Hyperfine Structure and Nuclear Moments of Gadolinium from Paramagnetic Resonance Spectrum*

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(Received May 7, 1956)

The hyperfine structure in the paramagnetic resonance spectrum of Gd^{3+} was resolved and a nuclear spin of $\frac{3}{2}$ was found for each of the two odd isotopes Gd^{155} and Gd^{157}. The ratio of the nuclear magnetic moments is $\mu_I(Gd^{155})/\mu_I(Gd^{157})=0.75\pm0.07$. The hyperfine structure in the $^2S_{7/2}$ state of Gd^{3+} arises probably from unpaired s-electron states which are admixed to the ground state by configurational interaction. Assuming the same degree of configurational interaction in Gd^{3+} as in isoelectronic Eu^{2+}, one finds the ratio $\mu_I(Eu^{151})/\mu_I(Gd^{157})=11.3$. If one takes $\mu_I(Eu^{151})=3.6$ nm, the values of the moments of Gd are $\mu_I(Gd^{157})=0.32$ and $\mu_I(Gd^{155})=0.24$ nm. The experiments were made on single crystals of $LaCl_3\cdot7D_2O$ and $Bi_2Mg_3(NO_3)_{12}\cdot24H_2O$ using enriched isotopes.

THE detection[1] of hyperfine structure in the paramagnetic resonance spectrum of Eu^{2+} indicated a possibility of determining the spins and magnetic moments of the odd isotopes of gadolinium in Gd^{3+}. Previous work[1,2] had indicated that such a hyperfine splitting would be less than 40 gauss.

We have detected and resolved the hyperfine structure resulting from the odd isotopes 155 and 157 of Gd in the electronic transition $\frac{1}{2}\rightarrow-\frac{1}{2}$. Nuclear spins of $\frac{3}{2}$ were found for both isotopes. The ratio of the nuclear magnetic moments is $\mu(Gd^{155})/\mu(Gd^{157})=0.75\pm0.07$.

Measurements were made at room and liquid nitrogen temperatures at 3.2 and 1.2 cm on single crystals of bismuth magnesium nitrate $(Bi_2Mg_3(NO_3)_{12}\cdot24H_2O)$ and deuterated lanthanum chloride $(LaCl_3\cdot7D_2O)$ containing about 1 part in 5000 gadolinium enriched to about 70% in either 155 or 157. Four hyperfine lines due to the isotope 157, and a central line with intensity of about 1.6 that of the hyperfine lines due to the even isotopes, were completely resolved in the double nitrate salts. The line width between points of maximum slope of the hyperfine lines was about two gauss. In lanthanum chloride the lines were partially resolved, the line width apparently larger, of about 3–4 gauss. For the isotope 155, only the two outer hyperfine lines and the central line were completely resolved. The only possible assignment of the spin of this isotope consistent with the observed line shape in the double nitrate salt is $\frac{3}{2}$. The hyperfine structure constants are:

Bismuth magnesium nitrate:

$$A_{155}=4.0\pm0.3 \text{ gauss},$$
$$A_{157}=5.34\pm0.17 \text{ gauss}, \quad g=1.991,$$

Lanthanum chloride:

$$A_{157}=5.7\pm0.3 \text{ gauss}, \quad g=1.99.$$

Gd^{3+}, like the isoelectronic Eu^{2+}, has $4f^7$ electrons, a half-filled shell and, therefore, a ground state of $^8S_{7/2}$. No hyperfine structure should be present in an ion in an S state. Presumably the hyperfine structure in Gd^{3+}, as in the case of Eu^{2+}, results from unpaired s electron states such as $4f\,5s\,6s$ which are mixed to $4f\,5s^2$ by configurational interaction.[3] This hyperfine structure is expected to be only slightly dependent on the crystalline environment. This can be seen for the two gadolinium salts, from their approximately equal hyperfine structure constants. For Eu^{2+} it has similarly been shown[4] that the hyperfine structure varies by less than 5% (SrS: $A_{151}=30.8$, $SrCl_2$: $A_{151}=32.1$, in units of 10^{-4} cm^{-1}). Assuming the same degree of configurational interaction in Gd^{3+} and in Eu^{2+}, one can calculate the ratio of the nuclear magnetic moments of gadolinium and europium. Taking $\langle 1/r^3\rangle_{Av}$ to be 62 A^{-3} for Gd and 57 A^{-3} for Eu,[5] one finds the ratio of the nuclear magnetic moments to be $\mu(Eu^{151})/\mu(Gd^{157})=11.3$. With a nuclear magnetic moment of 3.6 nm for Eu^{151},[6,7] the nuclear magnetic moments of the gadolinium isotopes are $|\mu(Gd^{157})|=0.32$ and $|\mu(Gd^{155})|=0.24$, with an error of probably less than 15%.

Recent optical hyperfine structure measurements on GdI by Speck[8] yielded also spins of $\frac{3}{2}$ for Gd^{155} and Gd^{157}, the ratio $\mu(Gd^{155})/\mu(Gd^{157})=0.80\pm0.02$, and $\mu(Gd^{157})=-0.37\pm0.04$ nm. Our results are within the limits of the combined errors, but are in somewhat better agreement with the earlier results of Murakawa[9] who found $\mu(Gd^{157})=-0.33\pm0.06$ and $\mu(Gd^{155})=-0.19\pm0.05$ nm.

These results indicate that configurational interaction is a general phenomenon in paramagnetic resonance spectra and may play a role in spectra of the $5f$ electron shell as well.

The author is grateful to Professor C. A. Hutchison, Jr., for kind encouragement.

* This work was supported by the U. S. Atomic Energy Commission.
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