Magnetic Resonance Determination of the Nuclear Moment of Tantalum-181 in $KTaO_3$†

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(Received July 29, 1960)

The nuclear magnetic moment of Ta^{181} is found from the nuclear magnetic resonance of Ta^{181} in $KTaO_3$. The uncorrected value of the moment is 2.340 ± 0.001 nm. Consideration of diamagnetic shielding effects and a possible second order paramagnetic correction leads to the estimated value of $\mu=2.35\pm0.01$ nm.

INTRODUCTION

IN recent years considerable interest has been shown in a precise determination of the ground-state nuclear magnetic moment μ of trantalum-181 (Ta^{181}) both for its application to the solid state[1,2] and for its importance in the theory of nuclear structure.[3] The observation of the nuclear magnetic resonance of Ta^{181} in potassium tantalate, $KTaO_3$, which was briefly reported earlier,[4] permits a much more precise value of the ground-state nuclear magnetic moment of Ta^{181} to be obtained than was previously available from optical data. Although Ta^{181} has a 100% natural isotopic abundance and a nuclear gyromagnetic ratio almost as large as that of deuterium, the broadening of the resonance line due to the interaction between the exceptionally large electric quadrupole moment of Ta^{181} and internal electric field gradients may be the reason that its resonance had not been previously observed. In the specimens of $KTaO_3$ investigated here, the cubic environment of the tantalum was sufficiently perfect so that the resonance of the Ta^{181} was not "washed out" by random quadrupole interactions.

EXPERIMENTAL PROCEDURE AND RESULTS

The nuclear magnetic resonances were observed by means of nuclear induction using a Varian wide-line nuclear magnetic resonance spectrometer, and a Varian electronically regulated electromagnet having 12-inch diameter poles and a 1.75-inch gap. Frequency determinations were made using a U. S. Navy Type LM-7 frequency meter calibrated with its internal crystal which was checked against the National Bureau of Standards radio station WWV. The magnetic field was measured with a gaussmeter of the Pound-Watkins type using the lithium-7 nuclear magnetic resonance in a sealed probe placed near the spectrometer probe. Both the absorption and the dispersion modes were observed. The amplitude of the modulation field was less than one-half the linewidth in every case. The center of the resonance was determined by adjusting the magnetic field to the maximum value of the observed derivative of the dispersion. Repeated measurements of the center of the resonances agreed within one gauss or less. All measurements reported here were made at room temperature.

The magnetic resonances were observed in $KTaO_3$ which has the cubic perovskite structure shown in Fig. 1. $KTaO_3$ has a ferroelectric Curie point[5] at 13.2°K. Higher Curie points have been reported, but these were due to Na impurities.[5]

The specimen used for the measurements on which the value of the magnetic moment is deduced was composed of many very small colorless crystals of $KTaO_3$, which were grown from a melt consisting of a mixture of Ta_2O_5 and K_2CO_3. Spectroscopic examination of this specimen revealed between 0.01 and 0.1% each of calcium and aluminum impurities. All other impurities totalled under 0.02%.

Typical recorder traces of the absorption and dispersion derivatives of the nuclear magnetic resonance of Ta^{181} in $KTaO_3$ are shown in Fig. 2. The line width is roughly 10 gauss corresponding to a "spin-spin" interaction time, $T_2\cong10^{-5}$ second. Noting the near equality of the amplitude of the traces, it is concluded that the approximately $\frac{1}{2}$ gauss intensity of rf field does not cause appreciable saturation. This leads to a value of the spin lattice relaxation time, T_1, of about 10^{-3} second. It is understood that the values of T_1 and T_2 quoted here may be off by as much as an order of magnitude.

The magnetic resonance of Ta^{181} was also observed in a single crystal of $KTaO_3$ which was blue in color, indicating an oxygen deficiency. The signal to noise was too poor to make accurate measurements but a change in linewidth was noted as the crystal was rotated in the

† Supported in part by the Department of Defense.

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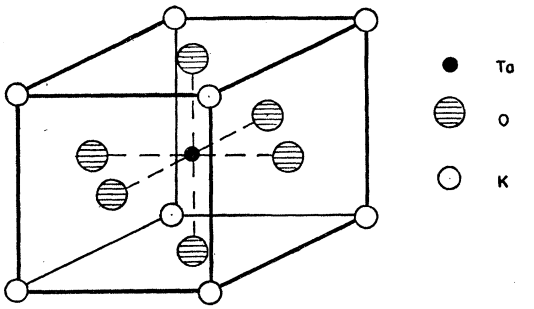

FIG. 1. Crystal structure (cubic perovskite) of $KTaO_3$.

magnetic field. This linewidth anisotropy is attributed to an orientation dependent strain in the crystal.

No resonance could be observed in a sample of $NaTaO_3$, which was composed of many very small colorless crystals. $NaTaO_3$ is ferroelectric at room temperature[6] and has orthorhombic symmetry. Cotts and Knight[7] observed the nuclear magnetic resonance of Nb^{93} in a single crystal of tetragonal $KNbO_3$, but the quadrupole moment of Ta^{181} is at least an order of magnitude larger than that of Nb^{93} whereas Nb^{93} has twice the magnetic moment of Ta^{181}; thus, it is not surprising that the resonance is broadened beyond observation by the quadrupolar interaction in the $NaTaO_3$ polycrystalline sample. The ferroelectric Curie point of $NaTaO_3$ is reported to be 475°C and is thought to be cubic above that temperature. The resonance may be observable in polycrystalline $NaTaO_3$ above the Curie point.

The frequency of the center of the Ta^{181} magnetic resonance in $KTaO_3$ was measured as a function of magnetic field. The experimental data are shown in Table I along with the calculated values of the uncorrected nuclear magnetic moment, assuming the nuclear spin $I=\frac{7}{2}$.

There does not appear to be any systematic field dependence of the nuclear magnetic moment, thus ruling out possible second order quadrupole shifts of the resonance. The uncorrected value for the magnetic moment of Ta^{181} obtained as the average of these values is

$$\mu(Ta^{181})=2.340\pm0.001 \text{ nm}.$$

DISCUSSION

The uncertainty shown in the observed magnetic moment represents the precision in locating the center of the broad resonance. The value of the magnetic moment can differ from the observed resonance value due to the magnetic properties of the sample, quadrupole effects, and "chemical shifts."

The addition of paramagnetic ions to a solution in order to broaden the resonance leads to shifts in the resonance frequency. Similarly the gross magnetic properties of the sample in the case of a solid may shift the resonance. The magnetic susceptibility of the $KTaO_3$ was measured by the Gouy method by Dr. G. Candella of the National Bureau of Standards, and found to be -0.13×10^{-6} cgs and is independent of magnetic field. Thus, we do not expect an appreciable shift from this cause.

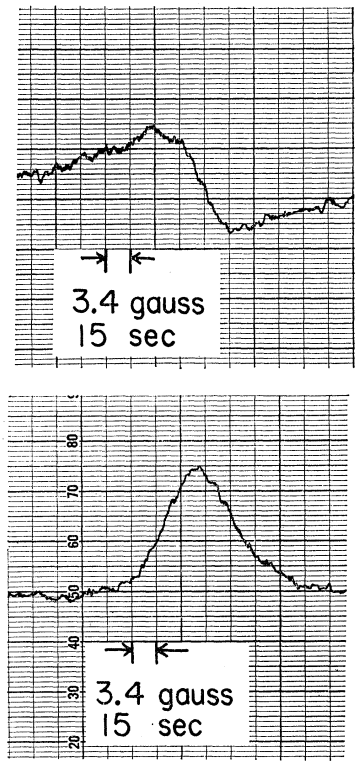

FIG. 2. Recorder traces of the dispersion (below) and absorption (above) derivatives of the nuclear magnetic resonance of Ta^{181} in $KTaO_3$.

As mentioned above, any quadrupole shift is ruled out by noting that the apparent moment is independent of magnetic field. However, chemical shifts are proportional to the magnetic field and hence cannot be measured by varying the field. The "chemical shift" arises from a magnetic shielding by the electrons of the atomic nuclei. Diamagnetic shielding causes the measured moment to appear to be smaller than it actually is. In the case of tantalum the observed value of the moment must be multiplied[8] by 1.0086 to correct for the diamagnetic shielding effect. Saha and Das[9] indicate that there is an uncertainty in this correction factor of 0.06%.

In addition to the diamagnetic contribution to the chemical shift there is a paramagnetic contribution

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which was first pointed out by Ramsey.[10] This contribution corresponds to the second order, temperature-independent paramagnetism which Van Vleck showed is expected in molecules having low-lying excited states. The theoretical evaluation of the shift expected from second order paramagnetism is very difficult, and has only been accomplished in a few simple cases. It is likely to be of the same order of magnitude as the diamagnetic shift, especially in the lighter elements. The paramagnetic contribution is, of course, in the opposite sense to the diamagnetic shift. Even if the resonance is at the same frequency in a number of different compounds, the shift may be present, leading Saha and Das to point out that the accuracy usually claimed for magnetic moments based on nuclear resonance measurements may not always be justified.

In the present case we state the moment corrected for the diamagnetic shift but with a possible error due to second order paramagnetic effects equal to the diamagnetic shift as

$$\mu(\mathrm{Ta}^{181})=2.35\pm0.01 \text{ nm}.$$

Prior to the work reported here, the ground-state nuclear magnetic moment of Ta^{181} was known only from optical hyperfine structure (hfs) measurements. Brown and Tomboulian[11] measured the hfs of Ta II and assuming $L-S$ coupling obtained the hyperfine coupling constant $a(s)=0.405$ cm^{-1}. They then used the Goudsmit formula and obtained a magnetic moment of 1.9 nuclear magnetons (nm). Taking into account the finite size of the nucleus then increased this value to 2.1 nm within an estimated uncertainty of 20%.

Recently, Murakawa[12] re-evaluated the magnetic moment of Ta^{181} using the experimental value for the hyperfine coupling constant of the $5d^36s\ 5f_1$ level of Ta II given by Brown and Tomboulian. Taking into account the work of Trees, Cahill, and Rabinowitz,[13] which showed that the Ta II level is not appreciably perturbed, Murakawa obtained $\mu=2.4\pm0.2$ nm.

Our value of the moment lends support to the calculations of Murakawa. In turn, the higher precision of our moment makes possible an improved calculation[14] of the screening correction of the $5d$ electron of the $5d^36s^2$ level of Ta II.

An accurate value of the nuclear magnetic moment has importance to the theory of nuclear structure. Tantalum is particularly interesting because its nucleus is strongly deformed and because a large amount of work has been done on the rotational spectrum of Ta^{181}. It is to be expected that the single-particle model of the nucleus would be inappropriate for strongly deformed nuclei. Bohr and Mottelson[3] have treated the nuclear core on the basis of a unified model. The nuclear gyromagnetic ratio of an odd-mass nucleus is treated as arising in part from the collective motion of the entire nucleus (g_R) and in part from the odd-particle motion (g_Ω). For strongly deformed nuclei, such as Ta^{181}, the ground-state magnetic moment can be expressed in a simple manner by the strong-coupling approximation of the unified model, as

$$\mu=\frac{I}{I+1}(Ig_\Omega+g_R).$$

Since the nucleus of Ta^{181} is deformed, the approximation for a uniformly charged nucleus $g_R=Z/A\simeq0.4$ is not likely to hold.

The value of $(g_\Omega-g_R)^2$ can be found from a study of the γ radiation emitted from the excited nuclear rotational levels due to Coulomb excitation. Angular correlation measurements for the transitions $(11/2\rightarrow9/2\rightarrow7/2)$ for Ta^{181} determine that $(g_\Omega-g_R)$ has the same sign as the quadrupole moment, which is positive. Using a reliable average value[15–18] for $g_\Omega-g_R=0.43$ and the optically determined value of $\mu=2.1$ nm, g_R is found to be 0.26 and $g_\Omega=0.69$. The same value for the difference $g_\Omega-g_R$ when used with the newly determined value of $\mu=2.35$ nm yields values of $g_R=0.34$ and $g_\Omega=0.77$. The increase of 12% in the value of the moment raises g_R by 31%. The higher value for g_R is not inconsistent with Gauvin's recent theory[19] of heavily deformed nuclei.

An accurate value for the magnetic moment of Ta^{181} is necessary in studies of the translational diffusion of protons in tantalum hydride.[1,2] Tantalum offers a good test for the application of the Torrey theory of translational diffusion which could enable one to deduce the interstitial positions of the protons from spin lattice relaxation measurements on the proton system. The theoretical estimate of the proton spin-lattice relaxation time is very sensitive to the value of the tantalum momentum since the large moment of the Ta^{181} produces about $\frac{2}{3}$ of the total relaxation of the proton spin. In concentrated hydrides of tantalum the new higher value of the Ta moment does not provide good agreement between theory and experiment for the two possible interstitial positions considered by Torrey. A study of dilute hydrides in this system would be most interesting, in order to clarify the source of this disagreement and to better decide between the possible proton sites.

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ACKNOWLEDGMENTS

Thanks are due to Dr. T. Dunne and Dr. G. Burns of the IBM Research Laboratory for providing the $KTaO_3$ and to Dr. F. Holtzberg of the IBM Research Laboratory for the $NaTaO_3$. Mr. V. M. Johnson assisted with some of the measurements. The spectrographic analysis was performed by the National Bureau of Standards Spectrochemistry Section. One of us (J.I.B.) acknowledges several helpful conversations with Dr. Burns, Dr. T. Dunne and Dr. D. R. Young. The other author (L.H.B.) thanks Dr. L. M. Kushner for several informative discussions.

PHYSICAL REVIEW VOLUME 120, NUMBER 5 DECEMBER 1, 1960

Decay of Ag^{104} and Levels in Pd^{104}†*

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(Received July 18, 1960)

The radioactive decay of the isomers of Ag^{104} has been investigated using scintillation spectrometers and a magnetic beta-ray spectrometer. Half-lives of (66±1) and (29.8±0.5) minutes were determined for the spin 5 and spin 2 isomers, respectively. Conversion electrons corresponding to 15 gamma rays assigned to Pd^{104} were observed. Two allowed positron transitions were detected: one of end-point energy (990±10) kev from the spin 5 isomer of Ag^{104}; and the other of end-point energy (2705±15) kev from the spin 2 isomer. Gamma-gamma and beta-gamma coincidences were observed. The experimental data together with data obtained by other investigators is used to determine the spins and parities of the low-lying excited states of Pd^{104}.

SINCE 1939 the neutron-deficient isotopes of silver have been the subject of many experimental investigations.[1–8] Because similar radiations and similar half-lives occur in the decays of these isotopes it has been difficult to assign the observed gamma and beta rays unambiguously to the silver isotopes of mass numbers 102, 103, and 104. The tentative assignment by Reynolds *et al.*[5] of two spin 2 activities to Ag^{104} with half-lives approximately one hour and one-half hour, respectively, stimulated the present work and also concurrent investigations in other laboratories. Ewbank *et al.*,[6] combining experimental excitation curves with atomic beam measurements, showed that one of the spin 2 activities assigned by Reynolds *et al.*[5] to Ag^{104} should be assigned instead to Ag^{102} and that Ag^{104} has spin 5 and spin 2 isomers. Girgis and van Lieshout,[7] using scintillation spectrometers, identified 10 gamma rays following the decay of the Ag^{104} spin 5 isomer and positrons from the decay of the Ag^{104} spin 2 isomer. Using these data they have proposed a level scheme for Pd^{104}. Ames *et al.*[8] demonstrated that the spin 2 level in Ag^{104} lies above the spin 5 level.

In the work described here Ag^{104} was studied using both scintillation spectrometers and a magnetic beta-ray spectrometer. We observed conversion electrons corresponding to all 10 gamma rays observed by Girgis and van Lieshout[7] and in addition, conversion electrons corresponding to several other gamma rays in Pd^{104} were observed. The 2.7-Mev positron transition from the spin 2 isomer of Ag^{104} detected previously by Johnson[4] and by Girgis and van Lieshout[7] was observed. A previosuly unknown 990-kev positron transition from the spin 5 isomer was discovered. Beta-gamma and gamma-gamma coincidences were obtained to confirm certain features of the Pd^{104} level scheme proposed by Girgis and van Lieshout.[7] By combining our data with those from other investigations we have confirmed the level order proposed by Girgis and van Lieshout and are able to make specific spin and parity assignments to the levels of Pd^{104}. The latter assignments differ somewhat from those suggested by Girgis and van Lieshout.

EXPERIMENTAL MEASUREMENTS

Ag^{104} was produced by the reaction $Rh^{103}(\alpha,3n)Ag^{104}$ using 38-Mev alpha particles (degraded from the 42-Mev alpha beam of the University of Washington cyclotron.) We chose this bombarding energy to obtain

† This work was supported in part by the U. S. Atomic Energy Commission.

* A preliminary account of this work was presented at the 1960 Spring Meeting of the American Physical Society [Bull. Am. Phys. Soc. **5**, 240 (1960)]. The material in this article is taken in part from a thesis submitted by H. Nutley in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Washington.

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