The Gyromagnetic Ratio for Paramagnetic Substances. III.—Results on Salts of the Rare Earth Group.

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In a previous paper* (referred to in what follows as I) a method for measuring the gyromagnetic ratio for paramagnetic substances was described, together with the results of experiments on a strongly paramagnetic substance, dysprosium oxide. The ratio of the angular momentum produced by a given change of magnetic moment gives the Landé splitting factor, which in the case of the Dy+++ ion was found to be 1·28. This indicates that the magnetic moment is composed of both orbital and spin contributions, and agrees well with the theoretical value of 1·33 for the state $^6H_{15/2}$ deduced by Hund† as being the most probable for this ion. In a further contribution‡ (II), the apparatus was used for similar measurements on some salts of the iron group, an account being given of the means used to obtain the necessary increased sensitivity. The results, taken as a whole, show that the only tenable view advanced to explain the magnetic susceptibilities of ions of this group is that of Stoner,§ i.e., that the spin and orbital moments are quantised separately relative to the field axis, and further, the orbital moment may be wholly or partially suppressed by the fields of neighbouring ions.

The present paper deals with measurements on some oxides of the rare earth group. The apparatus used was identical with that designed for increased sensitivity and described in II, so that no further description is necessary.

Measurements on some three oxides have been obtained, and it is shown below that the Van Vleck development of the Hund theory is most successful in explaining the experimental results. The expression developed by Van Vleck|| for the magnetic susceptibility is

$$\chi = \frac{N \sum_j \{g^2 \beta^2 j (j + 1)/3kT + a(j)\} (2j + 1) e^{-W/kT}}{\sum (2j + 1) e^{-W/kT}}, \quad (1)$$

† 'Z. Physik,' vol. 33, p. 855 (1925).
§ 'Phil. Mag.,' vol. 8, p. 250 (1929).
where \( j \) = the total quantum number, \( \beta \) = the Bohr magneton, \( W = h \omega \Delta \nu \) is the difference in energy between the particular \( j \) level concerned and the ground level, the overall multiplet separation being deduced from Goudsmit's equation.

The term \( \alpha (j) \) is due to the component of the magnetic moment perpendicular to the angular momentum vector, which gives rise to second order Zeeman terms. It is generally negligible, but in cases where the \( l \) and \( s \) vectors are large, the resultant \( j \) being small, the \( \alpha (j) \) term becomes important. This holds in the cases of Sm+++, and Eu++, and the previous discrepancies in the case of these ions in the Hund theory are completely removed.

If the term \( \alpha (j) \) is omitted from the equation, the expression for the susceptibility is identical with that previously obtained by Laporte and Sommerfeld.*

The gyromagnetic amplitude gives us a means of measuring the ratio of the change of magnetic moment to the angular momentum produced. The equation for this ratio corresponding to the expression for the magnetic susceptibility given in equation (1) is

\[
\frac{e}{2mc} \sum j \gamma j (j + 1)/3kT + \alpha (j)) \frac{(2j + 1)e^{-W/kT}}{(2j + 1)e^{-W/kT}} = \frac{\bar{g}}{2mc},
\]

the expression for the angular momentum in the denominator carrying no term corresponding to the \( \alpha (j) \) term in the susceptibility.

**Discussion of Results.**

The experimental results obtained are given in Table I, being calculated according to the formula†

\[
g = \frac{1}{\theta_M} \cdot \frac{2m}{e} \cdot \frac{2\gamma T m_0 H_0}{\pi \lambda I},
\]

where \( \theta_M \) is the double gyromagnetic amplitude produced at resonance by an alternating square wave magnetic field \( H_0 \); \( g \) is the Landé splitting factor; \( I \) the moment of the inertia of the specimen used containing \( m_0 \) gram of mass susceptibility \( \gamma \); \( T \) is the time of oscillation; and \( \lambda \) the logarithmic decrement of the suspended system.

† For full details see I and II.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Mass $\times 10^3$ gr.</th>
<th>$I \times 10^3$</th>
<th>$\chi \times 10^3$</th>
<th>$\lambda \times 10^3$</th>
<th>$T$ (sec.)</th>
<th>$\theta_{\nu} \times 10^2$ (theor.)</th>
<th>$\theta_{\nu} \times 10^2$ (exp.)</th>
<th>$H_0$ (gauss)</th>
<th>$g$ (theor.)</th>
<th>$g$ (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$_2$O$_3$</td>
<td>24.0</td>
<td>12.6</td>
<td>3.7</td>
<td>2.3</td>
<td>17.7</td>
<td>12.2</td>
<td>9.5</td>
<td>6.5</td>
<td>2.37</td>
<td>2.37</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>17.6</td>
<td>7.28</td>
<td>2.65</td>
<td>7.05</td>
<td>7.25</td>
<td>1.94</td>
<td>2.06</td>
<td>1.70</td>
<td>7.05</td>
<td>7.05</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>21.2</td>
<td>27.7</td>
<td>14.8</td>
<td>2.49</td>
<td>28.0</td>
<td>6.20</td>
<td>6.20</td>
<td>6.20</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>Dy$_2$O$_3$</td>
<td>31.4</td>
<td>27.1</td>
<td>12.1</td>
<td>2.25</td>
<td>28.0</td>
<td>6.40</td>
<td>6.40</td>
<td>6.40</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>

W. Sucksmith.
The last column gives the theoretical value of $g$ calculated by means of equation (2).

Gd$^{+++}$.—This ion was used in the form of the oxide.* In all cases $g$ is found to be 2·0 within the limits of experimental error. Hund obtained $8S_{7/2}$ as being the only possible ground state for this ion in the gaseous state, the magnetic electrons being seven in the $4f$ shell. The $g$ value is 2, since the whole of the moment is due to spin.†

Nd$^{+++}$.—Two specimens of Nd$_2$O$_3$ were employed and satisfactory measurements were made on both specimens. The mean of the experimental results gives $g = 0·77$. The original Hund theory gives $8/11 = 0·726$ for the $g$ value for this ion, assuming the ground state to be $4J_{9/2}$. The Van Vleck $\alpha (j)$ term increases this to 0·752 so that the results are in good agreement with the theory. Measurements on this oxide were particularly easy as the ratio of the angular to magnetic moment is relatively large, which means that the disturbing couples are proportionately reduced.

It is interesting to compare the variation of magnetic susceptibility with temperature as obtained from Van Vleck’s theory with experiment. Cabrera and Duperier‡ have measured the susceptibility of this oxide over a range of 400° C. above room temperature. Their results show that $1/\chi$ plotted against the absolute temperature $T$ does not give a linear relationship, but a curve convex towards the $1/\chi$ axis. The experimental results given are in fair agreement with the theoretical one, though the convexity is not so marked. The value of the mass susceptibility at 300° K. is $28·6 \times 10^{-6}$ according to Cabrera and Duperier, whilst theory gives $33·3 \times 10^{-6}$. The writer’s measurement on the Nd$_2$O$_3$ used was within 1 or 2 per cent. of the experimental value.

Eu$^{+++}$.—Four specimens of Eu$_2$O$_3$ were made, but owing to the relatively coarse nature of the powder, which causes a high horizontal magnetic moment due to non-uniformity in packing, only two could be used. A large number of experiments were carried out, of which the two given are indicative of the whole of the results. In no case was any amplitude greater than $\pm 0·3$ mm. obtained, whereas under approximately similar conditions Nd$_2$O$_3$ gave amplitudes 2·0 to 2·5 mm. It is only possible to put an upper limit to the amplitude,

* All the oxides used were obtained from Messrs. Adam Hilger, and were of a high degree of purity.
† In this connection the work of Freed and Spedding (‘Phys. Rev.,’ vol. 38, p. 670 (1931)) on the absorption spectra of GdCl$_3$ $6H_2O$ and GdBr$_3$ $6H_2O$, though the work is not as yet sufficiently developed to admit of any relevant conclusions being drawn.
‡ ‘C. R.,’ vol. 188, p. 1640 (1929).
i.e., 0·3 mm. on the scale. In the majority of cases this means that no
discernible periodic oscillation was observed, the sharpness of the image often
being slightly blurred by very small pendulum oscillations of the specimen.
The mean $g$ value calculated from the results is $> 4·5$.

If we calculate the susceptibility of Eu$_2$O$_3$ from the theory of Laporte and
Sommerfeld, the room temperature value is about one-quarter that given by
experiment. Inclusion of the $x(j)$ term of Van Vleck's theory brings the
susceptibility up to $30 \times 10^{-6}$ at 12° C., as against Cabrera and Duperier's
experimental value of 27·0 at the same temperature. As pointed out by the
writer elsewhere,* the agreement between the latter theory and experiment
over the range of temperature in which results are available is remarkably
good, especially considering the uncertainty in deducing the multiplet separa­
tion and the screening constant necessary for the calculation. The $\tilde{g}$ value
calculated from the Van Vleck formula is 6·4, whereas the Laporte-Sommerfeld
expression gives 1·5, corresponding to which an easily observable gyromagnetic
amplitude would be obtained. The magnitude of the effect observed is much
too small to admit of explanation by the Laporte-Sommerfeld theory and is
thus in agreement with that of Van Vleck.

The ion Eu$^{+++}$ differs from most other paramagnetic ions in that the varia­
tion of $g$ with temperature should be very considerable, so that it would be of
great interest if the ratio could be obtained over a range of tempera­
tures. Below 50° K., the amplitude should be zero, $\chi$ being $46 \times 10^{-6}$,
whilst at 600° K., $\tilde{g}$ decreases to 3·8, the calculated susceptibility being
$20 \times 10^{-6}$.

Dy$^{+++}$.—For the sake of completeness, two measurements on Dy$_2$O$_3$ are
included, the substance having been fully investigated in I. The data now
given serve as a check on the new apparatus, and further, give an idea of the
increased sensitivity. Comparison with the data given in I shows that whilst
the field strength has been increased from 500 to about 1200 gauss, the
logarithmic decrement has been nearly halved, thus giving an approximate
four-fold increase in sensitivity. The results agree with the $g$ value of 1·33
as deduced originally by Hund.

Sufficient material to make one specimen of Ytterbium oxide (Yb$_2$O$_3$) was
obtained, but unfortunately it received some ferromagnetic contamination
in the course of preparation, and it was found quite impossible to obtain any
satisfactory measurements.

Summary and Conclusions.

In two previous papers a description of an apparatus for the measurement of the gyromagnetic ratio for paramagnetic substances was given, together with results on some salts of the iron group. The measurements are here extended to some paramagnetic substances in the rare earth group.

The mean value of $g$, the Landé splitting factor, for different ions is found to be in agreement with the modification of the Hund theory of paramagnetism as modified by Van Vleck. For the ions Gd$^{+++}$, Nd$^{+++}$, Eu$^{+++}$, and Dy$^{+++}$, the theoretical values are $g = 2.0$, $0.75$, $6.4$, and $1.33$, whereas experiment gives $2.12$, $0.78$, $>4.5$, and $1.36$ respectively.

With the completion of the above measurements, as many paramagnetic substances have been investigated as appear necessary to decide on the correct theories of paramagnetism in the iron and rare earth groups. An apparatus with ten- or twenty-fold the present sensitivity would be an extremely valuable weapon for further investigation, but such an increase appears quite impossible on the lines of the present method.

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