PHYSICAL REVIEW VOLUME 126, NUMBER 4 MAY 15, 1962

Nuclear Magnetic Resonance of Lu^{175}

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(Received January 8, 1962)

The nuclear magnetic resonance of Lu^{175} has been discovered in LuB_{12} and LuSb. The lutetium-to-deuteron frequency ratios were found to be 0.73677±0.00002 and 0.73732±0.00002 in the respective compounds. The nuclear magnetic moment of Lu^{175} derived from these measurements is 2.230±0.011 nm.

I. INTRODUCTION

IN connection with an atomic beam study[1] of Lu^{175}, a search was made for the nuclear magnetic resonance of this nuclide. No resonances were found in lutetium solutions, presumably because of the rapid relaxation caused by the large nuclear quadrupole moment. For this reason it seemed necessary to work with a solid having cubic symmetry. An attempt was made to incorporate lutetium ions in NaCl, but no resonance was found probably because the NaCl did not dissolve sufficient $LuCl_3$. The cubic compound LuN was prepared, but no resonance was found because the preparation contained less than the stoichiometric amount of nitrogen. A series of unsuccessful attempts was made to prepare the cubic compound LuB_6 which has been reported by Neshpor and Samsonov.[2] These preparations yielded mixtures of LuB_4 and a phase identified as LuB_{12} which had the same structure as the cubic compound ZrB_{12}. La Placa, Binder, and Post[3] have recently described this lutetium compound. The Lu^{175} nuclear resonance was found in a sample of LuB_{12}.

The series of rare-earth antimonides prepared by Brixner[4] and having the NaCl structure suggested that it might be possible to prepare LuSb for this work. The compound was prepared[5] and the lutetium resonance was found in it.

In order to get some idea of the frequency shifts in the borides and antimonides, ScB_{12}, LaB_6, and LaSb were prepared and their nuclear resonances were measured.

II. EXPERIMENTAL

The lutetium, lanthanum, and scandium borides were prepared by heating compressed mixtures of boron and the appropiate oxide in a graphite furnace *in vacuo* for about 2 hr at about 1400°C. Stoichiometric amounts of boron and oxide were used for the hexaboride. Better yields of the dodecaborides were obtained by using about 50% more than the stoichiometric amount of boron.

The antimonides were prepared by heating the stoichiometric amounts of the elements in a sealed, evacuated quartz tube. The temperature was held at about 700°C for $\frac{1}{2}$ hr and then raised to 1000°C for about 2 hr. X-ray powder patterns were run on all samples using a 114.6-mm camera and Cu radiation. The lattice parameter of LuB_{12} was found to be 7.46 Å in agreement with Post's[3] value of 7.464 Å. The LuSb parameter was found to be 6.06 Å. This compound has not been previously reported. Extrapolation of Brixner's[4] parameters for TbSb, DySb, HoSb, ErSb, and TmSb suggests a value near 6.04 Å for LuSb. The powder pattern of ScB_{12} indicated a crystal structure similar to that of LuB_{12} and a lattice parameter of 7.39 Å. This compound has not been reported before, but the lattice parameter seems reasonable when compared with those of other dodecaborides. The LaB_6 was identified by its lattice parameter of 4.15 Å which agrees with that given by Post,[6] 4.153 Å. The LaSb sample had the NaCl structure with a lattice parameter of 6.48Å in agreement with the reported value[4] of 6.475Å.

A Varian Associates wide-line spectrometer was used in this study. Frequencies were measured with a Hewlett Packard HP524D frequency counter.

The boride and antimonide samples weighed about 2 g. They had an appreciable conductivity and for this reason were ground to fine powders. Some were embedded in paraffin wax, but this procedure did not seem to be necessary. All measurements were made at room temperature.

The resonances of the borides and antimonides were quite broad (about 5 to 10 gauss) and quite weak. It was necessary to use high rf power levels (1000–2000 μamp), wide modulations (4 to 8 gauss), and long time constants (10 to 25 sec). The resulting signal-to-noise ratio was of the order of 10 to 1.

The resonance frequencies of the solid boride and

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* National Research Council Postdoctorate Fellow 1959–1961. N.R.C. Contribution No. 6828.

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antimonide samples were compared in the same magnetic field with those in suitable solution samples. This was done by substitution. The resonances of the liquid samples were strong enough to be observed and measured on the oscilloscope. The resonances of the solid samples were recorded by slowly sweeping the magnetic field over a range of several times the linewidth. However, the long-time-constant filter used introduced a delay in response. The measurements were therefore made by sweeping the field back and forth over the resonance. This procedure introduced hysteresis effects; therefore, a simple average of the resonance frequencies obtained with the field current increasing and decreasing was subject to error from these effects. It was necessary to establish a reproducible hysteresis loop. Hence, the field current was always swept over a precisely defined range. The same range was cycled for the solid and liquid samples. Care was taken to use the same part of the hysteresis loop when comparing the resonance frequencies for the two types of samples in a single run. The frequency ratio for the two samples at resonance at a given magnet current was therefore determined separately for increasing and decreasing currents and finally the average of these two ratios was taken.

III. RESULTS AND DISCUSSION

The lutetium resonance frequencies were compared with the deuteron frequency in a 20% heavy water solution containing 0.5 M $MnSO_4$. The measured frequency ratios were:

$$\nu(\mathrm{Lu}^{175}\text{ in }\mathrm{LuB}_{12})/\nu(\mathrm{D})=0.73677\pm0.00002,$$
$$\nu(\mathrm{Lu}^{175}\text{ in }\mathrm{LuSb})/\nu(\mathrm{D})=0.73732\pm0.00002.$$

The limits quoted are the mean deviations of all measurements.

In order to estimate the nuclear magnetic moment of Lu^{175}, the possibility of environmental resonance frequency shifts must be considered. Some of the borides are reported[7] to be metallic conductors. Since the LuB_{12} sample had an appreciable conductivity, there is thus the possibility of a Knight shift of its resonance. Another source of frequency shifts is the second-order nuclear-quadrupole effect due to impurities. Such shifts have been reported by Oliver[8] for antimony in GaSb where they are of the order of 1 in 10^4. The shifts might be appreciably larger in the lutetium compounds because of the large quadrupole moment of Lu^{175}, which was reported[1] to be 5.68×10^{-24} cm^2. Finally, there are the chemical shifts due to shielding effects, which can be quite large for elements of higher atomic weight.

The lanthanide antimonides studied by Brixner[4] are reported to be semiconductors and should not have an appreciable Knight shift. A similar behavior may be anticipated for LuSb. Since the lutetium resonance in LuB_{12} is shifted to lower frequencies by 0.07% from that in LuSb, it may be concluded that a Knight shift, if present in LuB_{12}, is probably not larger than this amount.

Table I.

$\nu(\mathrm{Lu})/\nu(\mathrm{D})$	H_0 (gauss)	Number of measurements
0.736740 ± 0.000016	8600	2
0.736783 ± 0.000013	12 400	4

The frequency shift caused by impurities, through the second-order nuclear-quadrupole interaction, is negative and proportional to $(eqQ)^2/\mu H_0$, where eqQ is the quadrupolar interaction of the nucleus in question with the impurity and μH_0 is the magnetic interaction of the nucleus with the applied magnetic field in the absence of other interactions. The formulas have been given by Bloembergen and Rowland.[9] In the ratio of the frequencies of a solid and a liquid sample, the liquid frequency is not affected by quadrupolar interactions so that the ratio is shifted by an amount proportional to $(eqQ)^2/(\mu H_0)^2$. Thus the measured frequency ratio R_m may be written as $R_m=R_0+bH_0^{-2}$, where R_0 is the frequency ratio in the absence of quadrupolar shifts and b is a constant representing these shifts.

The LuB_{12} resonance frequencies were measured relative to those of the deuteron at two different fields with the results given in Table I.

These measurements permit the solution of above equation for the unshifted frequency ratio, R_0, yielding $R_0=0.736823$. The shifts are barely significant statistically, but they do indicate that if a second-order quadrupolar shift is present in LuB_{12}, it does not exceed about 0.01% in these measurements.

While the Knight shift and the quadrupolar shift do not seem to be significant in the compounds studied here, the chemical shift is a general phenomenon in nuclear magnetic resonance. Ramsey[10] has shown that the chemical shift results from two opposing effects: a diamagnetic shielding arising from induced electron circulation and a paramagnetic shielding arising from admixture of excited states with the ground state. Dickinson[11] has calculated a number of diamagnetic shielding corrections and found that they increase with increasing atomic number, reaching about 1% for the heaviest elements. These calculations show that the addition or subtraction of one electron from an atom changes the shielding factor by less than 1%, since it is determined mainly by the inner electrons. Thus while the chemical shift due to diamagnetic shielding may be as large as 1%, the resonance frequencies of an element in various compounds should not differ by more than about 0.01% because of such shielding. The diamagnetic shielding correction calculated for the free atom may thus be applied to compounds of the same element. Since the accuracy of the calculated correction is about

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5%, the corrected nuclear moment may have a corresponding error of up to 0.05%.

The paramagnetic corrections have not generally been calculated for lack of knowledge of the excited states involved, although they are probably smaller than the diamagnetic corrections (see for example Dickinson[12]), unless there are low-lying states as in cobalt. For free atoms and ions with spherical symmetry the paramagnetic corrections should be zero. Since the paramagnetic effects involve the outer electrons they should be fairly sensitive to the chemical environment. This is probably the reason for the chemical shifts in the heavier elements which, in those cases investigated, range up to about 0.2%, aside from cobalt.

The effect of chemical shifts in the lutetium compounds is not easily estimated because of the difficulty of finding compounds with observable resonances. To obtain some indication of the chemical shifts to be expected, resonances were measured in related compounds where it was possible to use ionic solutions for comparisons. For this purpose ScB_{12} and LaSb were used because they have structures similar to those of the corresponding lutetium compounds. It was not possible to prepare LaB_{12}. LaB_6 could be prepared and was used, although the crystal structure reported for it by Post *et al.*[6] is different from that of LuB_{12}.

The frequency of the cation resonance in each of these compounds was compared with that of the cation in an aqueous solution. The following results were obtained:

$$\nu(\mathrm{Sc}^{45}\text{ in }\mathrm{ScCl}_3,\text{ aq})/\nu(\mathrm{Sc}^{45}\text{ in }\mathrm{ScB}_{12}) = 1.00090\pm0.00005,$$

$$\nu(\mathrm{La}^{139}\text{ in }\mathrm{La(NO_3)_3},\text{ aq})/\nu(\mathrm{La}^{139}\text{ in }\mathrm{LaB}_6) = 1.000137\pm0.000007,$$

$$\nu(\mathrm{La}^{139}\text{ in }\mathrm{LaSb})/\nu(\mathrm{La}^{139}\text{ in }\mathrm{La(NO_3)_3},\text{ aq}) = 1.00156\pm0.00006.$$

None of the above shifts exceeds 0.2%, while the shift between the two lutetium compounds reported above is 0.07%. Thus it seems unlikely that there are unusually large paramagnetic effects in the lutetium compounds

If Dickinson's[11] diamagnetic correction, 0.820%, is applied to the lutetium resonances, the largest remaining uncertainty[13] in the calculation of the nuclear moment is the paramagnetic effect. This effect may be at least as large as the observed shifts, and if it is assumed to be smaller than the diamagnetic effect, then a reasonable limit of error for the calculated nuclear moment would be 0.5%.

The lutetium nuclear magnetic moment may be calculated from the average of the two lutetium-to-deuteron ratios given above together with Wimett's[14] value for the ratio of the deuteron and proton moments, 0.307012192; Sommer, Thomas, and Hipple's[15] uncorrected value for the proton moment, 2.79268 nm; and Dickinson's[11] diamagnetic shielding correction, 0.820%. The resulting corrected value for the Lu^{175} nuclear magnetic moment is 2.230 ± 0.011 nm. This result verifies the less accurate value $+(2.17\pm0.19)$ nm obtained from the atomic-beam magnetic-resonance study[1] of the electronic ground state of Lu^{175}.

ACKNOWLEDGMENTS

We are greatly indebted to Dr. Maria Przybylska of these Laboratories for her invaluable assistance in making the x-ray studies of the various compounds. We thank Dr. W. G. Schneider for his interest in the work.

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