DETERMINATION OF NUCLEAR MOMENTS OF Gd^{155} AND Gd^{157} FROM THE HYPERFINE STRUCTURE OF PARAMAGNETIC RESONANCE

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The nuclear spins (3/2) and the ratio of magnetic moments $|\mu(\mathrm{Gd}^{155})| : |\mu(\mathrm{Gd}^{157})| = 0.73 \pm 0.03$ are determined from the hyperfine structure of paramagnetic resonance in the phosphor SrS — Gd. A comparison of hyperfine splittings in the spectra of Eu^{2+} and Gd^{3+} in the phosphor SrS and assignment of a value of 3.6 nuclear magnetons for $\mu(\mathrm{Eu}^{151})$ yields $|\mu(\mathrm{Gd}^{155})| = 0.25$ and $|\mu(\mathrm{Gd}^{157})| = 0.34$ nuclear magnetons.

THE hyperfine structure in the optical spectrum of gadolinium has been investigated in several papers,[1-4] but the nuclear spins of Gd^{155} and Gd^{157} were not reliably determined for a long time, and only Speck[4] showed them to be equal to 3/2 for both odd isotopes. The values of the nuclear magnetic moments for the same gadolinium isotopes given in the various references quoted above differ widely among themselves. The table contains a summary of the data on the spins and the magnetic moments (in nuclear magnetons) of the isotopes Gd^{155} and Gd^{157} obtained in Refs.[1-4]

Nuclear spins and magnetic moments of Gd^{155} and Gd^{157} determined from the optical hyperfine structure.

Isotope	References quoted			
	1	2*	3	4
Gd^{155}	$I \geqslant 3/2$ $\lvert\mu\rvert = 0.25 \pm 0.15$	$I \geqslant 5/2$ $\mu = -0.19 \pm 0.05$	$I = 3/2$ $\mu = -0.31$	$I = 3/2$ $\mu = -0.30$
Gd^{157}	$I \geqslant 3/2$ $\lvert\mu\rvert = 0.3 \pm 0.2$	$I \geqslant 5/2$ $\lvert\mu\rvert = -0.33 \pm 0.06$	$I = 3/2$ $\mu = -0.38$	$I = 3/2$ $\mu = -0.37 \pm 0.04$

*The value of the magnetic moment is calculated on the assumption[2] that $I(\mathrm{Gd}^{155}) = I(\mathrm{Gd}^{157}) = 7/2$.

In Ref. 5 we have pointed out the possibility of determining the nuclear moments of Gd^{155} and Gd^{157} from the hyperfine structure of paramagnetic resonance in the phosphor SrS — Gd. In that reference it was possible to determine the values of the nuclear magnetic moments of Gd^{155} and Gd^{157} only approximately since the investigation was carried out on a natural mixture of gadolinium isotopes and the hyperfine structure was not completely resolved as a result of the overlapping of lines from different isotopes.

In the present work we have investigated the paramagnetic resonance in the phosphor SrS — Gd making use of separated isotopes Gd^{155} and Gd^{157}. The content of each of these isotopes in the corresponding enriched mixture was about 93%. The concentration of gadolinium in the phosphor was about 10^{-4} and at room temperature we observed a well resolved hyperfine structure for both odd gadolinium isotopes. The spectra were investigated at a frequency of 9383 Mcs with the aid of a superheterodyne radiospectroscope. The magnetic field was measured by means of proton resonance.

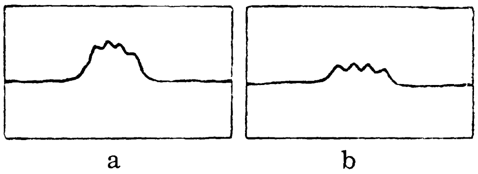
Oscillograms of the observed spectra are shown in the figure. The hyperfine structure consisting of four components for both the odd gadolinium isotopes shows that the nuclear spins of Gd^{155} and Gd^{157} are equal to 3/2. The total splittings (between the outermost hyperfine structure components) in the spectra of SrS — Gd^{155} and SrS — Gd^{157} are respectively equal to:

$$\Delta H(\mathrm{Gd}^{155}) = 11.C4 \pm 0.18\,\mathrm{G}, \quad \Delta H(\mathrm{Gd}^{157}) = 15{,}0 \pm 0.15\,\mathrm{G}.$$

From a comparison of the total splittings in the spectra of Gd^{155} and Gd^{157} we have obtained the ratio of the nuclear magnetic moments of Gd^{155} and Gd^{157}:

$$|\mu(\mathrm{Gd}^{155})/\mu(\mathrm{Gd}^{157})| = 0.73 \pm 0.03. \tag{1}$$

The magnitudes of the magnetic moments of Gd^{155} and Gd^{157} may be determined by means of comparing the hyperfine splittings due to gadolinium nuclei with the splittings due to europium nuclei. The hyperfine structure of the paramagnetic resonance spectrum of Eu^{2+} in the phosphor SrS — Eu was investigated in Refs.[6-8] The Gd^{3+} ion is isoelectric with the Eu^{2+} ion and both have the electronic ground state $4f^7\ {}^8S_{7/2}$. Therefore direct comparison of the hyperfine splittings observed in SrS — Eu and SrS — Gd gives for the ratio of the magnetic moments of Eu^{151} and Gd^{157} the value:*



Hyperfine structure for the electronic transition $M = \frac{1}{2} \longleftrightarrow -\frac{1}{2}$: a — $SrS - Gd^{155}$, b — $SrS - Gd^{157}$.

$$|\mu(\mathrm{Eu}^{151})/\mu(\mathrm{Gd}^{157})| = 10.60 \pm 0.03. \tag{2}$$

Using the value $\mu(Eu^{151}) = 3.6$ nuclear magnetons[9] we obtain from the ratios (1) and (2):

$$|\mu(\mathrm{Gd}^{155})| = 0.25, \ |\mu(\mathrm{Gd}^{157})| = 0.34 \text{ nuclear magnetons} \tag{3}$$

These values agree with the data obtained recently by Low[10] from the hyperfine structure of the paramagnetic resonance spectrum of gadolinium in single crystals of $LaCl_3 \cdot 7D_2O$ and $Bi_2Mg_3(NO_3)_{12} \cdot 24H_2O$. However, in Low's work[10] the hyperfine structure of Gd^{155} was not completely resolved and the conclusion with respect to the spin of Gd^{155} was made only on the basis of the shape of the observed line. Probably also due to the incomplete resolution of the hyperfine structure the ratio of the magnetic moments of Gd^{155} and Gd^{157} was found by Low[10] to be equal to 0.75 ± 0.07, i.e., its accuracy is lower than that of our ratio (1).

The ratio of the magnetic moments of Eu^{151} and Gd^{157} was found by Low to be equal to $\mu(Eu^{151})/\mu(Gd^{157}) = 11.3$ by comparing the hyperfine structure of europium and gadolinium in various compounds (and consequently in different crystalline surroundings). Since the hyperfine structure depends on the crystalline environment† the ratio of $\mu(Eu^{151})/\mu(Gd^{157})$ found by us is probably more accurate than that given by Low[10] since we compared the hyperfine splittings in the spectra of Eu and Gd in the same compound SrS.

In conclusion we would like to note the influence of the mechanical deformations of the crystal on the observed spectrum. In the sample of the phosphor SrS — Gd compressed into a tablet at a pressure of 150 atmos the resolution of the hyperfine structure of the spectrum is considerably worse than the resolution in the spectrum observed for a non-compressed sample. This is probably explained by the fact that at such a pressure a noticeable deformation of the crystalline lattice occurs which leads to a decrease in the symmetry of the crystalline electric field acting on the Gd^{3+} ion. Such changes in the electric field of the crystal lead to a larger anisotropic broadening of the paramagnetic resonance lines. It is also possible that in the case of such deformations of the crystalline lattice a change in the magnitude of the hyperfine splittings occurs, which can also lead to poorer resolution of the spectrum if non-uniform deformations take place over the whole sample. A similar effect of the influence of mechanical deformations of the crystal on the paramagnetic resonance spectrum was found by Van Wieringen[11] in the case of ZnS — Mn.

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*We assume here that the degree of configuration interaction on which the magnitude of the hyperfine structure depends[6] is the same for both ions.

†Although for ions in an S-state one should expect a weak dependence of the hyperfine splitting on the crystalline environment, nevertheless, for example, in SrS — Eu and in CaF_2 — Eu, a considerable difference was found[7] (about 15%) in the values of the hyperfine structure constants for Eu.

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AN ANOMALOUS MAGNETIC TRANSITION IN ANHYDROUS COPPER SULFATE

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We have investigated the magnetic properties of small crystals of anhydrous $CuSO_4$ from 1.5 to 300°K. Below $T_c = 34.4°K$ this substance shows antiferromagnetic properties. The transition to the antiferromagnetic state is accompanied by an anomalous, twofold increase of the susceptibility in a temperature interval of about 1.5°.

In a previous paper[1] we investigated the temperature dependence of the magnetic susceptibility of anhydrous copper sulfate in the temperature range from 14 to 300°K. At $T = 35°K$ the susceptibility showed a sharp increase, corresponding to a change of 30% over a temperature interval of about 2°K. A further lowering of the temperature was accompanied by a smoother increase of the susceptibility. The specimen of anhydrous copper sulfate we used in that experiment was obtained by heating copper sulfate to 300° C for two hours with constant stirring (see Ref. 2). All operations were performed in a current of dry nitrogen. The specimen was obtained in the form of a light blue, very hygroscopic powder.

Our investigations at helium temperatures have shown that the increase of the susceptibility which is observed below 35°K is apparently caused by the presence of paramagnetic impurities. The most likely impurity to be present can be assumed to be some singly hydrated copper sulfate. An approximate estimate showed that in the specimen used by us there could be found 20% singly hydrated copper sulfate.

The specimens of anhydrous copper sulfate used by us in the present experiment were obtained in two ways. The first specimen was obtained from a solution of copper sulfate in molten ammonium sulfate.[3] Above 360°C $(NH_4)_2SO_4$ decomposes and anhydrous copper sulfate remains in the form of a precipitation. In this case the specimen was obtained in the form of small transparent crystals of $1 \times 0.2 \times 0.2$ mm,