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PHYSICAL REVIEW B

VOLUME 3, NUMBER 11

1 JUNE 1971

Calculations of the Spectra of $\text{SrF}_2:\text{Gd}^{3+}$ in a Tetragonal Crystal Field*

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(Received 4 September 1970)

A theoretical calculation by means of parameter fitting to the experimentally observed crystal-field splittings of $\text{SrF}_2:\text{Gd}^{3+}$ for a tetragonal symmetry site is presented. The calculation uses free-ion wave functions which include spin-orbit, spin-other-orbit, spin-spin, and configuration interactions as basis vectors. The Stark splittings are calculated to all orders of the crystal field within the space defined by the first 15 free-ion states as basis. The tetragonal crystal-field coefficients were found to be $B_0^2=205.9$, $B_0^4=-1715.2$, $B_4^4=-1224.5$, $B_0^6=1874.6$, and $B_4^6=-499.5$ in cm^{-1} with a mean error of 7.0 cm^{-1} for 37 experimentally observed levels.

I. INTRODUCTION

The optical spectra of Gd^{3+} in crystals consist of transitions between the ground state ${}^8S_{7/2}$ and the nearest excited multiplets ${}^6(P, I, D)_J$. Theoretical calculations of the crystal-field spectra of Gd^{3+} in various MF_2 ($M = \text{Ca}, \text{Sr}, \text{or Ba}$) hosts and site symmetries have been the subject of recent investigations.¹⁻⁵ In Refs. 1 and 2, the cubic crystal-field splittings of the ${}^8S_{7/2}$ and ${}^6(P, I, D)_J$ multiplets of Gd^{3+} in MF_2 were determined by including all interactions between these multiplets to all orders throughout the crystal field. Nerenberg and Schlesinger³ and Nerenberg *et al.*⁴ have examined the tetragonal and trigonal sites of the 6P_J and 6I_J multiplets of Gd^{3+} in CaF_2 . Gilfanov *et al.*⁶ have experimentally observed tetragonal sites of the 6P_J and ${}^6I_{7/2}$ levels of Gd^{3+} in CaF_2 and SrF_2 , and Ivoilova⁵ has done some theoretical calculations on these levels. Recently, Detrio *et al.*⁷ have experimentally identified many of the tetragonal 6P_J , 6I_J , and 6D_J levels of Gd^{3+} in SrF_2 , thereby making it possible to do a detailed calculation to determine the tetragonal crystal-field coefficients of that system.

A number of calculations will be presented here in order to show the importance of including the interactions between all the ${}^8S_{7/2}$, ${}^6(P, I, D)_J$ free-

ion states when determining the crystal coefficients for any one of these multiplets. Firstly, the calculations were done for the 6P_J and 6I_J multiplets independently; that is, the matrix of the free ion plus the crystal-field interaction for the 6P_J multiplets was set up and diagonalized. By iterating this process, the eigenvalues were fitted to the experimental levels, with a similar procedure for the 6I_J multiplets. Next the splittings of the 6P_J multiplets were calculated by fitting the 6P_J eigenvalues of the matrix of the free-ion energy levels plus the crystal-field interaction between the ${}^8S_{7/2}$, ${}^6(P, I, D)_J$ free-ion states to the experimentally observed levels of 6P_J ; again the same calculation was done for the 6I_J and the 6D_J multiplets. Finally, in order to examine the possibility of fitting all of these levels simultaneously—that is, finding one set of crystal-field coefficients for all of these multiplets—the eigenvalues of the matrix of the free-ion energy levels and the crystal-field interaction between the ${}^8S_{7/2}$, ${}^6(P, I, D)_J$ free-ion states were fitted to the 6P_J and 6I_J experimental levels. The calculation was again repeated but with the addition of the ${}^6D_{9/2, 7/2}$ to the experimental lines included in the fitting procedure. No attempt to fit the ${}^8S_{7/2}$ levels was made; rather, it was of more interest to include them in the diagonalization and see how much ground-state splitting was produced by fitting the excited states.

II. CALCULATIONAL DETAILS

Since the electronic configuration of Gd^{3+} is f^7 , a half-filled shell, no first-order interactions occur for pure Russell-Saunders states. It is therefore necessary to obtain good intermediate coupled wave functions prior to calculating the crystal-field interaction. Several authors⁸⁻¹¹ have determined parameters necessary to calculate the free-ion wave functions of Gd^{3+} in various host crystals. These free-ion wave functions generally contain interaction terms due to Coulomb repulsion, spin-orbit, spin-other-orbit, spin-spin, and configuration interactions. We have obtained free-ion state vectors in essentially the same manner as Crosswhite, Schwiesow, and Carnall,¹¹ who determined the parameters necessary to reproduce the free-ion spectrum of $\text{CaF}_2:\text{Gd}^{3+}$.

The crystal-field Hamiltonian for tetragonal symmetry may be written as

$$H_{\text{cf}} = \sum_i [B_0^2(C_0^2)_i + B_0^4(C_0^4)_i + B_4^4(C_4^4)_i + B_0^6(C_0^6)_i + B_4^6(C_4^6)_i],$$

where the summation i is over the electrons of the Gd^{3+} ion and the C_q^k are tensor operators proportional to spherical harmonics,

$$C_q^k = [4\pi/(2k+1)]^{1/2} Y_{kq}(\theta, \mu).$$

In calculating the crystal-field splitting of the free-ion states, one may use standard Rayleigh-Schrödinger perturbation theory or one may calculate and diagonalize the matrix of the free-ion energies and the crystal-field Hamiltonian using the intermediate coupled wave functions as basis vectors. However, a complete diagonalization using all states within the f^7 configuration, because of the number of allowable states, involves matrices which are too large. The approach used here is to ignore most of the states that are separated from the ones of interest (6P_J and 6I_J) by large energy differences, thus giving much smaller matrices to diagonalize.

The simplest approximation, after first order, is to include only those states of a nominal LS multiplet as the basis states for calculating the crystal-field matrix. This means that for the 6P_J group, after applying Kramer's theorem and block diagonalizing according to the crystal quantum numbers μ of Hellwege,¹² one must diagonalize a 4×4 matrix for the $\mu = \frac{1}{2}$ crystal quantum number and a 5×5 matrix for the $\mu = \frac{3}{2}$ crystal quantum number. For the 6I_J group this results in a 20×20 matrix for the $\mu = \frac{1}{2}$ crystal quantum number and a 19×19 matrix for the $\mu = \frac{3}{2}$ crystal quantum number. It has been observed, however, that the contribution to the Stark splitting from other adjacent LS free-ion states is quite significant and therefore

that the crystal-field parameters obtained without taking these adjacent states into account are not accurate.^{1,2} To include these higher-order interactions from adjacent multiplets, the basis states were expanded to include the first 15 free-ion states of the f^7 configuration, that is, all of the J states of ${}^8S_{7/2}$ and ${}^6(P, I, D)_J$. Again applying Kramer's theorem and block diagonalizing by the μ 's, one obtains a 34×34 matrix for the $\mu = \frac{1}{2}$ and a 33×33 matrix for the $\mu = \frac{3}{2}$ crystal quantum numbers.

The procedure for fitting the eigenvalues of the matrix of the operator $H_{\text{fi}} + H_{\text{cf}}$ is to minimize a function of the five B_q^k parameters of tetragonal symmetry. The function minimized was

$$F(B_0^2 \cdots B_4^6) = \sum_i W_i [\Delta\lambda_i (B_0^2 \cdots B_4^6) - \Delta E_i]^2,$$

where $\Delta\lambda_i$ is the calculated theoretical splitting of the Stark component from the theoretical center of gravity of a particular $2S+1L_J$ state, ΔE_i is the experimental splitting of the i th component from the experimental center of gravity, and W_i is a weighting factor (taken to be zero or one in this calculation). It is important to fit splittings from the center of gravity rather than fitting the B_q^k 's to yield agreement with the actual experimental positions of the levels for the following reason: The free-ion basis vectors were obtained using the parameters of Crosswhite *et al.*,¹¹ which were fitted to $\text{CaF}_2:\text{Gd}^{3+}$ data; thus they are not "true" free-ion vectors because they include the shift in the center of gravity due to the CaF_2 crystal field. This will be true for any "free-ion" calculation that is fitted to crystalline or solution data.¹³ Therefore, if we fit the theoretical lines to the positions of the experimental lines, the B_q^k 's will try to accommodate this center-of-gravity shift and distort the B_q^k 's. An alternative way of overcoming this difficulty has been provided by Margolis,¹⁴ who added small correction terms along the diagonal to compensate for the center-of-gravity shift. This center-of-gravity shift will be different for different LS states, thus also making it difficult to determine if one set of crystal-field parameters can describe the Stark splittings for the first 15 multiplets of the free-ion configuration. Fitting to the splittings from the center of gravity will partially nullify this difficulty. Finally, in order to plot the experimental and theoretical lines on the same scale, the energy levels were shifted by an additive constant after the minimization for the B_q^k 's was carried out.

One other problem occurs in fitting the 6I_J group. Detrio *et al.*⁷ have experimentally identified most but not all of the lines of this group. Therefore, in the fitting procedure there are some experimental lines missing. The result of this is that one can obtain many fits which yield roughly the same size

TABLE I. Tetragonal crystal-field parameters for a $(2S+1)L$ multiplet using only the $(2S+1)L_J$ free-ion states of that multiplet as basis vectors.

	6P	6I
B_0^2	373.0	183.1
B_0^4	-1535.4	-1029.4
B_4^4	-1033.0	-1703.2
B_0^6	2390.0	7325.2
B_4^6	-2997.9	-2652.8
Mean error	0.01	7.1

residue but which give radically different values of the B_q^k 's. This may be contrasted to the cubic case, where fitting the 6P_J group yielded only two minima and one of these was not physically acceptable since the order of the irreducible representations was known.^{15,16} This, however, is not the case for tetragonal symmetry. To overcome this difficulty and fit the spectra in the manner described above, the following procedure was used. Several different fits that gave residues of about the same size, $F(B_0^2 \dots B_4^6)$, were found. Some were eliminated on the basis of their qualitative comparison with the observed spectra. Then the "best" fit was selected as the one which represented the smallest perturbation from the cubic parameters. The missing experimental lines were then assigned the theoretical value, the minimization procedure repeated but with these lines having zero weight, and a new value for the theoretical lines obtained. This process was repeated until there was self-consistent agreement between the calculated theoretical splitting of the missing lines and the assumed splitting.

III. RESULTS AND DISCUSSION

Table I gives the values of the B_q^k 's for the 6P_J group and the 6I_J group of lines when only crystal-field interactions within an LS multiplet are considered. Table II shows how these coefficients change when the first 15 free-ion states are allowed to interact through the crystal field. We see from Table I that a very large value of B_0^6 is required to fit the 6I_J group of lines. Schlesinger and Nerenberg³ and Nerenberg *et al.*⁴ also required very large values of both B_0^6 and B_4^6 in fitting the 6I_J spectra in $\text{CaF}_2:\text{Gd}^{3+}$; however, one sees from Table II that this problem disappears when we include interactions of the 6I_J multiplets with the adjacent ${}^6S_{7/2}$ and ${}^6(P, D)_J$ states. The need for including these higher-order interactions from other free-ion states is emphatically demonstrated in column B of Figs. 1 and 2. Column A of Figs. 1 and 2 shows the comparison between the theoretical

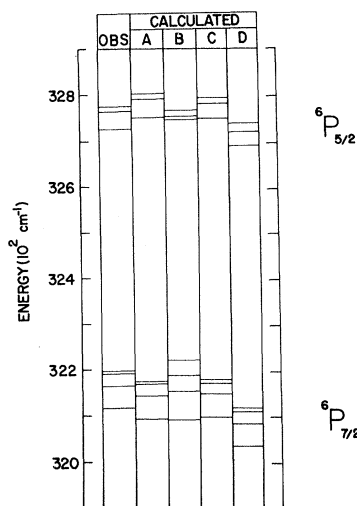


FIG. 1. Observed (Ref. 7) and calculated 6P_J multiplet spectrum of a tetragonal site in $\text{SrF}_2:\text{Gd}^{3+}$. See Sec. III for explanation of columns A-D.

and experimental splittings for the calculations expressed by Table I, whereas column B shows what happens to the quality of these fits if we use the coefficients obtained in Table I to calculate the crystal-field spectra of the 6P_J and 6I_J lines, but include all interactions from the first 15 free-ion states. That is, we diagonalize the matrix of $H_{t1} + H_{ct}$ with all states of ${}^6S_{7/2}$ and ${}^6(P, I, D)_J$ as basis, but use the coefficients of Table I, which were obtained from fitting the eigenstates of the smaller basis. Column B of Figs. 1 and 2 shows that the quality of agreement between theory and experiment has so deteriorated that coefficients obtained by the method used in obtaining Table I have little meaning. In fact, some of the ${}^6I_{13/2}$ lines in column B of Fig. 2 are 700 cm^{-1} above the scale of Fig. 2 and could not be included in the diagram.

Column C of Figs. 1 and 2 shows the comparison between the theoretical and experimental splittings

TABLE II. Tetragonal crystal-field parameters for a $(2S+1)L$ multiplet using the first 15 free-ion states as basis vectors but only the $(2S+1)L_J$ states as experimental data for the fitting procedure.

	6P	6I
B_0^2	194.0	257.5
B_0^4	-1658.3	-1679.8
B_4^4	-685.8	-1296.8
B_0^6	1985.2	1846.9
B_4^6	-910.1	-450.8
Mean error	0.4	7.8

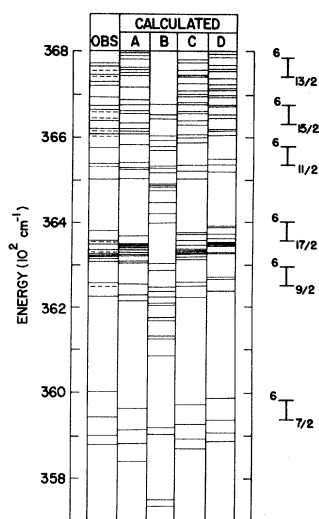


FIG. 2. Observed (Ref. 7) and calculated 6P_J multiplet spectrum of a tetragonal site in $\text{SrF}_2:\text{Gd}^{3+}$. See Sec. III for explanation of columns A–D. The dotted lines represent levels missing from the experimental observations.

expressed by the calculation of Table II. Here the first 15 free-ion states were used as basis vectors, but only the $(2S+1)L_J$ states of a particular $(2S+1)L$ multiplet were used as experimental data for the fitting procedure. Finally, even though the coefficients in Table II obtained for 6P_J lines differ from those for the 6I_J lines, it was of interest to see if one set of coefficients could be obtained for both 6P_J and 6I_J lines without causing a significant decrease in the quality of the fit. Here again the first 15 free-ion states were used as basis vectors, but now both the 6P_J and 6I_J experimental lines were used as data for the fitting procedure. The result of this calculation gave the following results for the B_q^k 's in cm^{-1} : $B_0^2 = 205.9$, $B_0^4 = -1715.2$, $B_4^4 = -1224.5$, $B_0^6 = 1874.6$, and $B_4^6 = -499.5$, with a mean error of 7.0 cm^{-1} . This calculation is shown in column D of Figs. 1 and 2.

Detrio *et al.*⁷ have identified what appear to be the nine lines belonging to the ${}^6D_{9/2,7/2}$ levels in $\text{SrF}_2:\text{Gd}^{3+}$. However, when attempting to fit these levels in the calculation, we could not obtain a fit which was consistent with those obtained for the 6P_J and 6I_J levels. This inability of one set of crystal-field parameters to account for the splitting

of different multiplets of a particular configuration has been previously noted by Eisenstein¹⁷ and is regarded as being due to neglect of interactions with higher configurations. Indeed, Rajnak and Wybourne¹⁸ have shown that an electrostatically correlated crystal-field interaction would differ for different LS multiplets in such a way that the crystal-field parameters could be different for each LS free-ion state, depending upon the strength of the interaction. In addition, however, there are other intraconfiguration states which could have significant effect on the 6D_J levels and thus in part explain our inability to find a reasonable fit for these levels. We have shown the necessity of including interactions of adjacent free-ion states when trying to calculate the crystal-field splitting of a particular LS multiplet. For the case of the 6D_J states there are f^7 states above the 6D_J levels (6G_J , 6F_J , 6H_J) which have not been included in the calculation and supposedly could noticeably affect the calculated splitting. However, to include these higher states would require extending the basis and result in untractably large matrices.

Finally, in the above calculations for the excited-state splittings, we also obtained a splitting for the ground state of 0.38 cm^{-1} . This represents 28% of the ground-state splitting of $\text{SrF}_2:\text{Gd}^{3+}$ found by Sierro.¹⁹ Thus, part of the ground state is accounted for by the crystal field seen by the excited states, but if crystal field alone were to account for the ground-state splitting, it would be necessary to assume a crystal-field interaction for the ground state which is three times larger than that seen by the excited states. This is, of course, unrealistic.

In conclusion, we have found a set of crystal-field coefficients for the tetragonal site of $\text{SrF}_2:\text{Gd}^{3+}$ which will, when we include crystal-field interactions between the ${}^8S_{7/2}$, ${}^6(P, I, D)_J$ states, give a good fit to the 6P_J and 6I_J levels, produce 28% of the ground-state splitting, but give a poor description of the ${}^6D_{9/2,7/2}$ levels observed by Detrio *et al.*⁷

ACKNOWLEDGMENTS

The author is indebted to J. A. Detrio, Dr. V. L. Donlon, and Dr. P. P. Yaney for useful discussions.

*Work supported by U. S. Air Force Contract No. F336515-69-C1172.

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Mössbauer-Effect Observations of Th²³² following Coulomb Excitation*

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(Received 29 January 1971)

Resonant absorption following Coulomb excitation has been observed for γ rays from the first excited state of Th²³² in Th metal and ThC targets with ThO₂, Th metal, ThN, and ThC₂ absorbers. Most spectra were obtained with targets at 30 °K and absorbers at 25 °K using 1- μ A beams of 6-MeV He⁴⁺ ions. Absorber and target recoilless fractions (f_a and f_s) and zero-thickness absorber linewidth (Γ_0) were determined from a series of measurements of the width (half-width at half-maximum) of absorption spectra versus absorber thickness. These spectra were obtained with Th metal targets and ThO₂ absorbers. We find that $f_a = 0.35 \pm 0.04$ and $f_s = 0.31 \pm 0.06$, which correspond to a Debye temperature of (121 ± 13) °K. The zero-thickness linewidth Γ_0 , uncorrected for target-absorber geometry, was found to be 11.35 ± 0.26 mm/sec. The value of Γ_0 , corrected for broadening due to the geometry of the experimental configuration, was estimated to be 9.6 ± 0.4 mm/sec.

I. INTRODUCTION

For several years it has been realized that, in principle, the Mössbauer effect could be used to study the actinide elements and their γ transitions from the low-lying levels.¹ With the exception of Np²³⁷,^{2,3} Am²⁴³,⁴ and U²³⁸,⁵ such studies have not been carried out because of the lack of suitable radioactive sources. Oleson *et al.*⁶ partially overcame this difficulty for U²³⁸ by using Coulomb excitation to excite the 2⁺ level. However, data accumulation was slow because of the large internal-conversion coefficient of U²³⁸ (approximately 600). Since large internal-conversion coefficients characterize nearly all actinide nuclei, Mössbauer-effect experiments utilizing resonant absorption following Coulomb excitation (RACE) inevitably encounter the same difficulty with count rates. Th²³² is suitable for RACE experiments because the ground state has an extremely long half-life (1.4×10^{10} yr) and the 49.8-keV E2 transition from the first excited state is relatively far from the

characteristic K and L x rays.

The first Mössbauer-effect measurements of Th²³² were made by Hershkowitz *et al.*⁷ following Coulomb excitation by a 1.5- μ A beam of 4.5-MeV He⁴⁺ ions. The absorber (ThO₂) and target (Th metal) were cooled to near liquid-nitrogen temperatures. The half-width at half-maximum (HWHM) of the observed Mössbauer line was found to be 8.35 mm/sec. We have reevaluated the uncertainty of this measurement using an improved statistical procedure and also taking into account some systematic errors and find that the HWHM was 8.4 ± 1.4 mm/sec which corresponds to a half-life of 0.33 ± 0.06 nsec. This result agrees with earlier electronic measurements of 0.345 ± 0.015 nsec.⁸

The primary difficulties encountered by Hershkowitz *et al.* were low count rate (about 120/sec) and a small percent effect (about 1.2%) which could be attributed, respectively, to substantial internal conversion (the internal-conversion coefficient for Th is approximately 255)⁹ and to small recoilless fraction at liquid-nitrogen temperature. The con-