Tensor polarizabilities of the $4f^7(8S)\,5d\,6s^2\,9D_{2,3,4,5,6}$ levels in Gd I

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Received: 17 December 1992

Abstract. The optical pumping method with rf detection and the nonlinear level crossing technique were used in parallel electric and magnetic fields to investigate the Stark splitting of all the fine structure levels of the ground multiplet $4f^7(8S)\,5d\,6s^2\,9D$ in Gd I. The tensor polarizabilities were deduced from the level crossing and the rf signals. The variation of the tensor polarizabilities is well reproduced by the LS coupling approximation, except for the small value of the $9D_5$ level. A value of the tensor polarizability of the $5d$ electron is evaluated from the experimental results, $\alpha(5d) = 2.00(6)\,\text{kHz/(kV/cm)}^2$. It is shown that the ratio between the electric quadrupole constant and the tensor polarizability is constant, except for the $9D_5$ ratio, which is caused by a breakdown of the central field model.

PACS: 32.60.+i; 32.80.Bx

Introduction

The polarizabilities appear in many formulae for low-energy processes involving the valence electrons of atoms or molecules, for instance the description of the dielectric constant, the diamagnetic susceptibility, the long-range electron- or ion-atom interaction energy, or the van der Waals constant between two systems. For further detailed information and references the reader is referred to [1, 2]. Nevertheless, experimentalists have determined ground state polarizabilities only for the extremities of the periodic table, and have hardly touched the interior columns [3]. Accurate values of atomic polarizabilities [2] exist primarily for the alkaline metals, the alkaline earths, the noble gases and some inroads as In and Tl. Therefore we have started a programme to study the Stark splitting of levels of the ground multiplet of atoms with open electron shells. Recently we reported on measurements of the tensor polarizabilities of the $4f^6\,6s^2\,7F_{1,2,3,4,5,6}$ levels in Sm I [4, 5].

The subject of the present paper is the first measurement of the tensor polarizabilities of all levels of the ground multiplet $4f^7(8S)\,5d\,6s^2\,9D_{2,3,4,5,6}$ in Gd I. Two essentially independent experimental methods were used to obtain the values of the polarizabilities. These are the optical pumping method with rf detection and the nonlinear level crossing technique [6, 7]. Using the experimental results the validity of the central field approximation in the ground multiplet of Gd I was discussed and confirmed, except for the $9D_5$ level.

Measurements and results

Our experimental investigations of the Stark effect were carried out mainly on the even isotopes of Gd. In the present experiment collinear electric and magnetic fields were used. The energy $\Delta W(JM)$ of a sublevel $|JM\rangle$ of a free atom in a magnetic and electric field has a linear dependence on the magnetic field $B$ and a quadratic dependence on the electric field $\delta$. It is given by

$$\Delta W(JM) = g_J \mu_B MB - \left[ \alpha_0(J) + \alpha_2(J) \right] \cdot \left[ 3 M^2 - J(J+1) \right] / \left[ J(2J-1) \right] \delta^2 / 2,$$

where $g_J$ is the Landé factor, $\mu_B$ the Bohr magneton, $\alpha_0(J)$ the scalar and $\alpha_2(J)$ the tensor polarizability.

In a $(\Delta J=0, \Delta M=2)$ or $(\Delta M=1)$-level crossing experiment or an optical pumping experiment with $(\Delta J=0, \Delta M=1)$ rf detection, $\alpha_0$ cannot be observed, since $\alpha_0$ describes an overall shift. The term with $\alpha_2$ causes a shift of the sublevels depending on the $M$ value. This results in a shift of the value of the magnetic field strength at which the level crossing signal or the rf signal occurs.

A scheme of the experimental set up of the experiments is shown in Fig. 1. The optical pumping experiments were performed by resonantly exciting atoms in an atomic beam of natural Gd by the light of a single mode cw dye laser linearly polarized parallel or perpendicular to the direction of the magnetic field in order to populate the different sublevels selectively. The fluo-
The resonant light was observed as a function of the magnetic field, whereas the static electric field and the rf field remained fixed. The magnetic field was produced across the interaction region by a pair of Helmholtz coils. The current through the Helmholtz coils was measured by means of a temperature-controlled high precision resistor and a voltmeter. The magnetic field was calibrated using an optical pumping experiment with rf detection in the $^{4f_6s_2}F_1$ level in Sm I, of which the $g_j$ value is known with high accuracy [8]. The current through the Helmholtz coils was generated by a power supply which was controlled by a computer.

Parallel to the magnetic field an electric field up to $\varepsilon = 200 \text{ kV/cm}$ was produced between the Stark plates. It was calibrated using the Stark effect of the Sm I line 572.0 nm, which is known with high accuracy [9]. The oscillating rf field perpendicular to the magnetic field was generated in the interaction region. The amplitude of the rf field was modulated for lock-in detection. The signal from the lock-in amplifier was stored on a computer. The conventional signal averaging technique was used to enhance the signal to noise ratio.

As an example, Fig. 2 shows an rf resonance signal of the $^{4f_7 5d 6s_2}g D_3$ level. The rf signal was subjected to a least squares fit procedure to extract the exact position of the resonance. Since the $g_j$ factors of the ground multiplet are known [10, 11], the tensor polarizability can be derived, using (1), from the magnetic field value at which the signal occurs. Only the absolute value of the tensor polarizability can be determined from the rf signal of an even isotope.

As a second experimental method we used the nonlinear level crossing technique. The level crossing signals occur whenever sublevels coupled by an optical transition are degenerated. The shape of the signal is determined by the level in which the degeneracy occurs, while the other level involved in the optical transition acts only as a coupler. In our experiment we have observed the level crossing signals in emission. Effects due to the crossing of sublevels in the lower level can therefore only appear by transferring their coherence to the upper level.

For a detailed discussion of the nonlinear level crossing effect the reader is referred to [12, 13]. The line shape of a level crossing signal in fluorescence depends on the direction of observation and polarization. Using the experimental setup described below, the line shape is Lorentzian or a sum of Lorentzians [12].

The experimental setup was the same as for the optical pumping experiment (Fig. 1), but no rf field was needed. An amplitude modulation was superimposed on the scanning magnetic field for lock-in detection. The modulation depth was chosen so that the observed signal could be related to the derivative of the level crossing resonance. The laser light was linearly polarized perpendicular or at an angle of 45° to the direction of the magnetic field in order to measure $(\Delta M = 2)$- or $(\Delta M = 1)$-level crossing signals.

Usually a superposition of level crossing signals of the upper and lower levels is observed. In this work contributions of the excited levels to the observed level crossing signals were suppressed by choosing suitable transitions. In these the polarizabilities of the excited levels were so large that the level crossings of the sublevels were at lower electric field strengths than the level crossings of the sublevels of the lower levels. Typical examples are given in Fig. 3. It shows the recording of $(\Delta M = 2)$-level crossing signals of the $^{4f_7 5d 6s}D_4$ and $^3D_4$ levels in electric and magnetic fields. The level crossing signals were subjected to a least squares fit procedure to extract the exact positions of the level crossings (Fig. 3). Using (1) the tensor polarizability was derived from the magnetic field value at which the signal occurs. As in the optical pumping experiment, only the absolute value of the tensor polarizabilities can be determined.

In order to derive the sign of the tensor polarizabilities of the levels of the ground multiplet, a level crossing signal of an odd Gd isotope was observed in parallel magnetic and electric fields. The sign and the absolute
Fig. 3. Dotted line, registration of nonlinear level crossing signals of the lower level in the transitions a) \(4f^7 5d 6s^2 9D_2 - 4f^7 5d 6s 6p 9D_2\) and b) \(4f^7 5d 6s^2 9D_2 - 4f^7 5d 6s 6p 9P_5\) of \(^{155}\text{Gd}\). Solid line, fit curve. G: \(\Delta M = 2\)-level crossing in the \(9D_2\) level between the Zeeman levels \(|2, 0\rangle, |2, 2\rangle\) at an electric field strength of \(E = 141\) kV/cm. J and K: \(\Delta M = 2\)-level crossings in the \(9D_4\) level between the Zeeman levels \(|4, 2\rangle, |4, 4\rangle\), and \(|4, 1\rangle, |4, 3\rangle\), respectively, at an electric field strength of \(E = 140\) kV/cm.

value of the tensor polarizability can be derived from this signal using the hyperfine constants of this level. The hyperfine structure was measured by Unsworth using atomic beam magnetic resonance [14], and by Niki et al. [15], and Jin et al. [16] using atomic beam laser spectroscopy. The hyperfine Zeeman splitting of the \(4f^7 5d 6s^2 9D_2\) level of \(^{155}\text{Gd}\) as function of the magnetic field \([\ldots] F = 3/2; \ldots F = 1/2\]. \(0(\Delta M = 2)\)- and \((\Delta M = 1)\)-level crossings.

Fig. 4. Hyperfine Zeeman levels of the \(4f^7 5d 6s^2 9D_2\) state of \(^{155}\text{Gd}\) as function of the magnetic field \([\ldots] F = 7/2; \ldots F = 5/2; \ldots F = 3/2; \ldots F = 1/2\]. \(0(\Delta M = 2)\)- and \((\Delta M = 1)\)-level crossings.

Fig. 5. Measured and calculated magnetic field positions of the level crossing signal between the hyperfine Zeeman levels \(|F, M\rangle = |3/2, 1/2\rangle, |5/2, 5/2\rangle\) of the \(4f^7 5d 6s^2 9D_2\) level of \(^{155}\text{Gd}\) in dependence on the electric field strengths. Dashdot line, for a positive value; solid line, for a negative value of the tensor polarizability. \(\Omega\) measured values.

Table 1. Tensor polarizabilities \(\alpha_2(J)\) of the fine structure levels \(4f^7(8S) 5d 6s^2 9D_{2,3,4,5,6}\) in \(^{155}\text{Gd}\) and derived \(\alpha_2(5d)\) values using wave functions (i) of Unsworth [14] and (ii) of Eremin and Maryakhina [18] (see text). Tensor polarizabilities in kHz/(kV/cm)^2.

<table>
<thead>
<tr>
<th>Level</th>
<th>Energy [cm(^{-1})]</th>
<th>(g_J) [17]</th>
<th>(\alpha_2(J))</th>
<th>(\alpha_2(5d)) (i)</th>
<th>(\alpha_2(5d)) (ii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9D_2)</td>
<td>0</td>
<td>2.6514</td>
<td>0.58(4)</td>
<td>2.03(14)</td>
<td>2.05(14)</td>
</tr>
<tr>
<td>(9D_3)</td>
<td>215</td>
<td>2.0708</td>
<td>-1.29(9)</td>
<td>2.04(14)</td>
<td>2.07(14)</td>
</tr>
<tr>
<td>(9D_4)</td>
<td>532</td>
<td>1.8392</td>
<td>-1.16(11)</td>
<td>1.93(18)</td>
<td>1.92(18)</td>
</tr>
<tr>
<td>(9D_5)</td>
<td>999</td>
<td>1.720</td>
<td>0.027(3)</td>
<td>1.25(14)</td>
<td>1.59(17)</td>
</tr>
<tr>
<td>(9D_6)</td>
<td>1719</td>
<td>1.660</td>
<td>1.91(16)</td>
<td>1.91(16)</td>
<td>1.91(16)</td>
</tr>
</tbody>
</table>
bility of $\alpha_2 = 0.58 \text{ kHz/(kV/cm)}^2$. It can be seen clearly that the sign of $\alpha_2(5d)$ is positive.

The results of the tensor polarizabilities of the levels of the configuration $4f^75d\,6s^2$ are given in Table 1. The quoted errors include the threefold parameter error of the fit procedure as well as systematic errors of the electric (1%) and magnetic (0.2%) field strengths. The sign of the polarizability of the $9D_5$ level was measured and the signs of the other levels were chosen in agreement with theory (5). The sign changes twice. The values of the tensor polarizabilities in the ground multiplet show strong variations, and the absolute values vary by about two orders of magnitude.

**Discussion**

The tensor polarizabilities of the investigated $4f^7(8S)$ $5d\,6s^2\,9D_j$ levels depend only on the $5d$ electron. Wave functions of the investigated levels are needed to determine the single electron tensor polarizability $\alpha_2(5d)$. The wave functions of Unsworth [14] or Eremin and Maryakhina [18] show that all levels of the ground multiplet are 98–99% pure LS coupled states. The two eigenvector sets contain only a little mixing with the $7D$ term of $4f^7(8S)$ $5d\,6s^2$.

To interpret the observed tensor polarizabilities we used the expression [19]

$$-\alpha_2(J) = \gamma_J \beta(J)(2J+1)/2,$$

where $\gamma_J = \delta(J)|4f^7(8S)\,5d\,9D_j \rangle + \beta(J)|4f^7(8S)\,5d\,7D_j \rangle$

where $\delta(J)$ and $\beta(J)$ are the mixing coefficients given by [14] or [18] and $H_{\text{ten}}$ is the Stark operator of the tensor polarizability. Since the fine structure splitting of the ground multiplet is small compared to the optical energy intervals, the spin dependence of the tensor polarizability can be eliminated by the LS coupling approximation [19]. One gets

$$\langle \gamma J | H_{\text{ten}} | \gamma J \rangle = \langle 5d | H_{\text{ten}} | 5d \rangle (-1)^l (2J+1)\left( \begin{array}{c} J \ 2 \ J \ 0 \ 0 \\ -J \end{array} \right) \left( \begin{array}{c} \delta^2(J) \{ 2 \ 4 \ 3 \} \\ -\beta^2(J) \{ 2 \ 2 \ 3 \} \end{array} \right).$$

Using the definition of the tensor polarizability of a single electron

$$-\alpha_2(nl) = \gamma_{nl} \beta_{nl}(2l+1)/2,$$

the relation between $\alpha_2(J)$ and $\alpha_2(5d)$ is given by

$$\alpha_2(J) = \alpha_2(5d)(-1)^l (2J+1) \left( \begin{array}{c} J \ 2 \ J \ 0 \ 0 \\ -J \end{array} \right) \left( \begin{array}{c} \delta^2(J) \{ 2 \ 4 \ 3 \} \\ -\beta^2(J) \{ 2 \ 2 \ 3 \} \end{array} \right).$$

The tensor polarizabilities $\alpha_2(5d)$ obtained by means of the two different wave function sets [14, 18] are presented in Table 1. The values of $\alpha_2(5d)$ show only a significant difference for the $J=5$ level. When the value of the $J=5$ level is omitted, the tensor polarizabilities of the levels of the ground multiplet can be described by one value. The average value is $\alpha_2(5d) = 2.00(6) \text{ kHz/(kV/cm)}^2$. From (5) it follows that the tensor polarizability of the $4f^75d\,6s^2\,9D_5$ level is caused only by the small admixture of the $4f^75d\,6s^2\,7D_5$ level, since the $6-j$ symbol $\{ 2 \ 5 \ 4 \ \{ 5 \ 2 \ 2 \}$ is zero. From the values $\alpha_2(5d)$ of the $J=5$ level (Table 1) it is seen that the $4f^75d\,6s^2\,9D_5$ level is described better by the wave function of [18] than [14], whereas the wave function of [14] provides a better reproduction of the fine structure energies and $g_j$ values of the ground multiplet $9D_j$. The difference between both wave function sets for the $J=5$ level is the smaller admixture of the $7D_5$ level in the $9D_5$ level in [18]. Nevertheless, the wave function [18] does not describe the $4f^75d\,6s^2\,9D_5$ level satisfactorily. A still smaller admixture of the $7D_5$ level or a configuration interaction could give a better agreement with the other $\alpha_2(5d)$ values. In the following it will be shown that configuration interaction has to be considered in the wave function of the $9D_5$ level.

We now discuss the relation between the experimental values of the tensor polarizabilities and of the quadrupole coupling constant $B$ in the central field model. Since $H_{\text{ten}}$ is a tensor of rank two, (4) can be written in the form [4]

$$-\alpha_2(nl) = \langle nll \ | C^2 | nll \rangle K_{nl} \delta^2.$$

$K_{nl}$ is a function of $n$ and $l$. Since the tensor polarizabilities of the investigated levels depend only on the polarizability of a single electron, the tensor polarizabilities of the fine structure levels are given through

$$-\alpha_2(J) = \langle nll \ | C^2 | nll \rangle K_{nl} \delta^2.$$

Using (5–7) and the relation between the quadrupole coupling constant $B$ and the quadrupole moment $Q$

$$B(J) = -2e^2Q (\langle JJ \rangle \sum_i C^2(i)\langle JJ \rangle K_{ni} \delta^2.$$

one gets

$$B(J)/\alpha_2(J) = -\langle nll \ | C^2 | nll \rangle /2e^2Q /\alpha_2(nl).$$

For any configuration containing only one open shell with $L=0$, the ratio $B(J)/\alpha_2(J)$ should be a constant for all levels. Any deviation implies a breakdown of the central field model. The values of this ratio are given in Table 2. The data found confirm the chosen sign of the experimental $\alpha_2(J)$ values. There is good agreement for this ratio (9), except for the value of the $J=5$ level. So far, the ratio $B(J)/\alpha_2(J)$ has been studied only for all the levels of the ground multiplet $4f^66s^2\,9F$ in Sm I [4]. The values found for this ratio in Sm show very good agreement, which indicates that the levels are all unperturbed to a good approximation.

The results (Table 2) indicate that the perturbation in the $4f^7(8S)\,5d\,6s^2\,9D_5$ level can not be described completely with wave functions, which contain only term
Table 2. Values of the ratio $B(J)/\alpha_2(J)$ for all levels of the Gd ground multiplet $4f^7(^8S)\ 5d\ 6s^2\ 9D$

<table>
<thead>
<tr>
<th>Level</th>
<th>$\alpha_2(J)$ [kHz]</th>
<th>$155B(J)$ [MHz]</th>
<th>$157B(J)$ [MHz]</th>
<th>$155B(J)/\alpha_2(J)$ [(MV/cm)²]</th>
<th>$157B(J)/\alpha_2(J)$ [(MV/cm)²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^9D_2$</td>
<td>0.58(4)</td>
<td>179.407(44)</td>
<td>191.161(72)</td>
<td>0.31(2)</td>
<td>0.33(2)</td>
</tr>
<tr>
<td>$^9D_3$</td>
<td>-1.29(9)</td>
<td>-406.663(2)</td>
<td>-433.234(13)</td>
<td>0.31(2)</td>
<td>0.33(2)</td>
</tr>
<tr>
<td>$^9D_4$</td>
<td>-1.16(11)</td>
<td>-352.834(38)</td>
<td>-375.884(38)</td>
<td>0.30(3)</td>
<td>0.32(3)</td>
</tr>
<tr>
<td>$^9D_5$</td>
<td>0.027(3)</td>
<td>41.977(40)</td>
<td>44.744(39)</td>
<td>1.5(2)</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>$^9D_6$</td>
<td>1.91(16)</td>
<td>587.893(12)</td>
<td>623.275(60)</td>
<td>0.31(3)</td>
<td>0.33(3)</td>
</tr>
</tbody>
</table>

mixing with the $4f^7(^8S)\ 5d\ 6s\ ^2D_3$ level, since the ratio of $B(J)/\alpha_2(J)$ is independent of term mixing with levels of the same configuration. Configuration interaction, however, can change the ratio $B(J)/\alpha_2(J)$ in a multiplet. From Stark effect investigations, for example in high lying levels in the $msnd\ ^1D_2$ series of the alkaline earth atoms, it is known that the strong variations of the tensor polarizabilities in these series can be described rather precisely by theoretical values calculated with wave functions taking account of configuration interactions (see, e.g., [20-22]). Therefore we expect that a discussion of the results of Gd with new wave functions which consider configuration interactions should give a still better agreement between theory and experiment.

This paper demonstrates that the optical pumping technique with rf detection and the nonlinear level crossing technique in parallel electric and magnetic fields are powerful experimental methods for measuring small tensor polarizabilities occurring in the ground multiplets. The actual knowledge of the wave functions in the case of Gd is not sufficient for interpreting the observed tensor polarizabilities completely.

We would like to thank Prof. Dr. A. Steudel for his interest in this work and for many helpful discussions.

References


