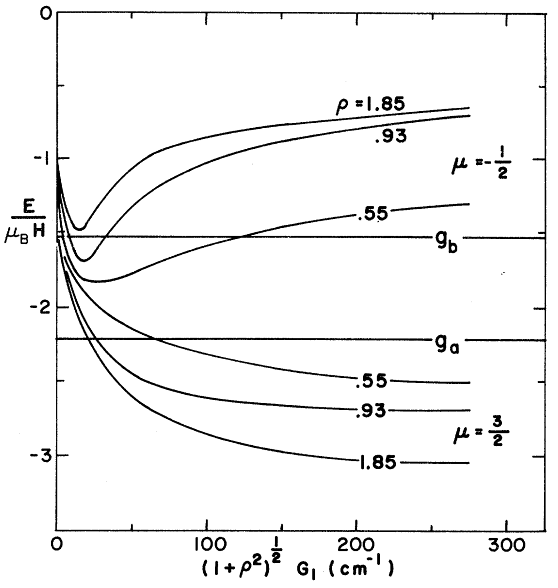

FIG. 2. Zeeman energies of the lowest G state of $4f^6\,({}^7F_J)^2e_g$ as a function of the f-d Coulomb interaction. As the pattern is symmetric about zero energy, only the lowest pair of Zeeman levels, $\mu=\frac{3}{2}, -\frac{1}{2}$, are shown. The energies are given for three different ratios $F_2/G_1 = \rho$.

configuration. The polarized relative intensities of transitions from the ground-state ${}^8S_{7/2}$ Zeeman level $M_J = -\frac{7}{2}$ to each calculated eigenstate of ${}^7F_J^2e_g$ were calculated along with the eigenvalues. These calculated spectra were compared with the low-temperature high-magnetic-field MCD and MLD spectra[6] of CaF_2: Eu^{2+}. A good detailed fit is not possible for any region of the Coulomb parameters, low, intermediate, or free ion, but the spectra calculated for intermediate cases most closely resemble the observed spectra. We shall not show spectra for each of the regimes, but will briefly describe the most salient features. The resonance line appears as a strong right circularly polarized (RCP) line in all cases, having very little left circularly polarized (LCP) or π intensity. In the case of small Coulomb interaction, the RCP intensities fall off rapidly with increasing energy, the LCP intensity is contained mostly in the high-energy components ($J = 5, 6$), and the π-polarized intensity is grouped toward the middle. The spectrum calculated using the free-ion values has a much more uniform spread of energy levels. There are several intense RCP lines 1500–2000 cm^{-1} above the resonance line and the π-polarized lines are more uniformly spread over the band.

We found that a much better match to the calculated spectra was obtained by using intermediate Coulomb parameters and the empirical spin-orbit J spacing[11] of ${}^7F$ found for Eu^{3+}. The observed spacing markedly departs from the Landé interval of pure Russell-Saunders coupling and is the result of strong spin-orbit interaction with ${}^5D$, which lies some 16 000–20 000 cm^{-1} above ${}^7F$. We expect that the spin-orbit interaction within the core $4f^6$ terms is relatively unaffected by coupling to $5d$, and using the empirical J spacing of Eu^{3+} partially takes into account the configuration interaction with ${}^5D_J^2e_g$. By using the approximations for both the configuration interactions which we discussed, we find that the polarized spectra and the resonance-line g values are best fit by the Coulomb parameters $F_2 = 65$ cm^{-1} and $G_1 = 110$ cm^{-1}, having fixed F_4/F_2, G_3/G_1, and G_5/G_1 at the free-ion ratios. The calculated g values of the excited state of the resonance line are $g_a = 2.20$ and $g_b = 1.51$. The calculated spectra, together with the observed low-temperature polarized spectra, are shown in Figs. 3 and 4.

It is quite difficult to interpret the higher-energy structure in the band because of the large number of electronic states and the associated and overlapping vibronic levels. The 4130-Å resonance line has a sideband structure extending to 400 cm^{-1} in absorption which is very similar to that observed to accompany the 6905-Å (L_3)[17] resonance line of CaF_2: Sm^{2+}. We know that for both Sm^{2+} and Eu^{2+} the excited state is the lowest $f^{n-1}d$ state to which transitions are allowed, so the vi-

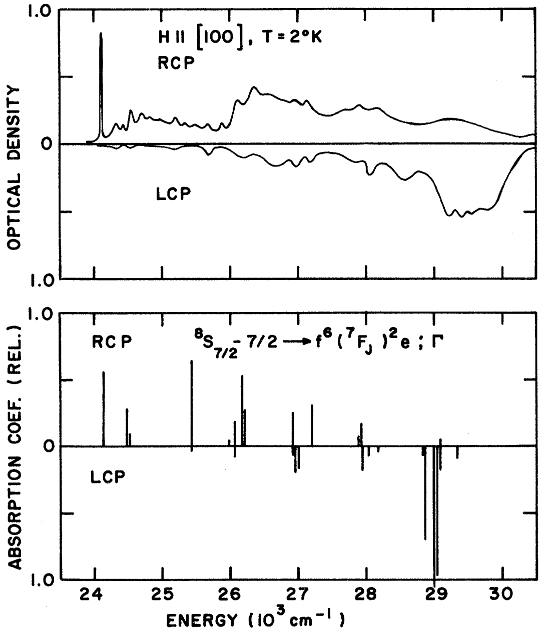

FIG. 3. MCD spectra for the magnetic field along a fourfold axis. The measured spectra for $T = 2$ °K and $H = 29$ kOe are at the top. The calculated relative absorption intensity pattern for the parameters given in the text is at the bottom.

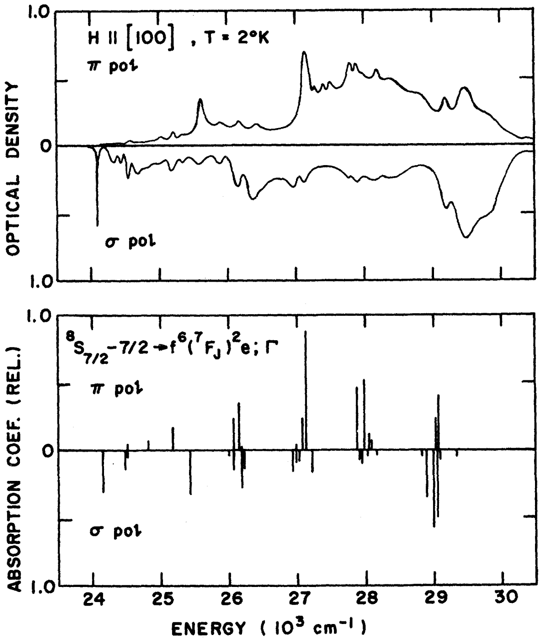

FIG. 4. Polarized linear Zeeman spectrum for H along a fourfold axis. The measured spectra for $T = 2$ °K and $H = 29$ kOe are at the top, and the calculated relative absorption intensity pattern for the parameters given in the text is at the bottom.

bronic structure is expected to be similar. At higher energy the band becomes a complicated composite owing to the similar values of electronic and vibrational energy spacings. We think that the vibronic coupling is generally weak, but not insignificant. This is supported by Chases's findings that certain aspects of the anisotropy in line shape of the excited resonance state were consistent with a dynamic Jahn-Teller distortion of ^2e_g.[7]

The "staircase" spectrum[8] of EuF_2 can be qualitatively accounted for by the intermediate Coulomb parameters, as can be seen by examination of Fig. 1. The energy levels are grouped into six bands of $S = \frac{7}{2}$ states for G_1 near 100 cm^{-1}, whereas the states are more uniformly spread near the free-ion value. Of course, six bands are also seen for small G_1, but the calculated polarized intensity distribution does not resemble the observed spectrum as well as that for $G_1 \sim 100$ cm^{-1}. Similar considerations are primarily the basis on which Yanase and Kasuya[9] deduced intermediate coupling. They used a generalized Hamiltonian for the Coulomb interaction and had four parameters appropriate for $S = \frac{7}{2}$ terms. If we assume no configuration interaction and take $G_5/G_1 = 0.02$, the f-d parameters they obtain are $F_2 = 65$ cm^{-1}, $F_4 = 7$ cm^{-1}, $G_1 = 95$ cm^{-1}, and $G_3 = 13$ cm^{-1}, which are in rather good agreement with the parameters obtained in this study.

IV. SUMMARY AND CONCLUSIONS

We have shown that the magneto-optic spectra and the Zeeman splittings of the resonance line are well accounted for by a strong crystal field split $5d$ electron having a Coulomb interaction with the $4f^6$ core about one-half the free-ion value. The effects of configuration interaction have been examined by perturbation theory and approximate corrections have been obtained. The apparent reduction in the f-d Coulomb interaction may be the result of neglected configuration interactions peculiar to Eu^{2+} or may result from the effect of the crystal environment on the $4f^6\,5d$ configuration. We cannot rule out the former with complete assurance, since the free-ion parameters have not been directly determined from spectra, and we relied on interpolation between data for other lanthanides to obtain them. Nevertheless, we think that the free-ion values quoted are within 10% of the correct ones, since usually there are not abrupt jumps as a function of atomic number, unless half-filled shells are involved. The interaction of $5d$ with crystal bonding electrons is a possible source of reduction of the $4f$-$5d$ interaction. The $5d$ function is less well shielded than $4f$ and the former has a maximum in its probability distribution near 1 Å. The vibronic coupling with the $4f$ electrons is certainly different from that with the crystal field orbitals of $5d$. The sideband structure of the resonance line of $CaF_2:Eu^{2+}$ differs quite a lot between emission and absorption. The vibronic spectrum seen in emission has been correlated with the lattice modes of CaF_2.[18] On the other hand, it has been found that the Jahn-Teller effect is manifest in the lowest state of the excited $4f^6(^7F_J)^2e_g$ configuration.[7] The coupling to a particular set of phonons is dictated by the symmetry requirements and the interaction with the ^2e_g orbital.

If the reduced Coulomb parameters do indeed reflect a real physical reduction of the f-d interaction owing to the lanthanide ion being in a crystal environment, we should inquire why the reduction has not been found elsewhere. We know of only two detailed studies of other rare-earth $4f^{n-1}\,5d$ configurations, $CaF_2:Ce^{2+}$[19] and $SrCl_2:Yb^{2+}$,[20] and in both cases the Coulomb parameters were taken as fixed and the best value of Dq for the d electron was sought. In neither case is the resulting analysis fully satisfactory. The ground state of Ce^{2+} is fd and the excited states seen in the spectrum are f^2. No other states of fd were observed and the only directly observable effect of the f-d Coulomb interaction is on the ground-state g value, whose calculated value does not agree well with the experimental one. The visible bands of $SrCl_2:Yb^{2+}$ are due to the excited configuration $f^{13}d$ and the calculated spectrum is certainly in reasonable agreement with the observed one.[20] It seems not improbable from an examination of the published plot of the energy levels as a function of Dq [20] and from observations made in this work that a good fit to the observed energies could be made by using reduced electrostatic f-d parameters and a larger value of Dq. Of course, this is mere speculation and intensity and eigenvalue calculations are both needed. It would certainly be instructive to reexamine these two cases, particularly since they are much simpler two-particle problems and complete diagonalization of the Hamiltonian, including all electronic interactions, can be done.

Recent calculations on the MCD of $\mathrm{CaF}_2:\mathrm{Tm}^{2+}$ have also supported the model of coupling the crystal field split $5d$ orbitals to the f^{n-1} core terms.[21] It may be possible to account for the observed bandwidths by including the Coulomb f-d interaction. It is certainly of interest to know how the $5d$ electron is affected by, and interacts with, the other electrons in the crystal, and we believe that future studies along the lines discussed will shed much light on the problem.

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Pressure Dependence of Acoustic-Mode–Soft-Optic-Mode Interactions in Ferroelectric BaTiO_3[†]

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Measurements of the pressure dependence of the Raman and Brillouin spectra of tetragonal BaTiO_3 at 296 K have shown that the frequency separation between the two branches of the coupled acoustic-mode–soft-optic-mode system increases and the mode coupling decreases with increasing pressure. The results yield independent quantitative support for the model recently discussed by Fleury and Lazay and demonstrate the utility of pressure studies as a unique means of investigating coupled-mode interactions.

We report the first measurements of the effect of hydrostatic pressure on the coupled acoustic-optic modes in ferroelectric BaTiO_3. These experiments provide a direct measurement of the pressure dependence of the acoustic- and optic-mode frequencies and dampings and yield the pressure dependence of the coupling between the soft TO mode and the acoustic mode of the same symmetry. The results quantitatively support the harmonically coupled acoustic-mode–optic-mode description for this important ferroelectric. In addition, these results demonstrate the importance of pressure as a general variable for investigating coupled-mode interactions of this type.