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Nuclear quadrupole moment of the ^{99}Tc ground state

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By combining first-principles calculations and existing nuclear magnetic resonance (NMR) experiments, we determine the quadrupole moment of the $9/2^{+}$ ground state of ^{99}Tc to be $(-)0.14(3)b$. This confirms the value of $-0.129(20)b$, which is currently believed to be the most reliable experimental determination, and disagrees with two earlier experimental values. We supply *ab initio* calculated electric-field gradients for Tc in $\mathrm{YTc_2}$ and $\mathrm{ZrTc_2}$. If this calculated information would be combined with yet to be performed Tc-NMR experiments in these compounds, the error bar on the ^{99}Tc ground state quadrupole moment could be further reduced.

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I. INTRODUCTION

In the words of Pyykkö,[1] the study of nuclear quadrupole moments of the elements is a "tiny science, having less than 100 objects, each characterized by a single number, usually known with less than three-figure accuracy." The (spectroscopic) nuclear quadrupole moment Q expresses how much the charge distribution within a nucleus deviates from spherical symmetry and, therefore, serves as a test for predictions from nuclear models. Knowledge of Q is important for chemical spectroscopy as well, especially for nuclear magnetic resonance (NMR) of quadrupolar nuclei.[1,2] Ratios between the quadrupole moments of different isotopes of the same element are easier to experimentally access than the quadrupole moment itself. Therefore, accurate knowledge of the quadrupole moment for one isotope paves the way for the knowledge of Q for many more isotopes, and this "tiny science" turns out to be not so tiny after all. The present work assesses the quadrupole moment of the $9/2^{+}$ ground state of the isotope ^{99}Tc. As the following historical survey shows, knowledge on this quadrupole moment is not complete.

The first estimate of the nuclear quadrupole moment Q for the ground state of ^{99}Tc goes back to the observed systematics of quadrupole moments as a function of atomic number Z by Townes *et al.*[3] in 1949. Although no experimental data for ^{99}Tc were available at that time, an interpolation of the existing data suggested a small and negative value, which was used as a benchmark in later studies.[4] The first explicit determination was made by Kessler and Trees[4] by examining the hyperfine structure in the optical spectrum of free Tc. They found a value of $+0.34\pm0.17$ b but did not rule out the possibility that the true result might be negative. Three decades later, Kidd[5] performed NMR on TcO_4^{-n} molecules in solution and based on the assumption that the electric-field gradient (EFG) on M in the $M\mathrm{O}_4^{-n}$ is small and constant for a large group of M ions, a value of $+0.28\pm0.10$ b was found. It was stressed that this value does not depend on any calculation of electric-field gradients. The value that has made it into the tabulations[1,2,6,7] of quadrupole moments is $-0.129(6)$ b, which was found by Büttgenbach[8] in 1982. It was determined by an analysis of optical hyperfine measurements on atoms due to Wendlandt *et al.*[9] five years earlier. Several approximations entered this analysis: the effective radial parameters b^{02} were calculated by neglecting relativistic effects and a theoretical value has been used to evaluate $\langle r^{-3}\rangle$. Moreover, the experimental uncertainties on the electric quadrupole hyperfine interaction constants B that were used to fit the b^{02} are large. Therefore, the reported error bar of 0.006 b or 5% might well be too low and the real uncertainty can amount to 10%–20% (0.01–0.02 b).[10] In summary, the current knowledge on the ^{99}Tc ground state quadrupole moment is as follows: There are three reported values with a similar order of magnitude and conflicting signs [+0.34(17), +0.28(10), and −0.129(6−20)], with the latter result being definitely the most reliable one. There is no independent verification of the −0.129 b value adopted in tabulations;[1,2,6,7] hence, its reliability does not stand beyond any doubt.

The present paper does provide such an independent verification by using the common procedure[11–16] of correlating *ab initio* calculated electric-field gradients and experimentally determined quadrupole coupling constants. The error bar on our result will be properly assessed, and ^{99}Tc experiments will be proposed that can further increase the accuracy of this quadrupole moment.

II. COMPUTATIONAL METHOD

Experimental methods such as NMR, Mössbauer spectroscopy, and time-differential perturbed angular correlation spectroscopy (TDPAC) can measure the interaction energy between the quadrupole moment Q of a nucleus and the gradient of the electric field this nucleus experiences at a particular place in a solid. This interaction energy is characterized by the quadrupole coupling constant C_Q,

$$C_Q = \frac{eQV_{ZZ}}{h}, \tag{1}$$

where e is the electron charge (Coulomb), Q is the spectroscopic quadrupole moment (barn), h is Planck's constant (J s), and V_{ZZ} is the main component of the EFG tensor (10^{21} V/m^2). C_Q is expressed in frequency units. Only the product between Q and V_{ZZ} is experimentally accessible; V_{ZZ} itself is not. However, if the quadrupole moment is known, V_{ZZ} can be obtained from C_Q. Alternatively, if V_{ZZ} can be calculated from first principles, a plot of the experimental C_Q versus the calculated V_{ZZ} should be a straight line with a slope determined by Q. This is a way to "measure" a quadrupole moment by using a combination of theory and experiment.

In the present work, electric-field gradients are calculated within density functional theory (DFT) [17–19] by using the Wu–Cohen exchange-correlation functional.[20] This recently proposed GGA-based functional has been shown[21] to be especially good for 4*d* transition metals, such as the hcp-Tc in the present paper. For solving the scalar-relativistic Kohn–Sham equations, we have employed the augmented plane waves+local orbital (APW+lo) method[19,22,23] as implemented in the WIEN2K package.[24] In this method, the wave functions are expanded in spherical harmonics inside nonoverlapping atomic spheres of radius R_{MT} and in plane waves in the remaining space of the unit cell (the interstitial region). For all elements that appear in this work, R_{MT} were taken in the range from 1.99 a_0 (Be) to 2.50 a_0. The maximum ℓ for the expansion of the wave function in spherical harmonics inside the spheres was taken to be $\ell_{\max}=10$. The charge density was Fourier expanded up to $G_{\max}=16\sqrt{Ry}$. Atomic positions were relaxed until the forces were below 0.5 mRy/au. The plane wave expansion of the wave function in the interstitial region was truncated at $K_{\max}=7.5/R_{\mathrm{MT}}^{\min}$ for the hcp metals and at $K_{\max}=8.0/R_{\mathrm{MT}}^{\min}$ for $\mathrm{KTcO_4}$, $\mathrm{RbTcO_4}$, and the Laves phases ($R_{\mathrm{MT}}^{\min}$ is the minimal muffin-tin radius in the considered solid). A converged k mesh of 264–312 k points in the irreducible part of Brillouin zone was used for the hcp structures, 143 k points were used for $\mathrm{KTcO_4}$ and $\mathrm{RbTcO_4}$, and 288 k points for the Laves phases.

III. AVAILABLE EXPERIMENTS

In order to have a nonzero electric-field gradient tensor, the Tc atom should be at a site with less than cubic symmetry. This is the case for the 2*c* (−6*m*2) site in plain hcp-Tc metal, the 4*a* (−4) Tc site in $\mathrm{XTcO_4}$ pertechnates, and the Tc sites in $\mathrm{Mg(TcO_4)_2}$ and $\mathrm{Tc_2O_7\cdot H_2O}$. As far as we could verify, these are the only cases for which the quadrupole coupling constant C_Q has been determined by ^{99}Tc NMR.

A. ^{99}Tc NMR experiments in hcp-Tc metal

Several ^{99}Tc NMR experiments in hcp-Tc metal are published. Jones and Milford[25] obtained C_Q=5.9(2) MHz in 1962 (our average over the different values reported in their paper). Van Ostenburg *et al.*[26] found shortly thereafter a slightly deviating value of 5.05 MHz. A few years later, McCart and Barnes[27] confirmed the measurement of Jones and Milford, although without explicitly quoting a value for the coupling constant. They demonstrated that the distribution of the quadrupole coupling constant is below 5%. All of these experiments were performed at room temperature. Experiments as a function of temperature were not done until 2001 when Tarasov *et al.*[28] found a nearly constant quadrupole coupling constant of 5.74(5) MHz over the range of 120–400 K. This value is in perfect agreement with the value of Jones and Milford but with a considerably smaller error bar.

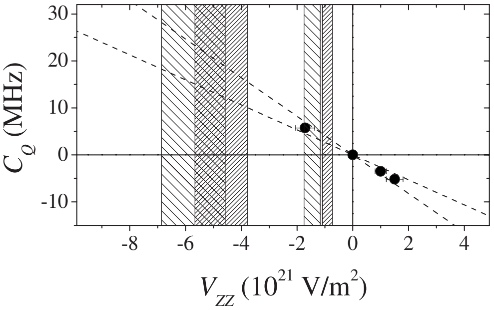

FIG. 1. Experimental quadrupole coupling constant C_Q (MHz) versus theoretical electric-field gradient component V_{ZZ} (10^{21} V/m^2). The dashed lines indicate the range in which the linear correlation can fall for extreme values of the quadrupole moment. For $\mathrm{YTc_2}$ and $\mathrm{ZrTc_2}$, the shaded areas indicate the assessed error bar in the calculated V_{ZZ} (see text). Up-to-down hatching indicates $\mathrm{ZrTc_2}$ and down-to-up hatching corresponds to $\mathrm{YTc_2}$. A negative sign for Q, according to Büttgenbach (Ref. 8), was assumed.

B. ^{99}Tc NMR experiments in $\mathrm{KTcO_4}$ and $\mathrm{RbTcO_4}$

The quadrupole coupling constants and asymmetry parameters of ^{99}Tc nuclei in 12 polycrystalline pertechnetates, as well as in $\mathrm{Mg(TcO_4)_2}$ and $\mathrm{Tc_2O_7\cdot H_2O}$, were determined by Tarasov *et al.*[29] The compounds with the highest experimental quadrupole coupling constants are $\mathrm{KTcO_4}$ and $\mathrm{RbTcO_4}$ [C_Q=5.2(1) and 3.5(2) MHz, respectively, both axially symmetric]. All other materials have smaller coupling constants, which will not contribute to a greater accuracy in our quadrupole moment determination (they will cluster near the origin in Fig. 1). Moreover, the majority of them do not lend themselves to a reliable treatment by our *ab initio* method as they contain hydrogen, water, or organic molecules or have very low crystal symmetry. $\mathrm{KTcO_4}$ and $\mathrm{RbTcO_4}$, on the other hand, have a simple unit cell with a small number of atoms and high symmetry, which allows high numerical precision in the calculations.

IV. RESULTS

A. Determination of Q

When plotting the experimental C_Q versus the calculated V_{ZZ}, a linear correlation that goes through the origin should appear (Fig. 1). The slope determines the quadrupole moment. Given the fact that we have three data points that lie

TABLE I. Comparison of the calculated and experimental values of V_{ZZ} for a series of elemental hcp-metals by using the Wu–Cohen functional (Ref. 20). The quadrupole moments Q are given in barn and V_{ZZ} in 10^{21} V/m^2. All experimental values for Q are taken from Ref. 36, except for ^{99}Tc where the value derived in this paper is given, and for ^{44}Sc where the recent and more accurate value from Ref. 16 is given. Experimental values for V_{ZZ} are derived from the quadrupole coupling constants given in Ref. 36 and from the quadrupole moments listed in the present table. The lattice constants are the experimentally determined lattice constants (Ref. 30). The sign of the experimental values for V_{ZZ} is unknown when not explicitly given. The error bars on V_{ZZ}^{expt} take the uncertainty in Q, as well as in C_Q, into account. The reported values for V_{ZZ} can be compared to seminal calculations by Blaha *et al.*(Ref. 31) 20 years ago on the same set of structures by using the local density approximation.

			I^{π}	Q (b)	V_{ZZ}^{calc}	V_{ZZ}^{expt}	a (Å)	c (Å)
^{9}Be	g. st.		$3/2^-$	$Q=+0.053(3)$	−0.052	0.048(4)	2.280(5)	3.600(7)
^{25}Mg	g. st.		$5/2^+$	$Q=+0.22(-)$	+0.038	0.061(7)	3.20944	5.21076
^{44}Sc	ex. st.	68 keV	1^-	$Q\pm0.214(3)$	+0.973	0.37(2)	3.3088(2)	5.2680(3)
^{45}Sc	g. st.		$7/2^-$	$Q=-0.22(1)$		0.38(2)		
^{43}Ti	ex. st.	3 066 keV	$19/2^-$	$Q\pm0.30(7)$	+1.698	1.1(5)	2.9508(2)	4.6855(3)
^{67}Zn	g. st.		$5/2^-$	$Q=+0.150(15)$	+4.084	+3.3(5)	2.665	4.947
^{67}Zn	ex. st.	605 keV	$9/2^+$	$Q=+0.60(7)$		3.1(4)		
^{69}Zn	ex. st.	439 keV	$9/2^+$	$Q=-0.45(7)$		4.2(8)		
^{90}Zr	ex. st.	3 589 keV	8^+	$Q\pm0.51(6)$	+4.116	3.7(4)	3.2331	5.1480
^{91}Zr	g. st.		$5/2^+$	$Q=-0.21(2)$		3.7(3)		
^{99}Tc	g. st.		$9/2^+$	$Q=-0.129(20)$	−1.709	1.84(30)	2.7407(1)	4.3980(1)
^{99}Ru	ex. st.	90 keV	$3/2^+$	$Q=+0.23(5)$	−1.605	−1.0(3)	2.7053	4.2820
^{111}Cd	ex. st.	247 keV	$5/2^+$	$Q=+0.83(13)$	+8.226	+7.3(9)	2.979	5.617

relatively close to the origin, uncertainties in C_Q, as well as in V_{ZZ}, will sensitively influence the value of the quadrupole moment. The experimental error bar on C_Q is fortunately quite small, especially for hcp Tc. In order to assess the spread on the calculated electric-field gradients, we will examine the case of hcp Tc, wherein our computational method is most reliable (GGA-based functionals are more reliable for metals than for oxides). In Table I, we list the calculated and experimental values of V_{ZZ} for a series of hcp metals including hcp-Tc. The lattice constants at which the calculations are done are the experimentally determined lattice constants.[30] From Table I, we can try to estimate the error bar on our calculated V_{ZZ} for Tc in hcp Tc. If we neglect the strongly deviating case of Sc—something that obviously deserves further attention—and attribute greater importance to cases wherein V_{ZZ} is not very small, an estimate of 20% uncertainty in the calculated V_{ZZ} seems to be conservatively safe (it is almost for sure an overestimation of the error bar as the deviations between calculated and experimental V_{ZZ} in Table I are dominated by uncertainties in the nuclear quadrupole moments). Given the fact that the calculated V_{ZZ} for Tc in hcp is -1.709×10^{21} V/m^2, a 20% uncertainty would mean the true value is within -1.37×10^{21} and -2.05×10^{21} V/m^2.

$KTcO_4$ and $RbTcO_4$ crystallize in the scheelite structure (space group $I4_1/a$). The lattice constants are experimentally known for both compounds while the coordinates of the atomic positions are experimentally determined only for $KTcO_4$ (see Table II for crystallographic details). Tc appears at the noncubic $4a$ position in this structure. We have optimized the internal positions in these crystals at fixed experimental lattice constants and calculated the EFG tensor at the Tc sites. The obtained results for the internal parameters x, y, and z, for V_{ZZ}, and for the asymmetry parameter η are given in Table II. We take as error bar on V_{ZZ} the same conservatively safe spread of 20%.

TABLE II. Calculated and experimental structural data for $KTcO_4$ and $RbTcO_4$ and predictions for V_{ZZ} and the asymmetry parameter $\eta=(V_{XX}-V_{YY})/V_{ZZ}$ $(|V_{ZZ}|>|V_{YY}|>|V_{XX}|)$ at the Tc site in these compounds that were obtained by using the experimentally determined lattice parameters. The parameters x, y, and z determine the positions of O atoms.

	$KTcO_4$	$RbTcO_4$
a_{expt} (Å)	5.630(2)[a]	5.758[b]
c_{expt} (Å)	12.867(4)[a]	13.540[b]
x_{expt}	0.1089(4)[a]	
y_{expt}	0.0254(4)[a]	
z_{expt}	0.2008(2)[a]	
x_{calc}	0.1170	0.1100
y_{calc}	0.0273	0.0308
z_{calc}	0.2015	0.1980
V_{zz}^{calc}	+1.45	+0.98
η^{calc}	0.00	0.00

[a] Reference 32.
[b] Reference 33.

TABLE III. Calculated and experimental structural data for YTc_2 and $ZrTc_2$ and predictions for V_{ZZ} and the asymmetry parameter η at the two Tc sites in these compounds that were obtained by using the experimentally determined lattice parameters. The parameters x and z determine the positions of Y (or Zr) and Tc atoms, respectively.

	YTc_2	$ZrTc_2$
a_{expt} (Å)	5.373[a]	5.2185(4)[b]
c_{expt} (Å)	8.847[a]	8.6527(7)[b]
x_{calc}^{6h}	−0.17080	−0.17105
z_{calc}^{4f}	0.06358	0.06243
V_{zz}^{calc} (Tc−6h)	−0.91	−1.46
η^{calc} (Tc−6h)	0.83	0.05
V_{zz}^{calc} (Tc−2a)	−4.72	−5.72
η^{calc} (Tc−2a)	0.00	0.00

[a] Reference 34.
[b] Reference 35.

All of these results lead to a value of (−)0.14(3) b for the quadrupole moment, which graphically allows for any straight line between the dashed lines in Fig. 1. Within the mutual error bars, this quadrupole moment is in perfect agreement with the most reliable experimental value of −0.129(20) b by Büttgenbach[8] (Sec. I). As the NMR experiments that we used in our derivation were powder experiments, they were not sensitive to the sign of the quadrupole coupling constant. We therefore do not know the sign of Q either (the data points in Fig. 1 could in principle be mirrored across the horizontal axis) but given the negative sign of the value by Büttgenbach,[8] a negative quadrupole moment is most likely—that is how it is plotted in Fig. 1.

B. Proposed NMR experiments

The fact that the data points in Fig. 1 lie close to the origin yields a large uncertainty in the determined Q. Experiments in Tc compounds, wherein the Tc atom is at a noncubic site and feels a much larger V_{ZZ}, could considerably lower the error bar on Q. Two suitable candidates are YTc_2 and $ZrTc_2$. Both crystallize in the $MgZn_2$-type structure (see Table III for crystallographic details). Tc appears at two inequivalent noncubic positions in this structure (2a and 6h) such that an experiment on one compound immediately provides us with two data points. We have optimized the internal positions in these crystals at fixed experimental lattice constants and calculated the EFG tensor at the Tc sites. The obtained results for the internal parameters x and z, V_{ZZ}, and the asymmetry parameter η are given in Table III. The results corresponding to V_{ZZ} are also indicated in Fig. 1 by vertical shaded areas (we take the conservatively safe spread of 20% on V_{ZZ} here; see Sec. IV A). It is clear from Fig. 1 what the expected quadrupole coupling constants are. These values provide complementary information and would allow fitting the quadrupole moment through several well-spread data points and the origin. If this measurement would be done with the same relative error of 0.9% as in the Tarasov experiment for hcp Tc, the error bar on Q could be considerably reduced. Moreover, if the experiment is set up such that the sign of the quadrupole interaction can be measured, then the sign of the quadrupole moment will be verified as well (we repeat here that the negative sign used in this work is not theoretically determined but is taken from the experiment by Büttgenbach[8]).

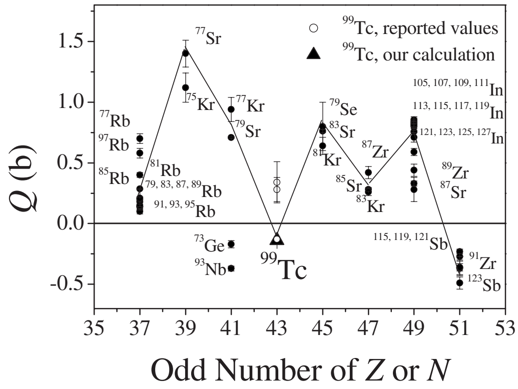

FIG. 2. Experimental trend for the nuclear quadrupole moments of isotopes with odd Z or N in the neighborhood of ^{99}Tc (recreated from Ref. 7).

C. Q trend in the Tc region

In Fig. 2, the quadrupole moments for isotopes with odd Z or N in the neighborhood of ^{99}Tc are given (data taken from the recent compilation by Stone[7]). This is a very much updated version of a similar picture published by Townes *et al.*[3] in 1949, which was used for the first estimate of a negative quadrupole moment for ^{99}Tc (Ref. 4, see Sec. I). When more than one value is available, the line connects the most plausible values. The previous positive estimates for the ^{99}Tc quadrupole moment are shown as well. The almost coinciding values from the most reliable experiment [−0.129(20)] and from the present work [(−)0.14(3)] fit into the general trend, but the less reliable previous experimental values [+0.34(17) and +0.28(10)] would also provide an acceptable trend.

V. CONCLUSIONS

Based on accurate NMR experiments found in literature and accurate first-principles electric-field gradient calculations, we have determined the quadrupole moment of the $9/2^+$ ground state of ^{99}Tc to be (−)0.14(3) b. This value deviates in magnitude and sign from two earlier experimental determinations but agrees nicely with −0.129(20) b, which is so far considered to be the most reliable value. We supply calculated values for the electric-field-gradient on two Tc sites in YTc_2 and $ZrTc_2$. A NMR measurement on ^{99}Tc in these compounds would allow to further reduce the error bar on this quadrupole moment.

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