

Dependence of the Stark structure on the energies of the multiplets

A. A. Kornienko and E. B. Dunina

Vitebsk Pedagogical Institute, 210022 Vitebsk, Belarus

(Submitted 26 November 1993)

Pis'ma Zh. Eksp. Teor. Fiz. **59**, No. 6, 385–388 (25 March 1994)

A detailed study of configurational-mixing effects in f systems reveals that the crystal-field Hamiltonian contains some new terms, which depend on the energies of the multiplets. When these terms are taken into account, it becomes possible to resolve some experimental data, on the Stark splitting of low- and high-lying multiplets, which have looked contradictory from the standpoint of the ordinary theory. These new terms can be thought of as corrections to the parameters of the even crystal field which depend on the energies of the multiplets. Analytic expressions are derived for these terms. These expressions make it possible, for the first time, to work from an analysis of the energy spectrum to determine the parameters of the odd crystal field, which is responsible for intensity characteristics of the optical spectra of f systems.

1. The search for new active media for UV lasers is attracting much theoretical and experimental interest to the Stark structure of crystals activated by ions with unfilled f shells (“ f systems”) over a broad energy range. It has been established that the standard crystal-field Hamiltonian

$$H_{cf} = \sum_{k=2,4,6} \sum_{q=-k}^k B_q^k C_q^k \quad (1)$$

is not always successful in describing the Stark splitting of low- and high-lying multiplets simultaneously.^{1–4} As Esterowitz *et al.*¹ have suggested, a possible reason for this difficulty is that high-lying multiplets lie closer to the excited configurations, and mixing effects should have a greater influence on them than on other multiplets. Effects of a mixing of configurations have been studied in many places (e.g., Refs. 5–7), but the fact that different multiplets are separated from the excited configurations by different energy intervals is not reflected in the form of the effective Hamiltonian. The influence of mixing effects reduces to simply a renormalization of the parameters B_q^k in Hamiltonian (1) and to the addition to this Hamiltonian of terms with a complex tensor structure. The values of these terms are determined by some auxiliary parameters which are constant for all multiplets.

In this letter we propose one possible way to solve this problem. On the basis of a more detailed study of configurational-mixing effects, a new crystal-field Hamiltonian has been constructed. The primary distinguishing feature of this new Hamiltonian is that it contains terms which depend on the energies of the multiplets. We show, for the particular case of Pr^{3+} in LiYF_4 , that these new terms substantially improve the description of the energy spectrum. This approach involves a radical change in the

interpretation of the nature of the crystal field. We derive some analytic expressions which make it possible in principle, for the first time, to work from an analysis of the energy spectrum to determine the parameters of the odd crystal field, which is responsible for intensity characteristics of the optical spectra of f systems.

2. It would be possible to derive correct results from Hamiltonian (1) if the basis for the diagonalization of the matrices were made up of all the wave functions of the ground and excited configurations. For technical reasons, this simple method is often impossible to implement in practice, so an effective Hamiltonian algorithm looks more attractive. An effective Hamiltonian acting in a basis of considerably lower dimensionality has the same eigenvalues as the actual Hamiltonian. To derive an effective Hamiltonian, we work from Eq. (25) of Ref. 8, reproducing from that equation the most important terms:

$$\begin{aligned} \langle n | \hat{H}_{\text{eff}} | n' \rangle = & \langle n | \hat{H} | n' \rangle + \sum_b \frac{1}{\Delta_{nb}} \langle n | \hat{\mathcal{H}}_n | b \rangle \langle b | \hat{\mathcal{H}}_n | n' \rangle \\ & - \frac{1}{2} \sum_{b, n''} \frac{1}{\Delta_{nb}^2} [\langle n | \hat{\mathcal{H}}_n | b \rangle \langle b | \hat{\mathcal{H}}_n | n'' \rangle \langle n'' | \hat{W} | n' \rangle \\ & + \langle n | \hat{W} | n'' \rangle \langle n'' | \hat{\mathcal{H}}_n | b \rangle \langle b | \hat{\mathcal{H}}_n | n' \rangle], \end{aligned} \quad (2)$$

where

$$\langle n | \hat{\mathcal{H}}_n | b \rangle = \langle n | \hat{H} | b \rangle - \langle n | \hat{H}^0 | n \rangle \langle n | b \rangle,$$

\hat{W} is a perturbation operator, \hat{H}^0 is the Hamiltonian of the zeroth approximation, and n, n', n'' , and b represent the eigenstates of the ground and excited configurations, respectively.

It is a simple matter to go over to a description in terms of the spherical tensors C_q^k in expression (2) by some method, e.g., that described in Refs. 9 and 10. The primary difficulty here is in correctly choosing the zeroth-approximation Hamiltonian, which strongly influences the interpretation of matrix elements of the $\langle n | \hat{W} | n'' \rangle$ type. We have pointed out that the customary approximation in transformations of this sort (see Ref. 11, for example) is to assume that the energy differences Δ_{nb} are independent of the projections of the spin and orbital angular momentum of the electrons. Such an independence is possible if all states of the configuration have the same energy, i.e., if the configuration is completely degenerate. This situation would suggest the approximation of a centrally symmetric field. The perturbation operator $\hat{W} = \hat{H} - \hat{H}_0$ must therefore contain all the noncentrally symmetric interactions: a) the noncentral part of the intraatomic Coulomb interaction of the electrons and the spin-orbit interaction, which dominate the energies of the multiplets; b) the Coulomb interaction of the electrons of the activator ion with electrons and nuclei of the surrounding ions. These interactions are responsible for the onset of a Stark structure. From this standpoint it seems reasonable to write

$$\langle n | \hat{W} | n' \rangle = (E_J - E_f^0) \delta_{nn'} + \left\langle n \left| \sum_{k=2}^6 \sum_{q=-k}^k F_q^k C_q^k \right| n' \right\rangle, \quad (3)$$

TABLE I. Values of $(B_q^k)_{\text{opt}}$, determined separately for each multiplet with the help of Hamiltonian (1), and values of I_q^k calculated from expression (5) (all values are in units of cm^{-1}).

$S L J$	Energy	$(B_0^3)_{\text{opt}}$	I_0^2	$(B_0^4)_{\text{opt}}$	I_0^4	$(B_4^4)_{\text{opt}}$	I_4^4	$(B_0^6)_{\text{opt}}$	I_0^6	$(B_4^6)_{\text{opt}}$	I_4^6
3H_5	2382	374	502	-861	-861	616	834	-201	18	1308	1308
3H_6	4573	518	481	-559	-558	938	938	46	46	1127	1127
3F_4	7055	476	458	-216	-216	1056	1056	79	78	940	922
1G_4	10018	394	430	156	193	1197	1197	63	118	659	678
1D_2	17008	—	364	—	1157	—	1530	—	—	—	—

where E_J is the energy of the state $|n\rangle$, E_f^0 is the energy of the center of gravity of the ground configuration, and F_q^k are crystal-field parameters. The latter are determined primarily by interactions b) and by the effects resulting from the overlap of wave functions. After substituting (3) into (2) and going through some straightforward transformations, we find the following expression for the effective crystal-field Hamiltonian:

$$\begin{aligned}
 \langle n | \hat{H}_{\text{eff}} | n' \rangle = & (E_f^0 + E_J) \delta_{nn'} + \left\langle n \left| \sum_{k=2}^6 \sum_{q=-k}^k I_q^k C_q^k \right| n' \right\rangle \\
 & + \sum_{n''} \left\langle n \left| \sum_{k=2}^6 \sum_{q=-k}^k F_q^k C_q^k \right| n'' \right\rangle \left\langle n'' \left| \sum_{k=2}^6 \sum_{q=-k}^k G_q^k C_q^k \right| n' \right\rangle \\
 & + \sum_{n''} \left\langle n \left| \sum_{k=2}^6 \sum_{q=-k}^k G_q^k C_q^k \right| n'' \right\rangle \left\langle n'' \left| \sum_{k=2}^6 \sum_{q=-k}^k F_q^k C_q^k \right| n' \right\rangle + \dots,
 \end{aligned} \tag{4}$$

where

$$I_q^k = B_q^k + (E_J + E_{J'} - 2E_f^0) G_q^k. \tag{5}$$

The parameters B_q^k here, as in ordinary crystal-field theory, (1), are determined primarily by interactions b), by covalency effects, and by an admixture of excited configurations of the activator ion. The parameters G_q^k are determined solely by covalency effects and the mixing of configurations of the activator ion.

3. Expressions (4) and (5) differ from Hamiltonian (1) in that they explicitly depend on the energies of the multiplets and in having a "quadratic crystal field" [the last two lines in (4)]. A quadratic crystal field was studied in Ref. 12, and we will not discuss its role here. In a study of the Stark structure of the Pr^{3+} ion in LiYF_4 with the help of Hamiltonian (1), Esterowitz *et al.*¹ concluded that the optimum sets of parameters, $(B_q^k)_{\text{opt}}$, determined separately for the low- and high-lying multiplets differ markedly from each other (this assertion is supported by the results of our own calculations, shown in Table I). When Esterowitz *et al.*¹ described the Stark structure by a single set of parameters, they found a large standard deviation of the theoretical values of the energies from the experimental values ($\sigma = 54.7 \text{ cm}^{-1}$ for 44 Stark levels with $B_0^2 = 489$, $B_0^4 = -1043$, $B_4^4 = 1242$, $B_0^6 = -42$, $\text{Re} B_4^6 = 1213$, and $\text{Im} B_4^6 = 22$, where

all these quantities are in units of cm^{-1}). The use of expressions (4) and (5) makes it possible to reduce the standard deviation to $\sigma = 24.8 \text{ cm}^{-1}$ with $B_0^2 = 430$, $B_0^4 = 198$,

$B_4^4 = 1199$, $B_0^6 = 118$, $B_4^6 = 674$, $G_0^2 = -47 \times 10^{-4}$, $G_0^4 = 690 \times 10^{-4}$, $G_4^4 = 238 \times 10^{-4}$, $G_0^6 = 65 \times 10^{-4}$, and $G_4^6 = -413 \times 10^{-4}$, where the B_q^k are in cm^{-1} , and the G_q^k are dimensionless. The parameters I_q^k calculated with these values of B_q^k and G_q^k are in general agreement with $(B_q^k)_{\text{opt}}$ (Table I).

4. The contribution to the Stark structure, which depends on the energies of the multiplets, is governed by the second and third lines of expression (2). Consequently, it is inversely proportional to the square of the energy difference between the ground configuration and the excited configurations. The primary contribution to G_q^k is thus from an admixture of an excited configuration with the lowest energy. In the case of f systems, this is usually the $nf^{N-1}(n+1)d$ configuration. In this approximation, it is a simple matter to derive an analytic expression for G_q^k in terms of the nj symbols and the parameters B_q^k of the odd crystal field:

$$G_q^k = -\frac{2k+1}{2\Delta_{fd}^2 \langle f \| C^k \| f \rangle} \sum_{q_1, q_2} \sum_{k_1, k_2} (-1)^q \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \times \begin{pmatrix} k_1 & k_2 & k \\ f & f & d \end{pmatrix} \langle f \| C^{k_1} \| d \rangle \langle d \| C^{k_2} \| f \rangle B_{q_1}^{k_1} B_{q_2}^{k_2}, \quad (6)$$

where k_1 and k_2 are odd, and $\langle f \| C^k \| d \rangle$ are reduced matrix elements of the spherical tensor C^k . Using expression (6), we easily see that the values of G_q^k listed above correspond to values of B_q^{2k+1} in the range from 10 000 to 29 000 cm^{-1} . This result is in reasonable agreement with the range of 1300 to 13 000 cm^{-1} calculated in Ref. 13 by a different method.

¹L. Esterowitz *et al.*, Phys. Rev. B **19**, 6442 (1979).

²B. P. Singh *et al.*, J. Phys. C **19**, 6655 (1986).

³J. B. Gruber *et al.*, Phys. Rev. B **40**, 9464 (1980).

⁴D. Hua *et al.*, J. Chem. Phys. **89**, 5398 (1988).

⁵B. R. Judd, Phys. Rev. Lett. **39**, 242 (1988).

⁶B. Ng and D. J. Newman, J. Chem. Phys. **87**, 7110 (1984).

⁷C. L. Li and M. F. Reid, Phys. Rev. B **42**, 1903 (1990).

⁸A. A. Kornienko *et al.*, Phys. Status Solidi B **157**, 261 (1990).

⁹A. A. Kaminskii *et al.*, Phys. Status Solidi B **134**, 717 (1986).

¹⁰A. A. Kornienko *et al.*, Phys. Status Solidi B **157**, 267 (1990).

¹¹B. R. Judd, Phys. Rev. **127**, 750 (1962).

¹²A. A. Kornienko *et al.*, Phys. Status Solidi B **178**, 385 (1993).

¹³L. K. Aminov, in *Spectroscopy of Crystals* [in Russian] (Nauka, Leningrad, 1983), p. 36.

Translated by D. Parsons