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Energy Levels of Ce^{2+} in CaF_2†

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The absorption spectrum of cerium-doped CaF_2 has been observed at several temperatures. When the cerium is reduced to the divalent state at room temperature, the absorption spectrum of Ce^{2+} is found to be unstable against thermal decay or bleaching by visible light; furthermore, this spectrum is found to comprise one state of a photochromic system. The absorption spectrum of CaF_2:Ce^{2+} at low temperature is seen to consist of transitions to levels of the $4f^2$ configuration. This identification is confirmed by a conventional crystal-field calculation of the energy levels and wave functions of the $4f5d$ and $4f^2$ electronic configurations of Ce^{2+} occupying a cubic site in CaF_2, which shows that while the ground state of the free divalent cerium ion is a level of the $4f^2$ configuration, the ground state of this ion in a sufficiently strong crystal field ($Dq > 1000$ cm^{-1}) is a T_2 level of the $4f5d$ configuration. Observations of the Zeeman effect have been made which confirm the T_2 character of the ground state. The energies and relative intensities of the allowed transitions between this ground state and the levels of the $4f^2$ configuration which were calculated using these wave functions were found to be in good agreement with our optical and near-infrared absorption data, the agreement being especially good for the near-infrared portion of the spectrum.

INTRODUCTION

Anomalous behavior of the divalent ions of atoms lying near the beginning and the middle of the lanthanide series in a crystalline environment has been reported in connection with a number of observations. Perhaps the most notable of these is that of the crystal-field spectra of these ions as dilute solutes in alkaline earth halide solid solutions. For example, when most of the rare earths are incorporated into CaF_2 and reduced to the divalent state, they show virtually no optical absorption in the visible region of the spectrum; however, the divalent ions of La, Ce, Gd, and Tb possess strong absorption bands in the visible portion of their crystal spectra.[1] Furthermore, the absorption bands at the short-wavelength end of the visible spectrum of these latter ions may be bleached by irradiating the crystal with light at the absorption wavelength.[2,3] This bleaching results in the production of a new absorption band at a longer wavelength in the visible spectrum. Finally, this new absorption band can be bleached by irradiating it with light of its wavelength returning the absorption spectrum of these ions to their original state. A photochromic process of this nature is not found to occur when divalent lanthanide ions other than those just mentioned are incorporated into CaF_2. Among other observations in which the divalent ions of the rare earths fail to show similar behavior in a crystalline environment one should mention that the di-iodides of La, Ce, Pr, and Gd exhibit a metallike character in their specific resistivity and magnetic susceptibility while the di-iodides of Nd, Sm, Eu, Dy, Tm, and Yb exhibit insulatorlike behavior.[4]

For some time it has been conjectured that these differences in the observed properties of the divalent rare earths in a crystalline environment result from the presence of a d electron in the crystal-field ground-state configuration of the divalent ions of those atoms lying near the beginning and the middle of the lanthanide series.[5,6] Indeed, this has been observed to be the case for La^{2+} in CaF_2.[7] In a recent survey[6] of the spectra of divalent rare-earth ions in CaF_2, rough calculations of the excitation energy of these spectra were carried out on the assumption that the observed absorption bands were due to allowed transitions between the ground state, a level of the $4f^n$ configuration, and the lower-lying levels of the $4f^{n-1}5d$ configuration. Although the agreement between experiment and theory was found to be quite good, in general, there were marked disagreements for Ce^{2+}, Gd^{2+}, and Tb^{2+} which were explained if the ground state of these ions arose from the $4f^{n-1}5d$ configuration instead of from the $4f^n$ configuration. An examination[8] of the distribu-

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tion of energy levels of the $4f^n$ and $4f^{n-1}5d$ configuration of the free divalent rare-earth ions reveals that the lower levels of the $4f^{n-1}5d$ configuration lie quite close to the ground state in Ce^{2+} and Tb^{2+} and contain the ground state in La^{2+} and Gd^{2+}. Since the effect of a crystal field will be most noticeable on the d electron, it is not implausible to conclude that the ground states of La^{2+}, Ce^{2+}, Gd^{2+}, and Tb^{2+} will consist of a level of the $4f^{n-1}5d$ configuration in a sufficiently strong crystal field.

In this paper we shall present evidence that the ground state of Ce^{2+} in CaF_2 is a level of the $4f5d$ configuration transforming according to the cubic representation T_2. In the first part of the paper we shall describe the experimental optical-absorption spectra of Ce^{2+} on cubic sites in CaF_2 and Zeeman-effect measurements performed on some of the lower-energy absorption lines. Following this we shall present calculations of the energy levels, wave functions, and g factors of the $4f5d$ and $4f^2$ configurations and of the intensities for allowed transitions between the levels of the $4f^2$ and the ground state. A discussion of this work will be given in the last part.

EXPERIMENTAL

Crystals of CaF_2 were grown at RCA Laboratories and were doped with 0.1 $M\%$ of Ce^{3+}. The material was reduced either by heating in the presence of calcium vapor, i.e., additive coloration, or by irradiation with γ rays from a ^{60}Co source. The absorption spectra were obtained on a Cary 14 spectrophotometer.

The optical spectrum of CaF_2:Ce^{2+} is identical when obtained by either reduction technique. However, the spectrum is not stable and at room temperature it will decay both thermally and by bleaching with visible light. For the irradiated crystals the process is irreversible, that is, the number of Ce^{2+} ions decreases with time, while for the additively colored samples the process is reversible, that is, the absorption spectrum of Ce^{2+} can always be regained by irradiation with ultraviolet light. Figure 1 shows the absorption spectrum of additively colored CaF_2:Ce^{2+}. After

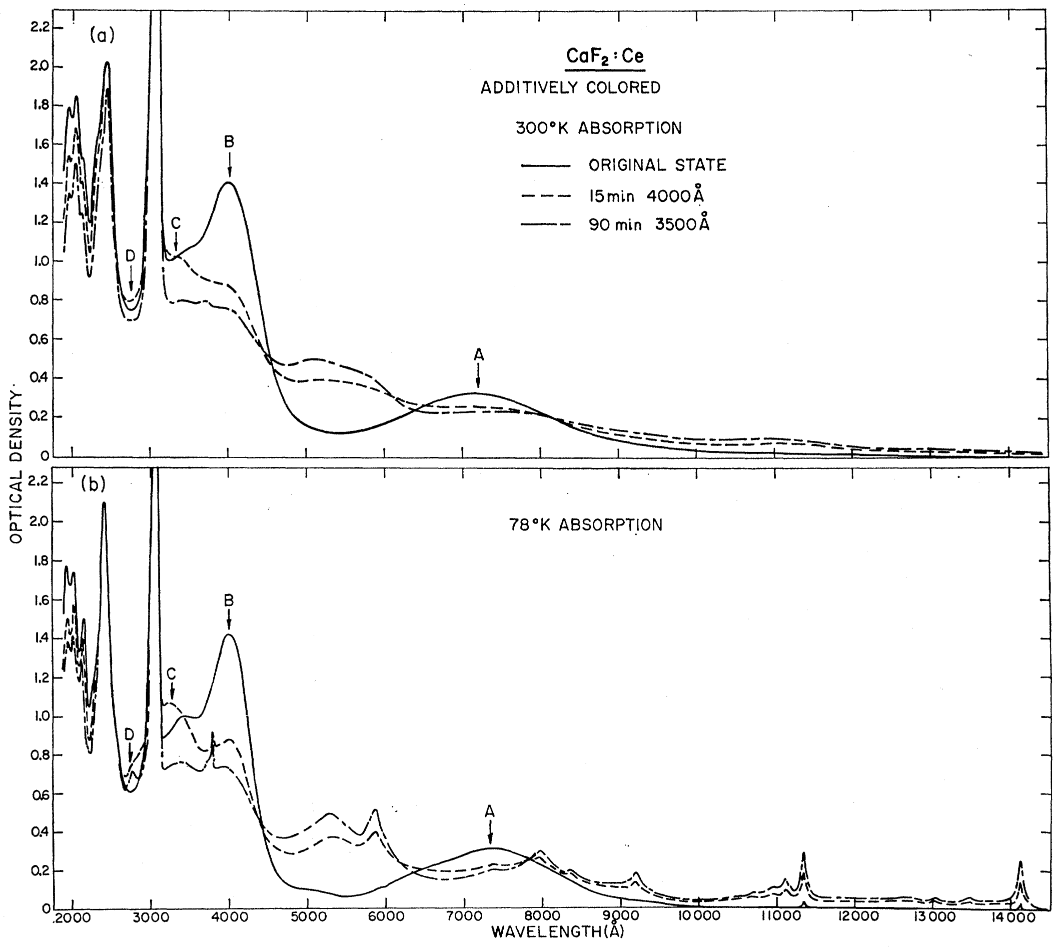

FIG. 1. Absorption spectrum of additively colored CaF_2:Ce^{2+} at 78 and 300°K after different photochemical treatments.

additive coloration, the stable spectrum appears as shown in the solid line. There are two characteristic absorption bands, one at 4000 Å and one at 7000 Å. The absorption bands at 3000 and 2400 Å are due[9] to $4f \rightarrow 5d$ absorption of Ce^{3+}. Most of the Ce^{3+} remains unconverted after additive coloration.[10] When the material is irradiated with light around 4000 Å the spectrum changes to that shown by the broken lines, which is the spectrum of Ce^{2+}. Although this spectrum will remain several days at room temperature in a dark ambient, it will slowly thermally reconvert to the stable spectrum shown by the solid line. The reconversion can also be accomplished in a matter of seconds by irradiating the sample with light of wavelength between 4500 and 7000 Å. This photochromic-charge transfer process is discussed elsewhere in some detail[3]; here we only note that the electron is transferred from the divalent rare earth to a color center associated with the trivalent rare earth and having a [111] symmetry.[11] When trivalent Ce is reduced by γ irradiation at 78°K, the spectrum of the divalent Ce appears first and remains relatively stable until the material is warmed to room temperature. In the warming process the spectrum is converted to the "stable" spectrum shown on Fig. 1. Some of the Ce^{2+} can again be regained by uv light irradiation but on each cycling some Ce^{2+} is lost and the material fatigues.

The absorption spectra of divalent Ce is shown in Fig. 2 at different temperatures. At low temperature, the absorption begins at around 1.4 μ and fills the whole visible region of the spectrum. There is also absorption in the near-ultraviolet, but it is covered by the more intense $4f$ to $5d$ absorption bands of Ce^{3+}. The spectrum exhibits a very strong temperature dependence which is shown in Table I. At 300°K, the various components can hardly be resolved, while at low temperature some of the lines are very sharp. This strong temperature dependence is reminiscent of other $5d \rightarrow 4f$ transitions in divalent rare-earth–doped CaF_2, e.g., the fluorescence spectrum[12] of Sm^{2+} in CaF_2. At low temperature most of the intensity of the transition is in a single line as contrasted to $4f$ to $5d$ transitions where the intensity is distributed over several vibrational states. The strong temperature dependence is certainly associated with populating only the lowest vibrational level of the $5d$ state from which a single transition is observed to all the very closely lying vibrational levels of the $4f$ configuration.

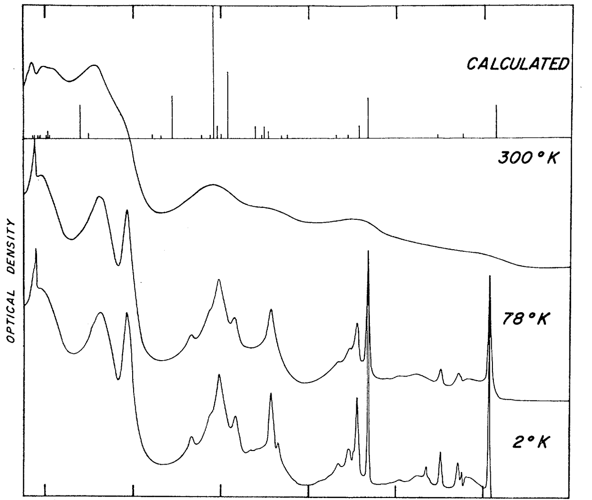

FIG. 2. Absorption spectrum of $CaF_2{:}Ce^{2+}$ at three different temperatures. The calculated positions and intensities of the $4f5d \rightarrow 4f^2$ transitions are shown at the top.

We have attempted to reduce Ce^{3+} in SrF_2, BaF_2, and $SrCl_2$ hosts without success. All these materials can be colored, but the absorption spectra obtained does not resemble Ce^{2+} in CaF_2. Of course, the possibility exists that Ce^{2+} is just not stable in these hosts or that the ground state is a level of the $4f^2$ configuration rather than the $4f5d$, thus producing an entirely different spectrum. We have also searched unsuccessfully for the $4f$ to $5d$ emission of Ce^{2+}. This result is perhaps not surprising since there are several levels of the $4f5d$ configuration below the lowest state of the $4f^2$ configuration through which nonradiative relaxation can take place very efficiently.

TABLE I. Half-width of the absorption spectrum of $CaF_2{:}Ce^{2+}$ at various temperatures.

Wavelength (μ)	Half-width (in cm^{-1}) at 300°K	78°K	2°K
1.41	~500	40	2.5
1.14	~500	60	10
0.91		160	100
0.79		300	200
0.52		~2000	~2000

Figure 3 shows the Zeeman effect of the 1.41-μ absorption line. The measurements were carried out using a superconducting solenoid and the Cary 14 spectrophotometer. The longitudinal Zeeman effect for both the field and the direction of observation along the [100] orientation is shown in Fig. 3. If one assumes the Ce^{2+} to be in cubic sites and that the representation of the excited state is T_2, then the Zeeman spectrum is consistent only with a ground state which transforms according to the representation T_2; the ground state is found to have a g value of 1.25 ± 0.1 and the excited state a g value of 1.43 ± 0.1. Different orientations of the magnetic field show the g value to be isotropic within the experimental errors. The calculated Zeeman pattern

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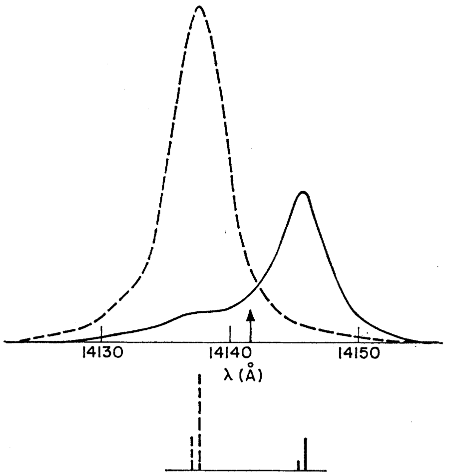

FIG. 3. Longitudinal Zeeman effect of the 1.41-μ transition $T_2 \rightarrow T_2$ for $H=25$ kG and $H \| [100]$ at 2.5°K. The calculated pattern is also shown. The solid curve corresponds to left circular polarization and the dashed curve to right circular polarization.

for the particular experimental conditions is also shown in Fig. 3. As can be noted, the agreement is reasonably good, considering that there is some uncertainty in the experimental intensity ratios, owing to the polarization properties of the spectrometer. Similar measurements were made on the 1.14-μ absorption line, and it is found that, if one assumes the excited level to transform as T_1, then the absorption pattern is only consistent with a ground state which transforms as T_2 and that the g value of the excited level is -1.15. Anderson and Sabisky of RCA Laboratories have searched by EPR techniques to observe this T_2 ground state without success.

THEORETICAL

The free-ion energy levels of the divalent cerium ion, which consists of two electrons outside a Xe closed shell, have been observed and identified by Sugar[13] and others.[14] The ground state of the free ion was found to be the $^3H_4$ level of the $4f^2$ configuration; the lowest-lying configuration of opposite parity to the ground state, i.e., the lowest-lying levels to which allowed transitions may be made from the ground state, was found to be the $4f5d$ configuration, the energy levels of which lie between 3277 and 18 444 cm^{-1} above the ground state. A theoretical interpretation of these free-ion configurations giving values of the spin-orbit parameters, the Slater parameters, and the $L(L+1)$ correction has been given by Spector.[15]

When Ce impurities enter into the fluorite lattice, it is found that the Ce, in a trivalent state, replaces a cation substitutionally. A fraction of these ions may be reduced to the divalent state by γ irradiation of the crystal, by additive coloration, or by electrolytic means. It has previously been shown for Dy, Tm, and Ho, that the divalent ions occupy cation lattice sites having the full O_h symmetry of the pure fluorite lattice.[16] We have therefore assumed that the divalent Ce impurities also occupy cation lattice sites having the full O_h symmetry of the pure lattice.

We shall describe the wave functions and energy levels of the valence electrons in terms of the $LSJM$ Russell-Saunders coupling scheme. The Hamiltonian for this system is

$$H=H_0+H_{ee}+H_L+H_{ls}-eV_{\mathrm{CF}}, \tag{1}$$

where $-e$ is the charge on an electron. The first term H_0 which describes the single-electron kinetic and potential energy and the second term H_{ee} which describes the electron-electron interaction are spherically symmetric and hence contribute only to the diagonal terms. These diagonal matrix elements are described in terms of the Slater parameters F_k and G_k, and in terms of the E_k, which are linear combinations of the F_k, introduced by Racah.[17] The linear combinations of these parameters appropriate to the permitted LS levels of the f^2 and fd configurations are given in Refs. 17 and 18. An empirical linear contribution to the energy of the system, called the $L(L+1)$ correction, is required to account for second-order effects in the electrostatic interaction[19]; this term is

$$H_L=\alpha L(L+1), \tag{2}$$

where α is an experimentally determined parameter. Since this correction is nonzero only for nl^m configurations where $m\geq 2$, it is used here only in the calculations for the $4f^2$ configuration. The spin-orbit interaction H_{ls} is

$$H_{ls}=\sum_i \zeta(r_i)\mathbf{l}_i\cdot\mathbf{s}_i, \tag{3}$$

where $\mathbf{l}_i$ and $\mathbf{s}_i$ are the orbital and spin angular momenta of electron i. Since this operation commutes with J, the total angular momentum, it is diagonal in the LSJ scheme. The radial integrals of the spin-orbit interaction, i.e., the spin-orbit parameters, are given by ζ_{nl} for each electron. The crystal-field potential V_{CF} is

$$V_{CF}=\sum_i (A_0+A_4r_i^4O_4(i)+A_6r_i^6O_6(i)). \tag{4}$$

For the case of eight identical point negative charges at the corners of a cube whose center coincides with the

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impurity ion,

$$A_0=-8e/R,\quad A_4=(4\pi/9)^{1/2}(28/9)e/R^5,\quad\text{and}\quad A_6=-(4\pi/13)^{1/2}(16/9)e/R^7, \tag{5}$$

where R is the ion-ligand separation. The angular dependence of the crystal-field potential is

$$O_4(i)=O_4(\theta_i,\phi_i)=Y_{40}(i)+(5/14)^{1/2}[Y_{44}(i)+Y_{4-4}(i)]$$

and (6)

$$O_6(i)=O_6(\theta_i,\phi_i)=Y_{60}(i)-(7/2)^{1/2}[Y_{64}(i)+Y_{6-4}(i)],$$

where (r_i,θ_i,ϕ_i) are the coordinates of the ith electron and $Y_{lm}(\theta,\phi)$ is a spherical harmonic. The crystal-field potential transforms according to the A_1 representation of the cubic symmetry group O_h, and thus, eV_{CF} will, in general, split each free-ion level, which was an eigenvalue of a spherically symmetric Hamiltonian, into a number of levels determined by the quantum number J assigned to the free-ion level. An orthonormal set of basis functions for each row of each irreducible representation of O_h for $J=0$ to 12 has been given by Polo.[20] For a single d electron only the first nonspherical term of eV_{CF} makes a nontrivial contribution to the energy; the radial matrix element for this term is commonly written

$$\langle d_0|-eV_4|d_0\rangle=-eA_4\langle r^4\rangle_d(9/4\pi)^{1/2}(2/7)\equiv-6Dq. \tag{7}$$

Here $\langle d_0|-eV_4|d_0\rangle$ represents the diagonal matrix element of the interaction $-eV_4=-eA_4r^4O_4(\theta,\phi)$ evaluated for the $m=0$ eigenfunction of a d electron, the radial integral being denoted $\langle r^4\rangle_d$. For a single f electron, both the fourth- and sixth-order terms of the crystal-field interaction contribute in a nontrivial manner to the energy levels of the system; the radial integrals for these terms are commonly written[21]

$$(\tfrac{11}{2})(4\pi/9)^{1/2}\langle f_0|-eV_4|f_0\rangle=-eA_4\langle r^4\rangle_f\equiv B_4$$

and (8)

$$(469/100)(4\pi/13)^{1/2}\langle f_0|-eV_6|F_0\rangle=-eA_6\langle r^6\rangle_f\equiv B_6.$$

In the *LSJM* Russel-Saunders coupling scheme, the levels arising from an *fd* electron configuration are $^{1,3}(PDFGH)$. In general, there will be matrix elements of the crystal-field interaction between each of these 140 levels giving rise to a 140×140 matrix which must be diagonalized to obtain the energy levels and wave functions of this configuration in a crystal field. However, since the crystal-field interaction is assumed to have O_h symmetry, simple group theoretical considerations may be used to reduce this problem to one of diagonalizing five matrices of dimensions 6, 5, 12, 18, and 17; these numbers correspond to the number of sets of levels in the configuration which transform according to the cubic representations A_1, A_2, E, T_1, and T_2, respectively. The Russell-Saunders levels arising from an f^2 configuration are $^1(SDGI)$ and $^3(PFH)$. There are 91 energy levels within this configuration; in a cubic field this configuration will contain 7, 3, 9, 9, and 12 sets of levels transforming according to the respective cubic representations A_1, A_2, E, T_1, and T_2.

There is no interaction between the eigenstates of the $4f5d$ and $4f^2$ configurations since these configurations are of opposite parity while the Hamiltonian H is of even parity. The lowest-lying configuration which couples to $4f^2$ is the $5d^2$ configuration; for the free ion the lowest level of the $5d^2$ configuration lies 20 000 cm^{-1} above the highest significant level of the $4f^2$ configuration. The lowest-lying configuration which couples to $4f5d$ is the $4f6s$; for the free ion the lowest level of the $4f6s$ lies above all the levels of the $4f5d$ configuration.[13] Thus, coupling between eigenstates of different configurations was ignored because of the relatively large energy separations between these configurations in the free ion.

For a given representation within a given configuration the matrix elements of H between the same row of each number of the set of free-ion levels which transform according to the given representation were calculated numerically using the radial parameters[22] given in Ref. 15, and the resulting matrices were diagonalized to obtain the energy levels and wave functions transforming according to the given representation. Independent calculations were also carried out for the *fd* configuration in a cubic crystalline field using the program of Piper, Brown, and McClure.[23] This calculation differs from the one they made for Yb^{2+} with configuration $f^{13}d$ only in that changes in the sign and magnitude of parameters which are different for a hole electron ($f^{13}d$) and two electrons (fd) were made. The two calculations gave nearly identical results for the crystal-field energy levels and thus serve as a check against numerical errors. In the divalent Yb calculation it was shown that the f-electron parameters had very little effect on the general features of the energy levels of the $4f5d$ configuration. By analogy one would expect no gross error in the level assignments for divalent Ce by only considering the effect of the crystal field on the d orbital in the $4f5d$ configuration, i.e., setting $B_4=B_6=0$. Thus, for the $4f5d$ configuration the crystal-field parameters B_4 and B_6 were put equal to zero, and the resulting energy levels are shown as a function of the parameter Dq in Figs. 4–7. In Fig. 8 the lower-lying energy levels of the $4f5d$ configuration

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[21] Z. J. Kiss, Phys. Rev. **137**, A1749 (1965).

[22] Although $\zeta_{4f}=547$ cm^{-1} in the free ion for the $4f^2$ configuration, $\zeta_{4f}=575$ cm^{-1} yields a better agreement with the crystal-field absorption spectrum.

[23] T. S. Piper, J. P. Brown, and D. S. McClure, J. Chem. Phys. **46**, 1353 (1967).

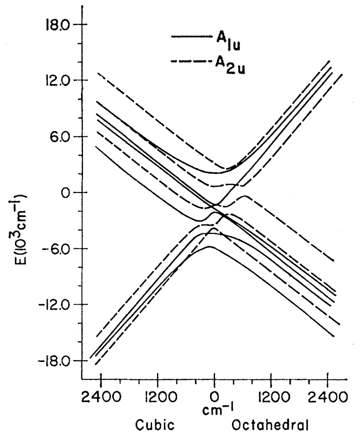

FIG. 4. Energy levels of the $4f5d$ configuration which transform according to the A_1 (solid lines) and A_2 (dashed lines) representations of the cubic group are shown as a function of the crystal-field parameter Dq. The parameters given in Ref. 15 together with $B_4=B_6=0$ were used in this calculation.

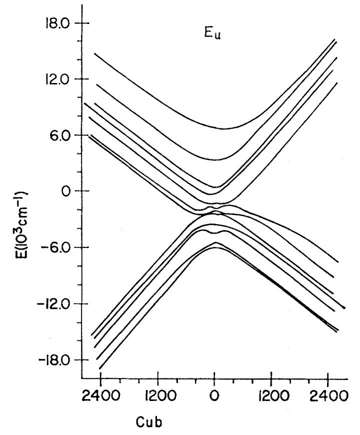

FIG. 5. Energy levels of the $4f5d$ configuration which transform according to E, calculated using the parameters described in Fig. 4, are shown as a function of Dq.

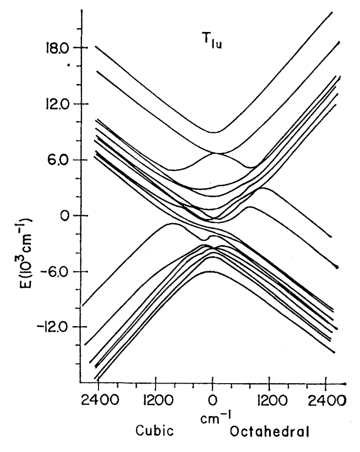

FIG. 6. Energy levels of the $4f5d$ configuration which transform according to T_1, calculated using the parameters described in FIG. 4, are shown as a function of Dq.

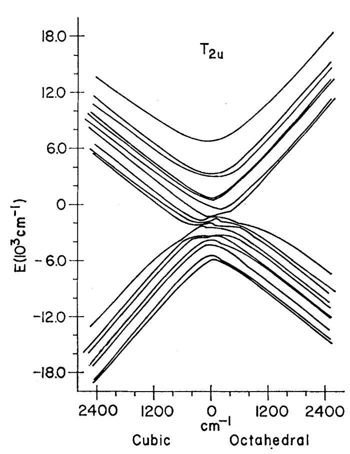

FIG. 7. Energy levels of the $4f5d$ configuration which transform according to T_2, calculated using the parameters described in Fig. 4, are shown as a function of Dq.

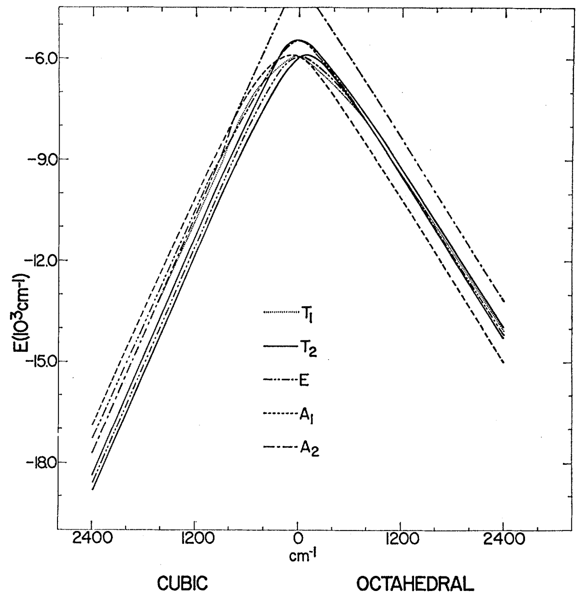

FIG. 8. Lowest energy levels of the $4f5d$ configuration, calculated using the parameters described in Fig. 4, are shown as a function of Dq. The abscissa is Dq in cm⁻¹.

are shown as a function of Dq. Negative values of Dq correspond to a physical arrangement of the negative point charges on the faces of a cube centered on the impurity ion, i.e., an octahedral coordination.

Although calculations[21] using the point-charge model give $B_6=-0.12B_4$ for the f electron in Ce^{3+}, we find that the observed splitting pattern of the $4f^2$ configuration can best be described by the relation $B_6=-0.05B_4$. The lower levels of this configuration are shown in Fig. 9 as a function of the parameter B_4. The crystal-field energy levels resulting from the $^3H_{4,5,6}$ free-ion levels of this configuration calculated here were found to be in general agreement with those given by Lea, Leask, and Wolf.[24] From Fig. 8 one notes that the lowest-lying level of the $4f5d$ configuration is a level transforming according to the T_2 cubic representation for nearly all positive values of Dq. The level is composed largely of the $^1G_4$ free-ion level.

Since the observed[21] magnitude of the crystal-field parameter B_4 for Dy^{2+} in CaF_2 is of the order 2000 cm^{-1}, we may conclude from Figs. 8 and 9, assuming that the magnitude of B_4 does not change radically as we go from Dy^{2+} to Ce^{2+} in CaF_2 and that there is no configuration shift, that the ground state of the divalent cerium ion moves from the $4f^2$ configuration to the $4f5d$ configuration when Dq exceeds 1000 cm^{-1}. If we assume the optical and near-infrared absorption spectrum results from transitions from the ground state in the $4f5d$ configuration to the levels of the $4f^2$ configuration, we observe that the experimental absorption spectrum is in good agreement with the levels given in Fig. 9 if we take $B_4 = -3000$ cm^{-1}. The calculated and experimental-absorption energies are tabulated in Table II and are shown diagrammatically in Fig. 2. The magnitude of the experimental absorption energies indicates that the ground state lies about 7000 cm^{-1} below the lowest $4f^2$ level. Thus, if we ignore configuration shifts, we are led to conclude that a crystal-field strength given by $Dq = 1800$ cm^{-1} is acting on the d electron of the ion. The energies and wave functions of some of the lower-lying levels of the $4f5d$ configuration are shown in Table III for $Dq = 1700$ cm^{-1}.

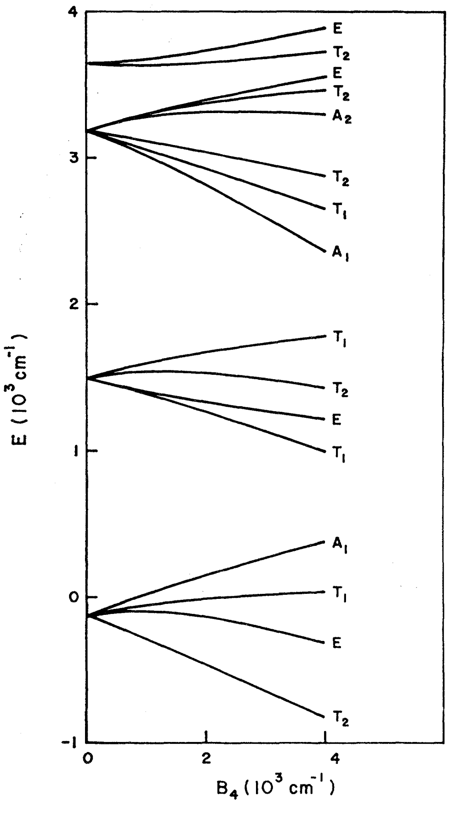

FIG. 9. Lower energy levels of the $4f^2$ configuration, calculated using the parameters given in Refs. 15 and 22 together with $B_6 = -0.05\ B_4$, are shown as a function of the crystal-field parameter B_4. In ascending order these levels derive from the $^3H_4$, $^3H_5$, $^3H_6$, and $^3F_2$ free-ion configurations. Each level is labeled with the representation according to which it transforms.

The intensities of the absorption bands were determined by obtaining the electric-dipole matrix elements between the ground state and the calculated crystal-field levels of the $4f^2$ configuration. These calculated intensities are tabulated in Table II and are shown diagramatically in Fig. 6.

The g factor of the $4f5d$ (T_2) ground state was calculated to be 1.94; the g factors of the T_2 and T_1 levels of the $4f^2$ configuration which correspond to the 1.41- and 1.14-μ absorption lines were calculated to be 2.01 and -2.42, respectively. Although these calculated g factors agree in sign with those observed experimentally, they all have magnitudes which are substantially larger than is observed experimentally; there is no apparent explanation for this magnitude discrepancy.

TABLE II. Observed and calculated absorption energies and relative intensities.

Level of f^2	Energy (cm^{-1}) Calculated	Energy (cm^{-1}) Observed	Intensity Calculated	Intensity Observed
$^3H_4$ T_2	7011	7080	(1.0)	(1.0)
E	7479	7460	0.03	~0.05
T_1	7715	7700	0.08	~0.05
A_1				
$^3H_5$ T_1	8818	8820	1.23	1.3
E	8954	9000	0.20	0.4
T_2	9174	9150	0	~0.02
T_1	9412	9410	0	~0.01
$^3H_6$ av	10 829	10 970	0.72	0.8
^3F, ^1G mixture	12 256	12 040	2.0	strong, broad shoulder
^3F, ^1G mixture	12 695	12 600	4.2	several broad peaks

DISCUSSION

After making a long and involved crystal-field calculation by computing machinery one looks at the results and wonders if enough parameters have been varied, and whether or not the order of levels has any fundamental significance.

The order of low-lying fd energy levels of Ce^{++} in cubal fields can be understood by making an analysis of the different factors entering into the energy-level scheme. The diagram of Fig. 8 shows that the limiting slope of the lower group of energy levels with crystal field is $\delta E/\delta Dq \cong -6$ for large Dq values. Therefore, a reasonable analysis of the energy-level problem would begin by electrostatically coupling a de electron with the cubic field components a_2, t_2, and t_1 of the f electron.

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[24] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

The results of this treatment are shown in Fig. 10. The $^1G_4$ term is lowest in zero crystal field, and gives rise to a $^1T_2$ term which even in the absence of spin-orbit coupling is the lowest term of all. It consists of a nearly equal mixture of the $^1T_2$ states arising from et_1 and et_2, where e refers to the d electron and t_1, t_2 are components of the f electron. The next higher term is $^3T_1$, again arising from a nearly equal mixture of these two configurations. In the presence of spin-orbit coupling $^3T_1$ splits into an inverted multiplet, having the pseudo-fivefold-degenerate component lowest and below $^1T_2$. This component is actually T_2+E, and in the presence of second-order spin-orbit coupling the $^1T_2$ level interacts with the T_2 component pushing it below the E level of $^3T_1$. The net result is that the level order $T_2—E—T_2$ is always maintained from moderate to strong crystal fields. Below $Dq\approx 400$ cm^{-1}, the de designation is not applicable to the split d orbital and the order of the lower levels begins to differ from that in the strong-field region.

TABLE III. Energy levels (in cm^{-1}) and the cubic representation to which they belong are given below for the $4f5d$ configuration with $Dq=1700$ cm^{-1}. The principal components of the wave function are given for some of the lower-lying levels.

Energy	Wave function
0 (T_2)	$0.72\,^1G_4+0.33\,^3F_3+0.33\,^3H_4$
192 (E)	$0.49\,^3H_4+0.33\,^3G_4-0.72\,^3F_2$
427 (T_2)	$0.33\,^3H_4+0.42\,^3G_3+0.38\,^3F_3+0.56\,^3F_2$
1074 (A_2)	$0.85\,^3G_3+0.52\,^3F_3$
1089 (T_1)	$0.41\,^3H_4+0.35\,^3H_5-0.31\,^1G_4+0.62\,^3F_3$

1448 (E),	1686 (T_1),	1837 (A_1),	2116 (T_2),	2404 (A_1),
2599 (T_2),	2644 (T_1),	3050 (T_1),	3071 (E),	3817 (A_2),
3821 (T_2),	3824 (E),	3946 (T_1),	4492 (T_2),	4516 (E),
6156 (T_2),	6217 (T_1),	10 687 (T_1),	19 331 (A_1),	19 837 (E),
19 943 (T_2),	20 182 (E),	20 307 (T_2),	20 660 (T_1),	20 964 (A_2),
21 093 (T_2),	21 221 (T_1),	21 515 (T_1),	21 986 (E),	22 348 (T_2),
22 374 (A_1),	22 570 (T_1),	22 952 (A_1),	22 965 (E),	22 986 (T_1),
23 107 (T_2),	23 214 (T_1),	23 679 (T_2),	23 810 (E),	23 952 (T_1),
24 090 (T_2),	24 223 (A_2),	24 527 (A_1),	24 759 (T_1),	24 991 (T_1),
25 391 (T_2),	25 940 (E),	26 121 (T_2),	27 340 (A_2),	28 480 (T_2),
29 010 (E),	30 056 (T_1),	32 443 (T_1).		

A further point of interest concerns the electrostatic interaction between $5de$ and $4f(a_2,t_1,t_2)$ electrons. The largest electrostatic repulsion occurs between the de $(3z^2-r^2)$ and the ft_1 $z(5z^2-3r^2)$ because these functions have the greatest overlap. The $^1T_1(et_1)$ level is therefore the highest by far of any of the $5de$, $4f$ singlets. The greatest exchange splitting occurs in this configuration, and the corresponding triplet $^3T_1(et_1)$ is among the lowest. The total exchange splitting is about 8200 cm^{-1}.

The configuration mixing between dt_2 and de orbitals is not large enough in high crystal fields to invalidate the foregoing description, although it has an appreciable effect on the level positions and some effect on their order. With no configuration mixing whatever, the levels derived from dt_2 would have their center of gravity $10Dq$ above those derived from de (omitting the spin-orbit coupling). In an actual calculation for $Dq=800$, these groups were found actually to be 9480 cm^{-1} apart rather than 8000 cm^{-1} apart (again omitting spin-orbit coupling).

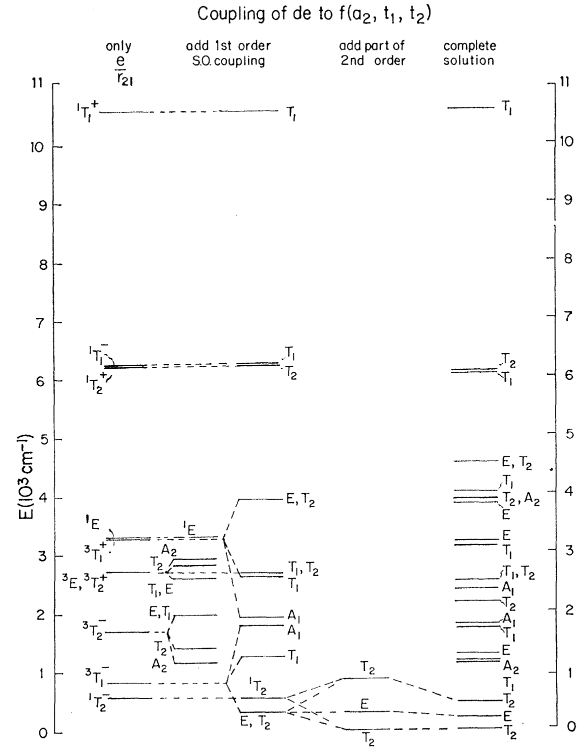

FIG. 10. Development of the ground state of Ce^{++} in CaF$_2$. The left-hand column shows the levels derived using the approximation of coupling de to $f(a_1, t_1)$ via electrostatic interaction only. The next column shows the effect of including first-order spin-orbit coupling for these levels, and the third column shows the additional effect of second-order spin-orbit coupling between $^1T_2^-$ and $^3T_1^-$. The final ground state is predominantly a mixture of $^1T_2^-$ and $^3T_1^-(T_2)$. The approximation $de\times f(a_2,t_1,t_2)$ yields $^{1,3}(E,2T_1,2T_2^-)$ or five singlets and five triplets, which yield $2A_1+2A_2+5E+7T_1+7T_2$, or 23 out of the 58 possible spin-orbit product states. The last column shows the complete set of 23 lower levels computed for $Dq=1600$. The approximate calculation bears considerable resemblance to the complete one, as a detailed examination of this figure will show.

The linewidths of the various absorption lines in Fig. 2 are seen to increase at higher energies (see Table I). Corresponding to this increase in the linewidths at higher energies there is also an increase in the oscillator strength of the transitions. For example, while the oscillator strength of the 1.41-μ line is 0.002, the strength of the 5000 Å band is 0.4. Admixture of the charge transfer states into the higher excited states of Ce^{2+} is likely to be responsible for both the increase in linewidth and oscillator strength. This interpretation has been confirmed by photoconductivity[25] and photochromic efficiency measurements. These measurements place the ground state of Ce^{2+} about 2.5 eV below the conduction band of CaF$_2$.

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[25] P. M. Heyman Appl. Phys. Letters **14**, 81 (1969).

In view of the large crystal-field strength acting on the d electron in the $4f5d$ configuration, it is possible that the higher excited states into which the charge-transfer states are mixed are levels of the $5d^2$ configuration. In the free ion the $5d^2$ configuration consists of 9 levels lying at energies of 40 000 cm^{-1} and greater above the ground state of the free ion.[13] The presence of a strong crystal field, however, causes two of these levels, transforming according to T_2 and E and composed primarily of ${}^3F_2$ and ${}^1D_2$, respectively, to be lowered in energy with a slope of $\delta E/\delta Dq \approx -12$; the remaining levels of the $5d^2$ configuration have a limiting slope with crystal field which is considerably larger than this. Thus, the presence of a very strong crystal field ($Dq \geq 2500$ cm^{-1}) or the presence of a moderately strong crystal field together with a downward shift of $5d^2$ configuration could lead to f to d transitions between the ground state and these levels of the $5d^2$ configuration which would lie in the visible.

Although coupling between eigenstates belonging to different electronic configurations was ignored because of the large separations in energy between configurations in the free ion, we have just noted that the crystal field may be strong enough to greatly reduce the energy separation between the levels of the $5d^2$ and $4f^2$ configurations, so that a significant amount of configuration mixing may occur. The effect of mixing will be to lower the observed absorption energies of transitions between the crystal-field ground state and the upper states of the $4f^2$ configuration below those calculated. Thus, the observation that the calculated absorption energies of the higher energy d to f transitions (see Table II) are larger than the corresponding observed absorption energies suggests that some mixing of the $5d^2$ and the $4f^2$ configurations does indeed occur. The magnitude of the matrix elements connecting states of different configurations is apparently not large enough, however, to appreciably alter the calculations that have been performed on the assumption that these matrix elements are zero.

The value of Dq for Ce^{2+} in CaF_2 cannot be obtained accurately from the spectrum. We know that by analogy to the transition-metal series the value of Dq should be larger for Ce^{2+} at the beginning of the rare earths than for Yb^{2+} at the end, for which values of Dq range from 800 cm^{-1} for[23] Yb^{2+} in SrCl_2 to 1700 cm^{-1} for Yb^{2+} in CaF_2.[26] The $5d$ electron is considerably more extended for Ce^{2+} than for Yb^{2+}; according to the tables of Herman and Skillman,[27] the outer maximum of $5d$ is 17% farther from the nucleus for the free La atom than for the free Lu atom. This may have a large effect on the value of Dq.

We know that in the free ion, the lowest state of the $4f^2$ configuration is 3277 cm^{-1} below that of the $4f5d$, and that in the crystal the difference is -7080 cm^{-1}. If this change is to be ascribed solely to crystal-field splitting, Dq must equal 1800 cm^{-1}. This cannot be entirely correct, however, because as was found for $\text{SrCl}_2\text{:Yb}^{2+}$, the $4f5d$ configuration shifts downward in going from vapor to crystal. In this case the shift was 6030 cm^{-1}. If the configuration shift were the same in $\text{CaF}_2\text{:Ce}^{2+}$, then Dq would equal 950 cm^{-1}. Several of the ef levels, i.e., the lower group, of the $4f5d$ configuration have been observed[28] via the electronic Raman effect; the influence of strains in the crystal was found to significantly alter the spectrum. Even if the positions of these levels could be accurately determined, however, they would still not yield an accurate Dq value since they all have nearly the same Dq dependence. The $ef \rightarrow t_2f$ transitions would give Dq accurately but they are probably obscured by the strong $ef \rightarrow 4f^2$ transitions. The most we can confidently say is $800 < Dq < 2000$, but there is a good probability that it is about 1700 cm^{-1}.

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[27] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

[28] A. Kiel and J. F. Scott, Bull. Am. Phys. Soc. 13, 1438 (1968).