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Calculation of the $^8S_{7/2}$ zero-field splitting for Gd^{3+}-doped LaF_3

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Calculations, based on crystal-field theory, are presented for the zero-field ground-state ($^8S_{7/2}$) splitting of Gd^{3+}-doped LaF_3 (single crystal). These agree, within experimental error, with those measured by electron paramagnetic resonance (EPR). This is the first case where a small (ground-state) zero-field splitting for Gd^{3+} can be explained through crystal-field theory alone, the results being in agreement with the excited-state splittings.

I. INTRODUCTION

It is well known that there exists a problem with the ground-state ($^8S_{7/2}$) splitting of Gd^{3+}. Specifically, the ground-state splittings as predicted by the use of the parameters derived from optical measurements on excited states do not agree with those obtained experimentally by EPR measurements. The debate over the S-state zero-field splitting (ZFS) problem goes back to Wybourne.[1] In considering the ZFS of gadolinium ethyl sulfate, he found that crystal-field theory (CFT) predicted that the $\pm\frac{7}{2}$ Kramers doublet is lowest, in contrast to the experimental result according to which the $\pm\frac{1}{2}$ Kramers doublet lies lowest. Wybourne concluded, as has since been consistently supported by theoretical calculations for various host crystals, that the observed ZFS cannot be explained by considering the ZFS to be a reflection of the splittings of the excited states of $4f^7$ into the ground state. Thus, if one were to find a case where the ZFS for the ground state, as computed by the use of parameters derived from optical measurements on excited states, was in agreement with those measured by EPR, the above contention would warrant a reexamination.

It is the purpose of the present paper to calculate the ground-state $^8S_{7/2}$ splittings for Gd^{3+}-doped LaF_3 (single crystal) using CFT for the excited-state parameters, and to compare them with those observed by EPR.

II. THEORY AND METHOD OF CALCULATION

A quick method of determining the ground-state splitting (using CFT), from measured excited-state splittings, has been developed by Antic-Fidancev, Lemaitre-Blaise, and Caro.[2] The next higher level (in Gd^{3+}) above the ground level ($^8S_{7/2}$) is $^6P_{7/2}$. They point out, from group-theory considerations (as originally discussed by Jones and Judd[3]), that the matrix elements for the crystal-field splittings of $^6P_{7/2}$ will be such that the second-order crystal-field parameters (CFP's) will be dominant, the fourth-order CFP's will be relatively small, and the sixth-order ones will be negligible. By giving appropriate values to Racah's parameters and the spin-orbit coupling constant, they find the energy solutions for the four $^6P_{7/2}$ Kramers doublets as functions of the second-order CFP's, A_2^0, and A_2^2. For axial symmetry ($A_2^2=0$), they thus get a graph of the $^6P_{7/2}$ splittings versus A_2^0. For a given case where the overall $^6P_{7/2}$ splitting is known from experiment, one can obtain, directly from the graph, the approximate A_2^0 value for that case. Similarly, by putting $A_2^0=0$ and plotting the splitting solution versus A_2^2, an approximate value for A_2^2 can be found. (N.B. There is no experimental example of a case where $A_2^0=0$.)

If the symmetry is low, then of course both A_2^0 and A_2^2 enter. To extract both of these from the data, the authors of Ref. 2 take the A_2^0 and A_2^2 values as derived using the method described above (A_2^0 for $A_2^2=0$ and A_2^2 for $A_2^0=0$) as defining the major and minor axes, respectively, of an ellipse. By plotting the positions of the two intermediate levels of $^6P_{7/2}$ (i.e., the $\pm\frac{5}{2}\leftrightarrow\pm\frac{1}{2}$ and $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ splittings as determined from optical data) as one goes around the ellipse and comparing these with the experimentally determined splittings, one gets three solutions for the pair (A_2^0,A_2^2). The correct solution can easily be determined using estimates based on point-charge-model calculations. Conversely, knowing the (A_2^0,A_2^2) so determined, and using graphs similar to those used for the $^6P_{7/2}$ multiplet, one could determine the $^8S_{7/2}$ ZFS. (This implies that the $^8S_{7/2}$ ZFS is a reflection of the $^6P_{7/2}$ ZFS via A_2^0, A_2^2.) In the case considered in Ref. 2, namely Gd^{3+}:La_2O_3, the predicted splittings did not agree with those determined from EPR measurements on the ground state.

III. APPLICATION TO THE CASE OF Gd^{3+}:LaF_3

The method of Ref. 2 was applied to the case of Gd^{3+}:LaF_3, truncating the Hamiltonian in the same way.

First, the measured $^6P_{7/2}$ splittings as reported by Caspers, Miller, and Rast,[4] (see Table I) were used to obtain the values of A_2^0 and A_2^2 using the graphs given in Ref. 2. These were found to be $A_2^0=-8700$ GHz $\pm5\%$,

TABLE I. Column 2 gives the $^6P_{7/2}$ splittings (Gd^{3+}:LaF_3) from Ref. 4. Column 3 gives the $^8S_{7/2}$ splittings as determined using the method of Ref. 2 (calc). Column 4 gives the measured $^8S_{7/2}$ splittings from Ref. 5 (expt).

Level	$^6P_{7/2}$ (GHz)	$^8S_{7/2}$ (calc) (GHz ±0.02 GHz)	$^8S_{7/2}$ (expt) (GHz ±0.01 GHz)
$\pm\frac{7}{2}$	1522.2	8.10	8.38
$\pm\frac{5}{2}$	734.7	4.05	3.93
$\pm\frac{3}{2}$	286.2	1.35	1.35

$A_2^2 = 1350$ GHz $\pm 12\%$. These values were then used to predict the (ground-state) $^8S_{7/2}$ splittings. The results are given in Table I. For this case, it was found that one does, indeed, reproduce the experimentally measured (by EPR) $^8S_{7/2}$ splittings as reported recently by Misra, Fabre, and Frandon.[5]

The ground-state $^8S_{7/2}$ splittings as measured by EPR for Eu^{2+}:LaF_3 have also been recently given in Ref. 5. These can be used as a means to check the applicability of the above method for a different case. Unfortunately, the method requires knowledge of the corresponding $^6P_{7/2}$ Eu^{2+}:LaF_3 ZFS obtained from optical data. These are not yet available. Furthermore, even if these were known, this case would present some problems as the charge of the doubly ionized Eu^{2+} is different from that of the triply ionized La^{3+} ion which Eu^{2+} replaces in the host lattice, causing local distortions which would significantly affect parameter values.[6]

IV. CONCLUSIONS

The present paper reports the first calculation on the basis of crystal-field theory which satisfactorily predicts the observed $^8S_{7/2}$ splitting. It should be noted that the Gd^{3+} zero-field splitting for the present case is rather small in contrast to those commonly observed.

It is hoped that the calculations of the present paper would stimulate a reexamination of the origin of the $^8S_{7/2}$ ground-state-splitting problem.

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