

Ligand dependence of the correlation crystal field

R. G. Denning, A. J. Berry, and C. S. McCaw

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, United Kingdom

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When the crystal-field components of 26 J multiplets in the elpasolites $\text{Cs}_2\text{NaTbX}_6$ ($X=\text{F,Cl,Br}$) are modeled by a one-electron crystal-field Hamiltonian, major variations are found in the accuracy with which the splitting of each multiplet is reproduced. The effective crystal field within each multiplet is quantified by a degeneracy-weighted standard deviation. Differences between experimental and calculated splittings of up to 80% of the theoretical value are observed. They provide the most extensive example so far reported of electron correlation induced by the crystal field (CCF). The percentage deviation of each multiplet from the one-electron model decreases in the order $\text{Br}>\text{Cl}>\text{F}$. This indicates the importance of covalency and/or ligand polarizability contributions to the CCF. [S0163-1829(98)50804-1]

The one-electron crystal-field Hamiltonian [expressed as the sum of one-electron operators,

$$H_{\text{CF}} = \sum_{k,q} B_Q^K C_Q^{(K)},$$

where

$$C_Q^{(K)} = \sum_i c_Q^{(K)}(i)$$

and $c_Q^{(K)}(i)$ is a spherical tensor operator for the i th f electron, of rank K where $K=2,4,6$, with Q restricted by symmetry] is used extensively in the assignment and interpretation of solid-state f - f spectra.^{1,2} However, the limitations of this model have been apparent for some time.³ For example, if the B_Q^K parameters are chosen to match the splitting of one subset of states, they often give a poor description of other multiplets. Typically the maximum spin multiplicity components of the ground state are well modeled in isolation, but the quality of the fit deteriorates with the inclusion of states associated with higher-energy terms. For Tb^{3+} and Eu^{3+} the 7F_J manifold can be accurately described in a variety of hosts; however, the splitting of the 5D_4 excited state for Tb^{3+} is much smaller than calculated, while for Eu^{3+} it is larger.^{4,5} Several ‘‘rogue multiplets’’ are found in other lanthanides; the measured crystal-field splitting being either too large or too small relative to that calculated using one-electron operators. These multiplets include 1D_2 in PrCl_3 ,⁶ $^2H(2)_{11/2}$ of Nd^{3+} in a variety of host crystals,⁷ and 3K_8 of Ho^{3+} and $^6I_{17/2}$ of Gd^{3+} in LaCl_3 .⁸

Various mechanisms have been suggested for improving the Hamiltonian.⁹ The most general arises from the correlation between pairs of electrons induced by the crystal field, and is termed the correlation crystal field (CCF). The CCF can be described in terms of orthogonal tensor operators $g_{iQ}^{(K)}$ with coefficients G_{iQ}^K as

$$H_{\text{CCF}} = \sum_{i,K,Q} G_{iQ}^K g_{iQ}^{(K)},$$

where i ranges from 1 to 11, K takes the values $0 < K \leq 12$, and the components Q are restricted by symmetry.¹⁰ In the absence of symmetry a total of 637 G_{iQ}^K parameters are required to specify this part of the Hamiltonian, but this number is reduced to 41 in O_h symmetry. The seven two-body scalar operators with $K=0$ describe the free-ion electrostatic interactions, while the $g_1^{(K)}$ are equivalent to unit tensor operators describing the one-electron crystal field. Ignoring these operators, which are already included in the Hamiltonian, the CCF can be specified by 603 additional parameters in the absence of symmetry, and 32 parameters in O_h symmetry.

Configuration interaction due to the Coulomb field is routinely incorporated in the free-ion Hamiltonian by means of effective operators, and the CCF operators handle the influence of the ligand field in an analogous way. In O_h symmetry, for example, the absence of spherical symmetry allows the radial functions for the a_2 , t_2 , and t_1 components of the f orbitals to be different. These become differentiated by interactions, induced by the ligand field with configurations corresponding to both excitations on the lanthanide ion and, as a result of covalency, from the ligand to the lanthanide.

The number of operators is large because they must be scalars in the appropriate finite group, in contrast to the small number required in the continuous groups R_7 , G_2 , and R_3 that apply to the free ion. Their intractable number has led to various attempts at simplification. Newman proposed a spin-correlated crystal field^{11,12} (SCCF) which merely introduces one further parameter for each one-electron crystal-field parameter. The effect is to scale the one-body parameters by a factor that depends on the total spin quantum number S . Because states with maximum spin-multiplicity experience a smaller interelectron repulsion energy than those of lower multiplicity, configuration interaction should manifest itself in more contracted radial functions, and thus smaller crystal-field splittings. In practice the SCCF has been used with some success for Gd^{3+} and Ho^{3+} in a variety of hosts^{8,13,14} and for Sm^{3+} and Dy^{3+} in $\text{Cs}_2\text{NaLnCl}_6$.¹ The sign of the additional sixth rank parameter does not agree with this simple interpretation, but the correct sign can be obtained if the energy denominators of covalency contributions are taken into account.¹⁵

A further possible simplification is the orbitally correlated crystal field (LCCF) in which multiplets with different orbital angular momenta interact differently with the ligand field.⁶ The success of this approach has been limited to correcting the anomaly in the 1D_2 multiplet of Pr^{3+} .⁶ More general investigations of the CCF parameters have been applied to $^2H(2)_{11/2}$ of Nd^{3+} (Ref. 16) and several Er^{3+} multiplets in $\text{Cs}_3\text{Lu}_2\text{Br}_9$.¹⁷

Some guidance as to the physical significance of the various CCF operators is provided by the *ab initio* calculations of Ng and Newman on the PrCl_2^{2+} unit.^{18,19} They examined contributions from a variety of excited configurations up to second order in perturbation theory, using a basis set in which the metal-ion excited states are orthogonalized to the outer occupied ligand orbitals as well as to the intermediate core states of the lanthanide and its $4f$ -valence shell. Contributions to both the one-electron and the correlation crystal field can then be classified according to the nature of the contributing configurations.¹⁸

In a first-order calculation that uses only the lanthanide valence shell, the contribution to the one-electron crystal field comes primarily from the ligand point charge. In addition, the distinction between valence-shell orbitals arising from the orthogonalization procedure makes possible a small first-order contribution to the CCF parameters. More important contributions arise in second order. The most significant of these come from two classes of excited configurations: (a) ligand to valence-shell excitations, which include the effect of covalency, and (b) metal core (primarily $5p$) to valence-shell excitations, which reflect the core polarization and consequent shielding of the ligand field. We also note that contributions from configurations corresponding to ligand polarization [type (c)] are found to be very small relative to their role in the one-body crystal field.¹⁹

The results of this calculation can be projected onto an octahedral site using the superposition model.²⁰ Among the CCF operators with $K \geq 4$ that are required in this site symmetry, the parameters specifying the magnitude of the fourth-, sixth-, and eighth-rank contributions predominate. Further, the importance of the CCF parameters relative to the one-body crystal-field parameters of the same rank is predicted to be greater in type (b) than type (a) excitations. This suggests that an experimental test of the mechanism of the CCF can be made, by comparing its relative importance for a series of ligands that differ in the covalency of their interaction with the lanthanide ion. We have therefore sought to analyze the influence of the CCF in an isostructural set of halides.

The most extensive lanthanide ion energy-level data sets come from ions doped into low-symmetry sites such as in LaF_3 and LaCl_3 , which require up to nine one-electron parameters and a prohibitive number of CCF parameters.^{2,21} However, in octahedral symmetry, the crystal field can be specified by only two one-electron parameters and 26 CCF parameters, if those of rank $K > 8$ are ignored. In lanthanides that have no linear absorption in the near infrared, a large number of excited states can be located by two-photon spectroscopy.²² Using a combination of emission and two-photon excitation (TPE) spectroscopies, we have identified the crystal-field components of 26 multiplets in $\text{Cs}_2\text{NaTbX}_6$ ($X = \text{F}, \text{Cl}, \text{Br}$) up to $35\,000\text{ cm}^{-1}$.^{23,24} Their symmetry is usu-

TABLE I. One-electron crystal-field parameters for $\text{Cs}_2\text{NaTbX}_6$. n is the number of experimental energy levels and σ the standard deviation of the fit.

X	$B_0^{(4)}$	$B_0^{(6)}$	n	σ
Br	-1676	227	90	18.5
Cl	-1889	259	100	19.0
F	-3573	298	90	26.8

ally uniquely determined by the optical polarization, and when taken with data on the Zeeman interaction,²⁵ the level assignments become essentially unambiguous. These levels provide the most extensive data set so far reported for a lanthanide ion in a cubic site. The optical experiments and sample preparation are described elsewhere.²³

The energy levels were fit to a combined free-ion and crystal-field Hamiltonian of the form used by Reid and Richardson.¹ The one-electron crystal-field model was fit to each data set and the resulting crystal-field parameters are given in Table I. The overall crystal-field splitting increases in the expected order $\text{Br} < \text{Cl} < \text{F}$, in agreement with previous comparative studies of the elpasolites.^{26,27}

The accuracy with which the one-electron model reproduces the crystal-field energy levels varies dramatically between multiplets. We choose to quantify this by comparing the degeneracy-weighted standard deviation of the experimental energies of the components of each multiplet σ_e , with the standard deviation of the equivalent calculated levels σ_c .²⁸ To first order σ_e provides a measure of the effective crystalline field within the multiplet. When assessed in this way, the deviations from the one-electron model ($\sigma_e - \sigma_c$) are largely independent of the free-ion Hamiltonian, which locates the center of gravity of the multiplets. This approach is similar to that of Leavitt²⁹ who uses the second moment (σ^2) of a number of multiplets to obtain the field strength parameters s_k , rather than fitting individual levels to the crystal-field Hamiltonian. The percentage deviation of a multiplet is $100(\sigma_e - \sigma_c)/\sigma_c$.

In some regions of the spectrum, there is extensive mixing of the multiplet components by the crystal field.²³ In particular, $^5G_{4,3,2}$ and $^5L_{9,8,7,6}$ interact strongly. In addition, in $\text{Cs}_2\text{NaTbF}_6$ the large crystalline field leads to extensive J mixing in 5D_3 , $^5L_{10}$, and 5G_6 . The SLJ labels applied to many of these levels are therefore an oversimplification, and we avoid a discussion of deviations between calculated and experimental splittings in those states where the underlying multiplet character is poorly defined. For multiplets with a clear SLJ parentage, the crystal-field levels could be accurately reproduced by fixing the free ion parameters and varying the crystal-field parameters to optimize the fit within that multiplet alone. For a few multiplets some of the crystal-field levels were not observed experimentally, and the determination of an effective crystal field by this method could be used to give an estimate of the energy of the missing levels. These estimates were used where necessary in the determination of σ_e .

The percentage deviation of the majority of multiplets is illustrated in Fig. 1. It is apparent that while the splitting of the 7F_J and 5L_J multiplets is calculated quite accurately, large positive and negative deviations, of up to 80% of the

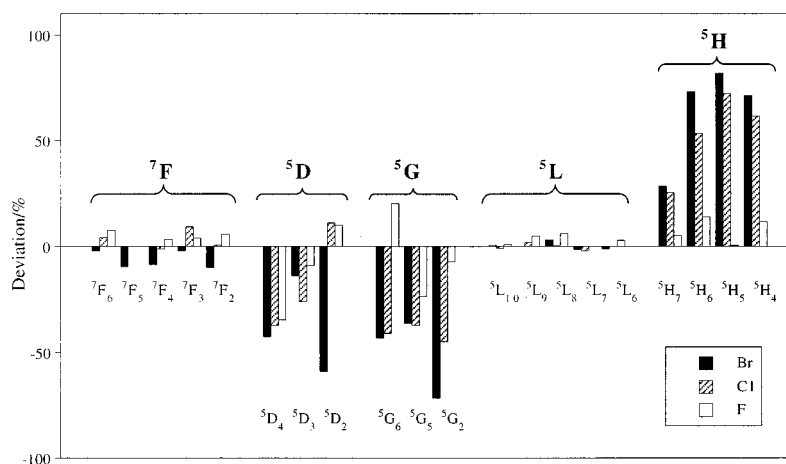


FIG. 1. The percentage deviation of each J multiplet in $\text{Cs}_2\text{NaTbX}_6$ ($X=\text{F}, \text{Cl}, \text{Br}$) from the one-electron crystal-field model.

theoretical value are observed in other cases. Together these provide a more comprehensive illustration of the role of the CCF than the data on solitary “rogue” multiplets. Only in the case of Er^{3+} in $\text{Cs}_3\text{Lu}_2\text{Br}_9$ have the CCF parameters been examined in the context of a number of multiplets.¹⁷ The extent of the effect in $\text{Cs}_2\text{NaTbX}_6$ suggests that the ${}^7\text{F}_J$ manifold and each excited-state multiplet experience a different effective crystal-field strength, and that the combined fit of all energy levels yields a weighted average value, about which systematic variations may be anticipated. Thus it is not surprising that the ${}^7\text{F}_J$ states are well described, due to their heavy weighting in the data set (20 levels out of 90) used to optimize the one-electron parameters.

The most significant feature of Fig. 1 is that the percentage deviations nearly always lie in the order $\text{Br} > \text{Cl} > \text{F}$, regardless of their sign. Among the multiplets shown in the figure, the significance of this trend is greatest when the SLJ parentage is well defined. This is true of all the ${}^7\text{F}_J$ states, as well as the ${}^5\text{D}_4$ and ${}^5\text{H}_{4,5,6,7}$ multiplets. In Fig. 1 we also include selected data on other multiplets, for which the eigenvectors indicate heavy J mixing, to illustrate that the trend broadly occurs in the same sense, even if the interpretation is not straightforward. For example, although ${}^5\text{G}_2$ is heavily mixed with ${}^5\text{L}$ states, the extent of the mixing is similar in all three compounds; since all ${}^5\text{L}$ states have small deviations, we believe that the trend in the deviations of the states labeled as ${}^5\text{G}_2$, is a true indication of the properties of this multiplet.

We have found that a SCCF Hamiltonian does not ac-

count for these deviations. As Reid⁸ has pointed out, the $g_{iQ}^{(K)}$ are orthogonal over the complete set of excited states, but the ninety states observed here represent only a small fraction of the total. Multiple parameter fits are therefore not satisfactorily convergent, and we continue to try to identify those $g_{iQ}^{(K)}$ that are important in modeling the observed deviations, by trial and error. Among the classes of excited configurations predicted to be important by Ng and Newman,¹⁹ those associated with core to valence excitations on the lanthanide ion [type (b)] are expected to be most significant with the strongly perturbing fluoride ion, but this is not substantiated by the data. On the contrary, the increasing importance of the CCF in the order $\text{F} < \text{Cl} < \text{Br}$ is consistent with large contributions from either covalent configurations [type (a)], or configurations describing ligand polarization [type (c)] or indeed both of these. The calculations of Ng and Newman, however, indicate that ligand polarization does not make a significant contribution to the CCF. If this is accepted, then the experimental data suggest a prominent role for covalency in the deviations from the one-electron model of the crystal field.

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¹M. F. Reid and F. S. Richardson, *J. Chem. Phys.* **83**, 3831 (1985).

²W. T. Carnall, G. L. Goodman, K. Rajnak, and R. S. Rana, *J. Chem. Phys.* **90**, 3443 (1989).

³D. Garcia and M. Faucher, in *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneider and L. Eyring (Elsevier, Amsterdam, 1995), Vol. 21, p. 263.

⁴P. A. Tanner, V. V. Ravi Kanth Kumar, C. K. Jayasankar, and M. F. Reid, *J. Alloys Compd.* **215**, 349 (1994).

⁵L. G. DeShazer and G. H. Dieke, *J. Chem. Phys.* **38**, 2190 (1963).

⁶Y. Y. Yeung and D. J. Newman, *J. Chem. Phys.* **86**, 6717 (1987).

⁷M. Faucher, D. Garcia, P. Caro, J. Derouet, and P. Porcher, *J. Phys. (France)* **50**, 219 (1989).

⁸M. F. Reid, *J. Chem. Phys.* **87**, 2875 (1987).

⁹B. R. Judd, *J. Lumin.* **18/19**, 604 (1979).

¹⁰B. R. Judd, *J. Chem. Phys.* **66**, 3163 (1977).

¹¹D. J. Newman, *Chem. Phys. Lett.* **6**, 288 (1970).

- ¹²B. R. Judd, Phys. Rev. Lett. **39**, 242 (1977).
- ¹³H. Crosswhite and D. J. Newman, J. Chem. Phys. **81**, 4959 (1984).
- ¹⁴Y. Y. Yeung and D. J. Newman, J. Phys. C **19**, 3877 (1986).
- ¹⁵D. J. Newman, G. G. Siu, and W. Y. P. Fung, J. Phys. C **15**, 3113 (1982).
- ¹⁶C. L. Li and M. F. Reid, Phys. Rev. B **42**, 1903 (1990).
- ¹⁷M. P. Hehlen, H. U. Güdel, and J. R. Quagliano, J. Chem. Phys. **101**, 10 303 (1994).
- ¹⁸B. Ng and D. J. Newman, J. Chem. Phys. **87**, 7096 (1987).
- ¹⁹B. Ng and D. J. Newman, J. Chem. Phys. **87**, 7110 (1987).
- ²⁰D. J. Newman, Adv. Phys. **20**, 197 (1971).
- ²¹G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley, New York, 1968).
- ²²A. J. Berry, R. G. Denning, and I. D. Morrison, Chem. Phys. Lett. **266**, 195 (1997).
- ²³A. J. Berry, I. D. Morrison, and R. G. Denning, Mol. Phys. **93**, 1 (1998).
- ²⁴A. J. Berry, R. G. Denning, C. S. McCaw, I. D. Morrison, and K. M. Murdoch (unpublished).
- ²⁵A. J. Berry, R. G. Denning, and I. D. Morrison, J. Chem. Phys. **106**, 8967 (1997).
- ²⁶M. F. Reid, F. S. Richardson, and P. A. Tanner, Mol. Phys. **60**, 881 (1987).
- ²⁷C. K. Jayasankar, F. S. Richardson, P. A. Tanner, and M. F. Reid, Mol. Phys. **61**, 635 (1987).
- ²⁸A. J. Berry, C. S. McCaw, I. D. Morrison, and R. G. Denning, J. Lumin. **66/67**, 272 (1996).
- ²⁹R. P. Leavitt, J. Chem. Phys. **77**, 1661 (1982).