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Theoretical Treatment of Gd^{+3} Terms Split in the Crystal Field of CaF_2†

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A theoretical treatment is given of the ${}^6P_J$ and ${}^6I_J$ terms of Gd^{+3} in CaF_2 split by either tetragonal or trigonal purely electrostatic crystal fields. A good fit with recently obtained experimental data is shown to exist for the ${}^6P_J$ case. In attempting to fit the ${}^6I_J$ terms with experiment we found it necessary to assume an unreasonably high crystal field. Thus, our conclusion that amendment to the ${}^6I_J$ free-ion energy eigenfunctions as given in the literature is needed.

1. INTRODUCTION

In a previous publication,[1] the spectral distribution of the thermoluminescent emission of Gd^{+3} in CaF_2 from different lattice sites was reported. The effect of the thermal history and differences of origin of crystals on the relative abundance of the rare-earth ion sites in the crystal matrix was shown.

Subsequently, the results of theoretical calculations pertaining to the ${}^9P_{7/2}\rightarrow{}^8S_{7/2}$ and ${}^6P_{5/2}\rightarrow{}^8S_{7/2}$ transitions of the Gd^{+3} ion in a tetragonal crystal field of CaF_2 were reported.[2] In those calculations, standard tensor operator methods[3] were employed to diagonalize the crystal-field Hamiltonian. The free-ion intermediate-coupling energy eigenfunctions published by Runciman[4] were used as base vectors.

The present work is an analysis of the Stark-split spectral lines of Gd^{+3} in crystals favoring the charge-compensating mechanism producing tetragonal point symmetry (Merz crystals[5]), and in those favoring trigonal symmetry (heat-treated 'Harshaw' crystals), of the local crystal field. Included are, with respect to the former, further calculations on the ${}^6P_J\rightarrow{}^8S_{7/2}$ transitions and the more complicated analysis of the observed ${}^6I_J\rightarrow{}^8S_{7/2}$ transitions. With respect to the latter, we deal with the Stark-splitting of the ${}^6P_J\rightarrow{}^8S_{7/2}$ lines that are observed experimentally.

One of the objectives of the present work was to test the applicability of the free-ion eigenfunctions of Runciman[4] and the improved version of these given by Wybourne.[6] Both sets of functions gave good agreement with experiment, when applied to the P-state spectrum, supporting the identification of the different point symmetries surrounding the rare-earth ion as a result of correspondingly different charge-compensating mechanisms.

The Runciman wave functions are inadequate to describe the I-state spectrum. Positive results, however, were obtained with the Wybourne set, although there are still some inconsistencies. A proposed identification of the origin of the groups of I lines that are illustrated in Fig. 5 of Ref. 1 (and reproduced here as Fig. 2) is given. The calculation allows us to comment on the relative positions of some of the free-ion excited I-states of Gd^{3+}. We find our interpretation to be in agreement with one investigator[7] and in slight disagreement with another.[8]

II. TETRAGONAL CRYSTAL FIELD

A. ${}^6P_J\rightarrow{}^8S_{7/2}$ Transitions

The tegragonal crystal field for the seven f electrons is given by

$$V=\sum_{i=1}^{7}\left[B_0{}^2(C_0{}^2)_i+B_0{}^4(C_0{}^{(4)})_i+B_4{}^4(C_4{}^{(4)}+C_{-4}{}^{(4)})_i\right.$$
$$\left.+B_0{}^6(C_0{}^{(6)})_i+B_4{}^6(C_4{}^{(6)}+C_{-4}{}^{(6)})_i\right],\quad(2.1)$$

where

$$(C_q{}^{(k)})_i=\frac{4\pi}{(2K+1)^{1/2}}Y_k{}^q(\theta_i,\phi_i).$$

With Runciman's wave functions, the quadrupole term is the only one of the field terms that has nonvanishing matrix elements in the P-state manifold. This is a consequence of Gd^{3+} having a half-filled shell (i.e., seven f electrons). A result of the admixture of the F-state component in Wybourne's P-state wave functions is that they do yield, in addition, nonzero matrix elements for the $C_0{}^4$ and $(C_4{}^4+C_{-4}{}^4)$ terms. Hence, the involvement of three free parameters rather than the single one in the Runciman case.

Figure 1 compares the experimentally[1] determined energy levels with both theoretical fits.

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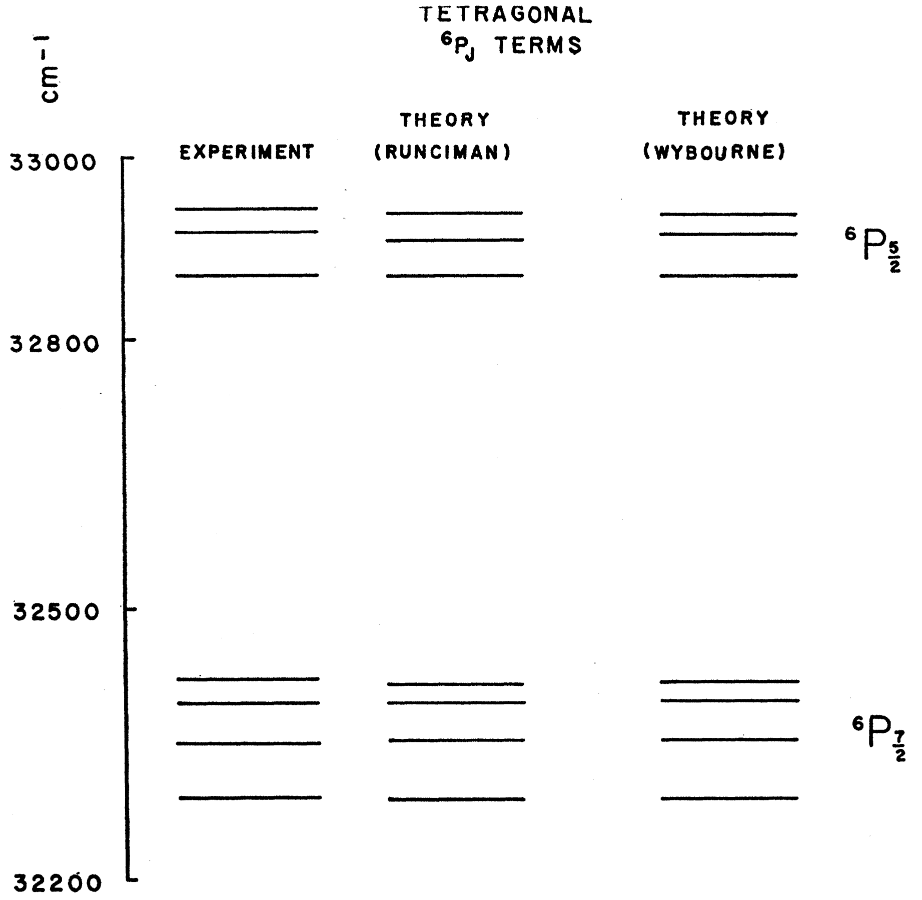

FIG. 1. Comparison of the experimentally determined energy levels with the two theoretical fits obtained using the wave functions of Runciman (Ref. 4) and Wybourne (Ref. 6), for the $^6P_J \to {}^8S_{7/2}$ transitions, in a tetragonal crystal field.

B. $^6I_J \to {}^8S_{7/2}$ Transitions

Figure 2 is the observed ^6I_J-$^8S_{7/2}$ thermoluminescent emission in the Merz crystal. Upon inspection, it is evident that the observed emission lines consist of three distinct groups. Our first objective was to determine whether each of these groups correspond to single ^6I_J manifolds (assuming that J is *approximately* a good quantum number). From the position of the center of gravity of the two lower energy emission line groups, their relative separations and as well the number of their components, we conclude that the lowest energy group corresponds to $^6I_{7/2} \to {}^8S_{7/2}$ transitions and the higher of the two to the $^6I_{9/2} \to {}^8S_{7/2}$ transitions. Our calculations imply, and we elaborate more fully below, that the remaining group (highest energy group) arises from states in the $^6I_{17/2}$-$^6I_{11/2}$ manifold (there is large admixture of the different J states here), and may include, perhaps, at the upper energy end some of the $^6I_{13/2}$ and $^6I_{15/2}$ states pushed down in energy by the crystal field (of course, one speaks here of the *major* J contribution to the given states as there is considerable mixing amongst the J-manifolds).

These identifications parallel those of Gilfanov *et al.*,[7] suggested by them for their absorption and constant-temperature luminescence results.

Figure 3 is a representation of the experimental results, and two attempted fits to the experimental data.

Once again the presence of a half-filled f-shell limits the numbers of nonvanishing matrix elements. Runciman's wave functions do not include any components which allow for nonzero matrix elements if we restrict ourselves to the total ^6I_J manifold. They, hence, could

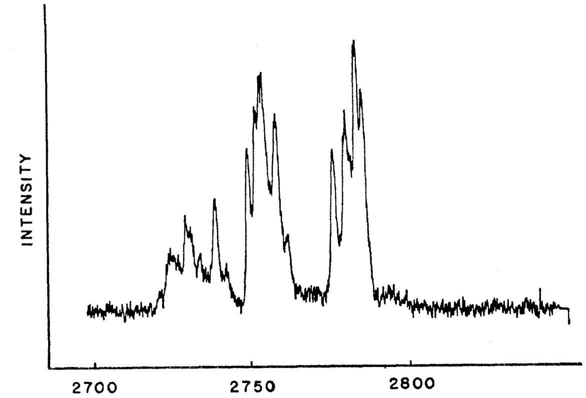

FIG. 2. Reproduction from Ref. 1 [Fig. 5(a)] of the observed $^6I_J \to {}^8S_{7/2}$ emission in the Merz crystals (tetragonal crystal field).

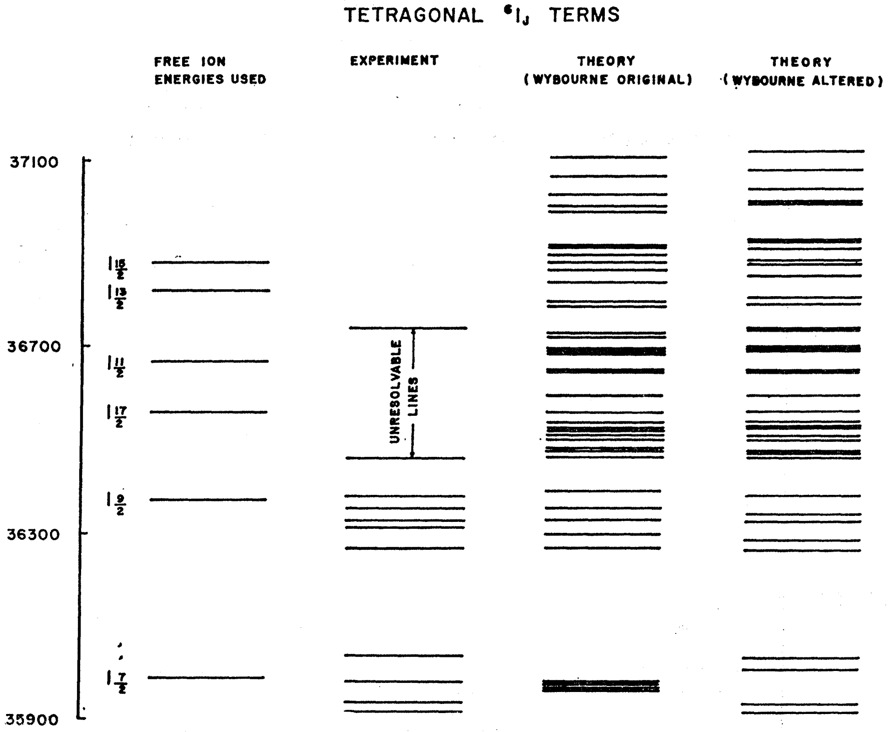

FIG. 3. Comparison of the experimental results with two different theoretical fits obtained using the wave functions of Wybourne for the observed $^6I_J \rightarrow {}^8S_{7/2}$ transitions in a tetragonal crystal field.

not possibly account for the large scale splittings that are observed.

Wybourne's energy eigenfunctions do contain an admixture of ^6H component in some of the ^6I states, which allows for nonzero matrix elements in this manifold. The results of our calculations make apparent, however, two shortcomings of these functions.

First, the lack in particular of any ^6H admixture in the $^6I_{7/2}$ manifold precludes obtaining theoretically stark-splitting to the extent observed experimentally for these states; e.g., our calculation indicates that a potential that gives the right-order-of-magnitude splitting for the 9/2 manifold would give for the 7/2 a theoretical splitting down by a factor of about 5 from the experimentally observed splitting (see Fig. 3). In one of our fits (see Fig. 3), a ^6H admixture (^6H coefficient $= -0.0317$) was artificially introduced to produce the right order of magnitude splitting for the $I_{7/2}$, the criterion for good fit, however, remained the minimization of the error for the $^6I_{9/2}$ states alone.

The second, and perhaps more serious, problem is an inconsistency between ^6P_J and the ^6I_J results. In fitting the ^6I_J data, a 39×39 matrix representing all the states of the ^6I manifold was diagonalized using the B_0^2, B_0^4,

TABLE I. Field coefficients used in the present calculations.

Transitions	Eigenvector set	Tetragonal field coefficients (cm⁻¹)	Trigonal field coefficients (cm⁻¹)
$^6P_J \rightarrow {}^8S_{7/2}$	Runciman[a]	$B_0^2 = -772$	$B_0^2 = -1630$ $B_2^2 = 275$
	Wybourne[b]	$B_0^2 = -657$ $B_0^4 = 389$ $B_4^4 = 466$	$B_0^2 = -1423$ $B_0^4 = -1798$ $B_3^4 = 0000$
$^6I_J \rightarrow {}^8S_{7/2}$	Wybourne[b] (original)	$B_0^2 = -657$ $B_0^4 = 389$ $B_4^4 = 466$ $B_0^6 = -18\,162$ $B_4^6 = -10\,498$	
	Wybourne[c] (altered) $^6I_{7/2} = -0.9644\,\vert {}_7{}^6I\rangle - 0.1884\,\vert {}_5{}^4H_{21}\rangle - 0.1579\,\vert {}_5{}^4H_{30}\rangle - 0.0317\,\vert {}^6H\rangle$	$B_0^2 = -657$ $B_0^4 = 389$ $B_4^4 = 466$ $B_0^6 = -18\,231$ $B_4^6 = -11\,442$	

[a] Reference 4. [b] Reference 6. [c] Present work.

and B_4^4 parameters as determined by the ^6P_J data. The additional terms of the potential which are operative for the ^6I states are so large to get the right magnitude of splitting (in both attempts) that, despite the fact that 3000 cm^{-1} separates the ^6I_J and ^6P_J manifolds, large mixing between them would theoretically occur. We do not think that this is the case in actuality, since a good fit was obtained in the ^6P_J transitions based on a diagonalization of the energy matrix within the ^6P_J manifold alone.

Perhaps different polarization effects could account for some difference of potential surrounding the ion in an I or P state, respectively, but there is no simple way of estimating this effect. A reasonably small increase in the ^6H admixture would undoubtedly lead to a fit with much smaller B_0^6 and B_4^6 coefficients; however, we did not feel justified in arbitrarily increasing the ^6H admixture without a detailed calculation of the free-ion energy eigenfunctions.

It is interesting that we noted in the diagonalization of the I-state energy matrix that, in order to obtain a reasonable interpretation of the data, the free-ion relative energies of the $I_{7/2} \leftrightarrow I_{9/2}$ and $I_{9/2} \leftrightarrow I_{17/2}$ (mainly the latter) needed to be closer to those reported by Gilfanov *et al.*[7] than to those of Hellwege *et al.*[8] In Table I, a summary is presented of the field parameters.

III. TRIGONAL CRYSTAL FIELD

As observed[1] experimentally, $GaF_2:Gd^{+3}$ crystals that have been heat-treated in the open air favor the charge-compensating mechanisms of a substitutional O^{-2} ion in nearest-neighbor lattice site. This results in a crystal field which is usually considered trigonal (C_{3v}). In these crystals, no emission due to transitions from the ^6I levels is observed.

In a first attempt, we employed Runciman's eigenfunctions in diagonalizing the energy matrix, but the results did not fit the experimental data. Because of the nature of this particular charge-compensating mechanism, the effect of the finite size of the ligand charges might be at least partially responsible for this lack of agreement. This effect might result in an additional small contribution to the local field in the form of an orthorhombic component. In keeping with this, a term $B_2^2(C_2^2+C_{-2}^2)$ was added to the crystal field resulting in a reasonable fit (Fig. 4).

An alternative explanation is allowed by the additional terms (^6F) of Wybourne's P-state wave functions which involve nonzero matrix elements of higher multiple terms in the potential. This permits one to preserve an interpretation involving a pure trigonal crystal field (see Fig. 4 and Table I).

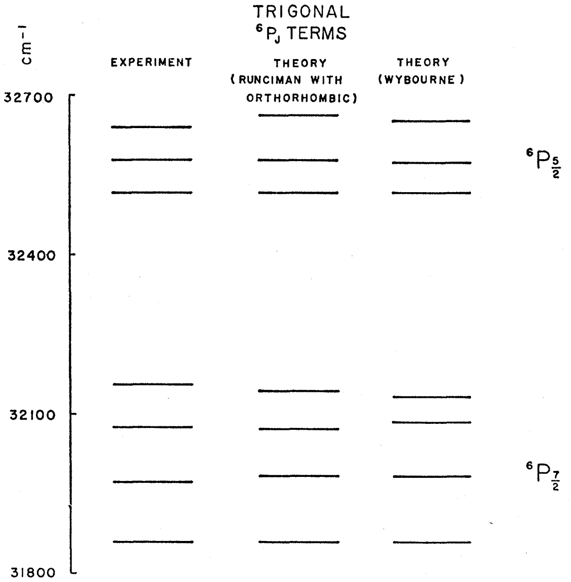

FIG. 4. Comparison of the experimental results with two theoretical fits obtained using the wave functions of Runciman (Ref. 4) and Wybourne (Ref. 6) (a small orthorhombic contribution was taken into account in the first) for the $^6P_J \rightarrow {}^8S_{7/2}$ transitions in a trigonal field.

IV. SUMMARY

An adequate description of the observed spectral lines corresponding to the $^6P \rightarrow {}^8S$ transitions was obtained in terms of a purely electrostatic model for both the tetragonal and trigonal point symmetries. In the latter case, however, the possibility of other symmetry potential terms being present was not ruled out.

In the case of the $^6I \rightarrow {}^8S$ transitions in tetragonal symmetries a reasonable fit to the observed spectra was obtained, requiring, however, unreasonably large fields which would produce considerable mixing with the ^6P states. But due to the good results obtained for the ^6P transitions based on a diagonalization of the energy matrix within the ^6P_J manifold alone, we feel that in reality the mixing between the ^6I and ^6P manifolds is small; and that the most probable answer to the ^6I problem of too-large fields is in improving the free-ion energy eigenfunctions.

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