



# *Ab-initio* calculations of electric field gradient in Ru compounds and their implication on the nuclear quadrupole moments of $^{99}\text{Ru}$ and $^{101}\text{Ru}$

S N MISHRA

Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India

E-mail: mishra@tifr.res.in

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**Abstract.** The nuclear quadrupole moments,  $Q$ , for the ground and first excited states in  $^{99}\text{Ru}$  and ground state of  $^{101}\text{Ru}$  have been determined by comparing the experimentally observed quadrupole interaction frequencies  $\nu_Q$  with calculated electric field gradient (EFG) for a large number of Ru-based compounds. The *ab-initio* calculations of EFG were performed using the all-electron augmented plane wave + local orbital (APW + lo) method of the density functional theory (DFT). From the slope of the linear correlation between theoretically calculated EFGs and experimentally observed  $\nu_Q$ , we obtain the quadrupole moment for the  $(5/2^+)$  ground state in  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  as 0.0734(17) b and 0.431(14) b respectively, showing excellent agreement with the values reported in literature. For  $3/2^+$ , the quadrupole moment of the first excited state in  $^{99}\text{Ru}$  is obtained as +0.203(3) b, which is considerably lower than the commonly accepted literature value of +0.231(12) b. The results presented in this paper would be useful for the precise determination of quadrupole moment of high spin states in other Ru isotopes and is likely to stimulate further shell model calculations for an improved understanding of nuclear shape in these nuclei.

**Keywords.** Hyperfine field; electric field gradient; density functional calculation; nuclear quadrupole moment.

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## 1. Introduction

Understanding the nuclear shape and structure of the excited states of the nuclei has been a topic of considerable interest for many years. Precise determination of nuclear quadrupole moment is crucial for understanding nuclear shape. Hyperfine interaction techniques such as nuclear magnetic/quadrupole resonance (NMR/NQR), Mössbauer spectroscopy (MS), perturbed angular correlation/distribution (PAC/PAD) etc. are often applied to determine quadrupole moments of the nuclei [1–5]. These techniques are also used for the microscopic investigation of electronic and magnetic properties of solids including novel phenomena like valence fluctuation, heavy fermion physics and superconductivity [6–8]. Experimentally, the nuclear quadrupole frequency is expressed through the coupling constant

$$\nu_Q = eQV_{zz}/h, \quad (1)$$

which depends on the product of the nuclear quadrupole moment  $Q$  and the gradient of the local electric field

at the site of the nucleus  $V_{zz}$  produced by the electron cloud of the solid. Determination of quadrupole moment  $Q$  from the experimentally observed  $\nu_Q$  requires prior knowledge about the electric field gradient (EFG)  $V_{zz}$ , which cannot be measured but calculated using different models. It can be immediately realized that precision calculation of EFG is essential to minimize the uncertainty in the quadrupole moment.

In the early years, calculation of EFG was made using the point charge model (PCM) [9]. In this model, the EFG is decomposed into two components: (i) a lattice contribution  $V_{zz}^{\text{lat}}$  assumed to stem from geometric arrangement of point-like electronic charges located at each lattice site and (ii) a valence electron contribution considered to be proportional to  $V_{zz}^{\text{lat}}$  such that the total field gradient is expressed as  $V_{zz}^{\text{tot}} = \alpha(1 - \gamma_\infty)V_{zz}^{\text{lat}}$ . Here,  $\gamma_\infty$  refers to the so-called Sternheimer antishielding factor and  $\alpha$  refers to the electronic enhancement factor. This model, though qualitatively reproduced the EFG in simple cases [9], it failed in many others, especially in alloys and compounds, as it neglected charge transfer, covalency and electron–electron correlation.

Modern methods based on density functional theory (DFT) have been shown to be successful in correctly predicting physical properties of solids and molecules [10]. In particular, the all-electron linearized augmented plane wave (LAPW) method has been found to accurately predict the EFGs in metals, alloys and compounds [10–16]. The precision calculation of EFGs through LAPW methods have been utilized to determine the quadrupole moments of several nuclei, including  $^{57}\text{Fe}$ , the celebrated nucleus in Mössbauer spectroscopy [11].

The  $5/2^+$  ground state in  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  are important nuclear probes for the measurements of quadrupole interaction via NMR and NQR spectroscopy. As such, they have been extensively utilized to get microscopic information regarding novel physical properties, e.g. heavy fermion behaviour in  $\text{CeRu}_2$ , unconventional superconductivity in  $\text{Sr}_2\text{RuO}_4$ , long-range magnetic ordering in  $\text{SrRuO}_3$ , etc. [7, 17–19]. Similarly, the  $3/2^+$  first excited state in  $^{99}\text{Ru}$  has served as the work horse in measurements employing Mössbauer and PAC spectroscopy [20–31]. In this respect, it is important to determine the quadrupole moments of these nuclear states with greater precision. Here, we present the *ab-initio* determination of nuclear quadrupole moment for the ground and first excited states in  $^{99}\text{Ru}$  and the ground state of  $^{101}\text{Ru}$  by comparing accurately measured quadrupole frequencies measured by different experimental techniques with precision calculation of electric field gradient in a number of Ru alloys and compounds. From the slope of the linear correlation between the calculated EFGs and the measured  $\nu_Q$ , we obtain the ground-state  $Q$  values for  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  as  $+0.0734(17)\text{b}$  and  $+0.431(14)\text{b}$  respectively, which show excellent agreement with the results reported in literature. The  $Q$  value for  $3/2^+$ , the first excited state in  $^{99}\text{Ru}$ , is found to be  $+0.203(3)\text{b}$ , which is lower than the commonly accepted literature value of  $+0.231(12)\text{b}$ .

## 2. Computational details

The EFG is a traceless second rank tensor defined by the second derivative (in Cartesian coordinates) of the Coulomb potential at the nuclear position. The Coulomb potential is calculated from the self-consistently obtained total charge distribution by solving the Poisson's equation. The EFG can be easily calculated, once the Coulomb potential is known. The field gradient tensor is diagonalized and principal components are rearranged such that  $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$  and the EFG is conventionally defined by  $V_{zz}$ , while  $(V_{xx} - V_{yy})/V_{zz}$  gives the asymmetry parameter related to the point symmetry of the atomic site. As the Coulomb potential is calculated from the total electronic charge

with the unit cell including the nucleus and no restriction is put on the nuclear shape, the derived EFG does rely on Sternheimer antishielding factor or any other arbitrary correction.

In the work presented here, we have performed EFG calculations for a large number of Ru-based alloys and compounds: elemental Ru metal; the rare-earth and actinide Laves phase compounds  $\text{RRu}_2$  with  $\text{R} = \text{La, Ce, Pr, Nd, Gd}$  and  $\text{Th}$ ; several oxides like  $\text{RuO}_2$ ,  $\text{CaRuO}_3$ ,  $\text{SrRuO}_3$  and  $\text{Sr}_2\text{RuO}_4$ ; and dilute Ru impurity in metallic hosts like  $\text{Ti, Re, Zn}$  and  $\text{Cd}$ , for which reliable and accurate experimental results for the quadrupole interaction frequency  $\nu_Q$  measured by different techniques like NMR/NQR, MS and PAC are available. Elemental Ru and  $\text{RuO}_2$  served as reference materials, which were earlier used for determining the quadrupole moments of the  $3/2^+$  state in  $^{99}\text{Ru}$  [32]. The Laves phase compounds  $\text{RRu}_2$  ( $\text{R} = \text{La, Ce, Pr, Nd, Gd}$  and  $\text{Th}$ ) are known to exhibit interesting electronic and magnetic properties and as such have been extensively studied by different experimental techniques including PAC spectroscopy. Amongst the Laves phase compounds,  $\text{RRu}_2$ ,  $\text{LaRu}_2$ ,  $\text{CeRu}_2$  and  $\text{ThRu}_2$  are known to be superconductors [33,34], while  $\text{PrRu}_2$ ,  $\text{NdRu}_2$ ,  $\text{GdRu}_2$  show long-range ferromagnetism [20,35]. Similarly,  $\text{SrRuO}_3$  is known to exhibit ferromagnetism [36] while  $\text{Sr}_2\text{RuO}_4$  has been observed to be an unconventional superconductor [37]. The selection of many compounds with widely different structural and electronic properties would allow the minimization of systematic error in the quadrupole moment derived from the linear correlation between  $\nu_Q$  and EFG.

For the calculations presented here, we have used the all-electron linearized augmented plane wave + local orbital (APW + lo) method as implemented in the WIEN2k code (2015 version) [38,39]. In this method, the unit cell is divided into non-overlapping atomic sphere of radius  $R_{\text{MT}}$  and the rest into interstitial region. The wave functions in the atomic spheres are expressed by spherical harmonics with maximum multipolarity  $l_{\text{max}} = 10$ , while the wave functions in the interstitial region are expanded in plane waves with the cut-off wave vector  $K_{\text{max}} = 8.0 \text{ a.u.}^{-1}$ . The  $R_{\text{MT}}$  values were chosen as:  $\text{Ru} = 2.0 \text{ a.u.}$ ; rare-earth (actinide) atoms ( $\text{La, Ce, Pr, Nd, Gd}$  and  $\text{Th}$ ) =  $2.5 \text{ a.u.}$ ; ( $\text{Ca, Sr}$ ) =  $2.3 \text{ a.u.}$ ; ( $\text{Zn, Cd}$ ) =  $2.4 \text{ a.u.}$  and  $\text{O} = 1.6 \text{ a.u.}$  The charge density was Fourier expanded up to  $G_{\text{max}} = 16\sqrt{\text{Ry}}$ . For the exchange correlation function, we have used the Perdew–Burke–Ernzerhof formalism of the generalized gradient approximation (GGA) [40]. Calculations were carried out after considering spin polarization using theoretical equilibrium lattice parameters and taking spin–orbit interaction into consideration. For the dilute impurity cases, Ru in  $\text{Ti, Re, Zn}$  and  $\text{Cd}$ , we used a supercell constructed with  $3 \times 3 \times 3$  units of the elemental

crystal structure. The integration in the reciprocal space was performed using the tetrahedron method using a  $k$ -mesh of size  $10 \times 10 \times 10$  in the full Brillouin zone. For the rare-earth Laves compounds  $RRu_2$ , a larger  $k$ -mesh of size  $20 \times 20 \times 20$  was used. The self-consistency of the calculations was ascertained from the charge and energy convergence criterion set to be 0.0001 and 0.01 mRy respectively. For the supercell calculations, lattice relaxation was considered to minimize the force on each of the atoms to less than 1 mRy/a.u.

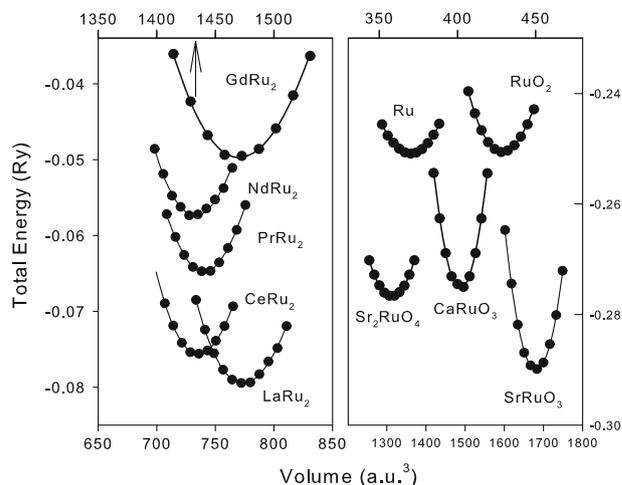
### 3. Results and discussion

For accurate calculation of EFG using DFT methods, one needs to provide precise values for the lattice constants of the unit cell of solids under investigation. As DFT calculations provide information regarding the ground-state ( $T = 0$  K) properties of solids, it is important to use lattice parameters measured at low temperatures, which may not be available for all the cases. Alternately, one can employ the DFT method itself to find the zero-temperature equilibrium lattice constants and use them for EFG calculations. It is generally observed that DFT calculations with the most commonly used GGA exchange correlation functional often overestimates the unit cell volume [41]. This would introduce a built-in error in the calculated EFG and hence the calculated  $Q$  value. However, as we shall see below, the calculated unit cell parameters of the compounds studied here agree with the experimental results within 1% and therefore does not pose serious problem towards obtaining quadrupole moments accurately.

The equilibrium lattice parameters of the compounds studied here were obtained by mapping the total energy surface as a function of unit cell volume,  $c/a$  (also  $b/a$  for orthorhombic structures) and internal coordinates. Figure 1 displays the total energy as a function of cell volume together with the fits to Birch–Murnaghan equation of state [42]. The lattice parameters obtained from the optimized structures are summarized in table 1 together with a few other properties like bulk modulus and magnetic moment. It is satisfying to note that the calculated lattice parameters are in good agreement with the experimental results [43–45]. This shows that the LAPW method correctly describes the structural as well as the magnetic properties of the materials and thus assures the reliability of the calculated EFGs.

#### 3.1 Determination of quadrupole moment for the $5/2^+$ ground state in $^{99}\text{Ru}$ and $^{101}\text{Ru}$

Let us first examine the quadrupole moment of the  $5/2^+$  ground state in  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$ . The nuclear quadrupole moments for the ground state of  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$



**Figure 1.** Variation of total energy as a function of unit cell volume. The vertical axis for each case has been shifted by an arbitrary value. Note that for Ru metal, we have multiplied the volume (top  $x$ -axis) by a factor 2 for aiding visual clarity.

were earlier determined from atomic beam magnetic resonance spectroscopy measurements and hyperfine-structure calculations with values  $Q = 0.076(7)$  b and  $0.44(4)$  b respectively [46]. These two nuclear states have been used extensively in NMR and NQR spectroscopies for studying quadrupole interaction in solids. In principle, the quadrupole moment can be derived from the experimentally observed  $\nu_Q$  of any one system. However, the  $Q$  value so determined may have systematic offset due to errors in measurement as well as calculation of EFG. We therefore have chosen sets of structurally different materials like Ru metal (hcp),  $\text{RuO}_2$  (orthorhombic),  $\text{CeRu}_2$  (C15 type cubic),  $\text{SrRuO}_3$  (orthorhombic) and  $\text{Sr}_2\text{RuO}_4$  (tetragonal) for which accurate  $\nu_Q$  measurements at low temperatures have been reported using NMR and NQR spectroscopies [7,17,19,47]. We have made precision EFG calculations for these materials. The measured  $\nu_Q$  and the calculated EFGs are listed in table 2 and displayed in figure 2. The EFG calculations have been performed previously for Ru metal and  $\text{Sr}_2\text{RuO}_4$  using FLAPW method [10,48]. The EFG values obtained from our calculations show excellent agreement with the results reported earlier. As expected,  $\nu_Q$  for both isotopes of Ru vary linearly with  $V_{zz}$ . The results were fitted to eq. (1), yielding the slope ( $= eQ/h$ ) to be  $1.774(42)$  MHz/ $\text{V m}^{-2}$  and  $10.416(25)$  MHz/ $\text{V m}^{-2}$  for  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  from which we determine the quadrupole moments of the  $I = 5/2^+$  ground state in  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  as  $Q_0 = 0.0734(17)$  b and  $0.431(14)$  b respectively, showing excellent agreement with the literature values.

**Table 1.** Summary of the calculated structural properties.

| Compound                         | Space group          | Properties | Lattice constant (Å)                       |                          | $B$ (GPa) | $M$ ( $\mu_B$ )                                |
|----------------------------------|----------------------|------------|--|--------------------------|-----------|--|
|                                  |                      |            | (Calc.)                                    | (Exp.)                   |           |  |
| Ru                               | P6 <sub>3</sub> /mmc | M; NM      | $a = 2.713$<br>$c = 4.294$                 | 2.706<br>4.282           | 187       | 0  |
| LaRu <sub>2</sub>                | Fd3m                 | M; NM      | $a = 7.707$                                | 7.702                    | 138       | 0  |
| CeRu <sub>2</sub>                | Fd3m                 | M; NM      | $a = 7.544$                                | 7.536                    | 168       | 0  |
| PrRu <sub>2</sub>                | Fd3m                 | M; FM      | $a = 7.603$                                | 7.624                    | 171       | $M_s^{\text{Pr}} = 1.8; M_o^{\text{Pr}} = 3.6$ |
| NdRu <sub>2</sub>                | Fd3m                 | M; FM      | $a = 7.590$                                | 6.614                    | 174       | $M_s^{\text{Nd}} = 2.9; M_o^{\text{Nd}} = 5.4$ |
| GdRu <sub>2</sub>                | P6 <sub>3</sub> /mmc | M; FM      | $a = 5.287$<br>$c = 8.926$                 | 5.271<br>8.904           | 175       | $M_s^{\text{Gd}} = 7.4; M_o^{\text{Gd}} = 0.0$ |
| ThRu <sub>2</sub>                | Fd3m                 | M; NM      | $a = 7.678$                                | 7.649                    | 169       | 0  |
| RuO <sub>2</sub>                 | P4 <sub>2</sub> /mnm | M; NM      | $a = 4.477$<br>$b = 4.477$<br>$c = 3.084$  | 4.497<br>4.497<br>3.105  | 261       | 0  |
| CaRuO <sub>3</sub>               | Pnma                 | M; FM      | $a = 5.507$<br>$b = 7.608$<br>$c = 5.318$  | 5.524<br>7.649<br>5.354  | 203       | $M_s^{\text{Ru}} = 0.48; M_o^{\text{Ru}} = 0$  |
| SrRuO <sub>3</sub>               | Pnma                 | M; FM      | $a = 5.612$<br>$b = 7.902$<br>$c = 5.572$  | 5.575<br>7.850<br>5.535  | 185       | $M_s^{\text{Ru}} = 1.20; M_o^{\text{Ru}} = 0$  |
| Sr <sub>2</sub> RuO <sub>4</sub> | I4/mmm               | M; SC      | $a = 3.898$<br>$b = 3.898$<br>$c = 12.806$ | 3.862<br>3.862<br>12.722 | 134       | $M_s^{\text{Ru}} = 0.36; M_o^{\text{Ru}} = 0$  |

$B$  and  $M$  are bulk modulus and magnetic moment respectively.  $M_s$  and  $M_o$  are spin and orbital moments.

$V_{zz}$  is the principal component of the calculated EFG.

M – metal; NM – nonmagnetic; FM – ferromagnetic; SC – superconductor.

**Table 2.** Calculated electric field gradient,  $V_{zz}$  ( $10^{21}$  V/m<sup>2</sup>) and experimental quadrupole interaction frequencies  $\nu_Q = eQV_{zz}/h$  for the ground ( $I = 5/2^+$ ) state in <sup>99</sup>Ru and <sup>101</sup>Ru obtained from NMR and NQR studies in Ru metal and compounds.

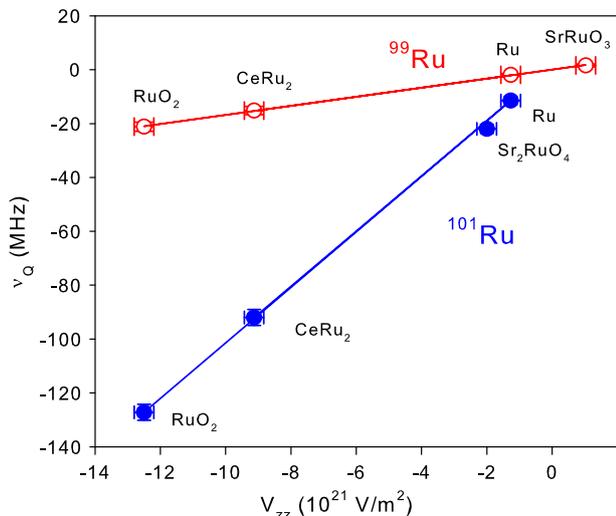
| Compound                         | $V_{zz}$ ( $10^{21}$ V/m <sup>2</sup> ) | $\nu_Q$ <sup>99</sup> Ru (MHz) | $\nu_Q$ <sup>101</sup> Ru (MHz) | Method | References |
|----------------------------------|---|--------------------------------|---------------------------------|--------|------------|
| Ru                               | -1.27                                   | -2.00                          | -11.60                          | NMR    | [7,47]     |
| CeRu <sub>2</sub>                | -8.48                                   | -15.20                         | -88.00                          | NQR    | [17]       |
| RuO <sub>2</sub>                 | -12.50                                  | -21.20                         | -127.2                          | NMR    | [7]        |
| SrRuO <sub>3</sub>               | 1.03                                    | 1.55                           |                                 | NMR    | [7]        |
| Sr <sub>2</sub> RuO <sub>4</sub> | -2.05                                   |                                | -22.00                          | NQR    | [7,19]     |

All  $\nu_Q$  data refer to measurements at temperatures below 4.2 K.

### 3.2 Quadrupole moment of the $3/2^+$ first excited state in <sup>99</sup>Ru

Next we come to the determination of the quadrupole moment of the  $3/2^+$  first excited state in <sup>99</sup>Ru. This nuclear state with the half-life  $T_{1/2} = 20.5$  ns is suitable for both Mössbauer spectroscopy and PAC studies. As such, it has been extensively used to study electronic and magnetic properties of different solids. The quadrupole moment of the  $3/2^+$  state in <sup>99</sup>Ru was first measured by Kistner using Mössbauer spectroscopy and reported a lower limit for the  $Q_e$  value as  $\geq 0.15$  b [32]. Later, Mössbauer measurements by Gib *et al* [49] and Kistner [50] reported the quadrupole moment to be  $Q_e = 0.23 \pm$

0.05 b which is now the most accepted value in literature. It should be noted that determination of quadrupole moment for the first excited state from Mössbauer measurements requires the prior knowledge of the ground-state moment  $Q_0$  as well as the ratio  $Q_e/Q_0$ . Gib *et al* and Kistner used the values  $Q_0 = 0.077$  b and  $Q_e/Q_0 = 2.93$  derived from atomic beam magnetic resonance studies [46]. On the other hand, the quadrupole interaction frequency obtained from PAC measurements does not depend on the ground-state properties of the nucleus. Thus,  $Q_e$  can be directly obtained from eq. (1) provided one knows the EFG values accurately. We have therefore calculated the EFG for a number of carefully selected Ru compounds (see table 1) for which



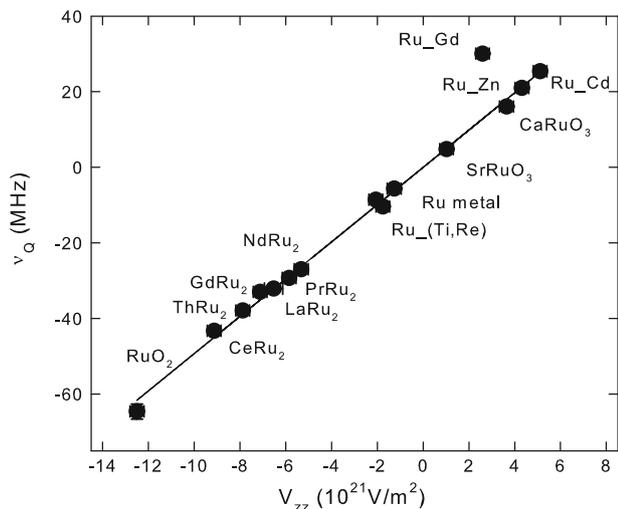
**Figure 2.** Experimental nuclear quadrupole frequency  $\nu_Q (=eQV_{zz}/h)$  for the  $5/2^+$  ground states in  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  obtained from high-resolution NMR and NQR measurements vs. calculated electric field gradient  $V_{zz}$  for Ru metal and some compounds.

$\nu_Q$  values have been accurately measured. The calculated  $V_{zz}$  and the measured  $\nu_Q$  results are summarized in table 3. Figure 3 displays the plot of the experimentally measured  $\nu_Q$  vs. the calculated  $V_{zz}$ . It can be noticed that most of the data points fall in a straight line with the lone case of Ru impurity in Gd being a clear outlier. In order to determine the quadrupole moment,

we first consider the data for Ru metal,  $\text{RuO}_2$ ,  $\text{GdRu}_2$ ,  $\text{CaRuO}_3$ ,  $\text{SrRuO}_3$  and dilute Ru impurity in Ti and Re for which experimental data are available at low temperatures. A linear regression fit of the data to eq. (1) gives the slope ( $=eQ/h$ ) =  $4.913 \pm 0.08$ , yielding the quadrupole moment of the first excited state in  $^{99}\text{Ru}$  as  $Q_e = 0.203(3)$  b.  $Q_e$  obtained from our *ab-initio* EFG calculations is lower compared to the literature value 0.231(12). It is satisfying to note that the EFG values calculated for the compounds  $\text{RRu}_2$  as well as the cases for dilute impurities Ru in Zn and Cd fall on the same linear curve. The deviation of Ru in Gd data from the above linear relation may be due to error in the experimental  $\nu_Q$  value or the calculated  $V_{zz}$ . It is possible that the experimental results may have some uncertainty due to the imprecise knowledge of the lattice site location of the Ru impurity. Considering that Ru has very low solubility in Gd, there may be clustering or alloy formation which may have different local surrounding and hence EFG. More precise measurement of  $\nu_Q$  of Ru in Gd is necessary to address this discrepancy. On the theoretical side, we have repeated our calculations using different exchange correlation functional. The effect of on-site Coulomb correlation (LSDA/GGA + U) was also considered. In all the cases, the calculated EFG is in the range of  $(2.4\text{--}2.8) \times 10^{21} \text{ V/m}^2$ . Further calculations using more modern exchange correlation functional like the hybrid functional may be useful to address the discrepancy observed for the EFG of dilute Ru impurity in Gd.

**Table 3.** Calculated electric field gradient,  $V_{zz}$  ( $10^{21} \text{ V/m}^2$ ) and experimental quadrupole interaction frequency  $\nu_Q (=eQV_{zz}/h)$  for the  $3/2^+$  state in  $^{99}\text{Ru}$  in different compounds. The temperature of  $\nu_Q$  measurements are listed in column 5.

| Compound                | $V_{zz}$ | $\nu_Q$ (MHz)    | Method | $T$ (K) | References |
|-------------------------|----------|------------------|--------|---------|------------|
| Ru                      | -1.27    | $5.67 \pm 0.16$  | PAC    | 15      | [28]       |
| $\text{LaRu}_2$         | -6.53    | $32.1 \pm 0.3$   | PAC    | 300     | [27,29]    |
| $\text{CeRu}_2$         | -8.48    | $43.3 \pm 0.3$   | PAC    | 300     | [27,29]    |
| $\text{PrRu}_2$         | -6.14    | $29.3 \pm 0.3$   | PAC    | 300     | [27,29]    |
| $\text{NdRu}_2$         | -5.42    | $27.0 \pm 0.3$   | PAC    | 300     | [27,29]    |
| $\text{GdRu}_2$         | -7.12    | $33.0 \pm 0.3$   | ME     | 4.2     | [20]       |
| $\text{ThRu}_2$         | -8.18    | $39.9 \pm 0.3$   | PAC    | 300     | [29]       |
| $\text{RuO}_2$          | -12.5    | $64.6 \pm 1.0$   | ME     | 4.2     | [32]       |
| $\text{CaRuO}_3$        | 4.02     | $16.95 \pm 0.3$  | PAC    | 20      | [24]       |
| $\text{SrRuO}_3$        | 1.03     | $4.77 \pm 0.2$   | PAC    | 26      | [24]       |
| Ru <sub>imp</sub> in Zn | 4.31     | $21.0 \pm 0.6$   | PAC    | 300     | [30]       |
| Ru <sub>imp</sub> in Cd | 5.11     | $25.4 \pm 1.0$   | PAC    | 300     | [30]       |
| Ru <sub>imp</sub> in Ti | -1.76    | $-10.40 \pm 0.4$ | ME     | 4.2     | [26]       |
| Ru <sub>imp</sub> in Re | -2.07    | $-8.60 \pm 0.4$  | ME     | 4.2     | [26]       |
| Ru <sub>imp</sub> in Gd | 2.59     | $30.06 \pm 0.6$  | PAC    | 300     | [31]       |



**Figure 3.** Quadrupole frequency  $\nu_Q$  of the  $3/2^+$  first excited state in  $^{99}\text{Ru}$  vs. calculated electric field gradient  $V_{zz}$  for Ru metal and compounds.

### 3.3 Error estimation

The error in the quadrupole moment determined from the above procedure depends on the uncertainty in the experimentally measured  $\nu_Q$  and the calculated EFG. The error bars quoted for  $\nu_Q$  are typically less than 1%. Normally, error bars are not quoted for DFT-calculated properties as it is an *ab-initio* approach and is expected to provide exact information. However, in recent times, efforts have been made to make estimates of error in DFT-calculated properties like lattice parameters and EFG [16,41]. Depending on the choice of the parameters like the muffin-tin radius of the atomic spheres  $R_{\text{MT}}$  and more importantly the size of the basis set controlled by the maximum value of the k-vector  $K_{\text{max}}$  and the density of the k-mesh used for Brillouin zone integration, one may find a small variation in physical properties, for example the electric field gradient. The precision of the calculated EFG was tested by examining the convergence with respect to variations in  $R_{\text{MT}}$ ,  $K_{\text{max}}$  and k-mesh size. The spread in the EFG tensor was found to be less than  $0.05 \times 10^{21} \text{ V/m}^2$ . Apart from these, the physical property under consideration, especially the EFG obtained from the self-consistent solution corresponding to the best set of the above-mentioned parameters can vary for different choices of exchange correlation functional. In order to check the error in our EFG values arising from the particular choice of exchange correlation functional, we carried out calculations using the two most commonly used exchange correlation functionals, namely, GGA and LDA. The results showed a maximum deviation of  $\approx 0.15 \times 10^{21} \text{ V/m}^2$  for the two extreme cases, i.e. for

$\text{RuO}_2$  and Ru impurity in Cd. Another major source of error can be due to uncertainty in the lattice parameters. For the calculations presented here, we have used the theoretical equilibrium lattice parameters, which deviated from the experimental values by less than 1%. To examine the deviation in the EFG with respect to this small change in the lattice constants, we performed calculations for a few selected compounds (Ru metal,  $\text{RuO}_2$ ,  $\text{LaRu}_2$ ,  $\text{CaRuO}_3$  and Ru impurity in Zn metal) using the experimental unit cell parameters shown in table 1. The maximum difference between the EFG calculated with theoretical and experimental values is  $\leq 0.3 \times 10^{21} \text{ V/m}^2$ . It is not clear how each of these error bars is related. Assuming that they are uncorrelated, we take the sum of all the contributions discussed above and the upper bound for error in our EFG values comes out to be  $0.5 \times 10^{21} \text{ V/m}^2$ . The error bar for the quadrupole moment quoted in this paper is obtained from the regression fit of all data points by taking into account the error bars in  $\nu_Q$  as well as the calculated EFG.

### 4. Conclusion

In conclusion, we have performed detailed *ab-initio* calculation of electric field gradient for a number of Ru compounds. By comparing the calculated EFGs with accurately measured nuclear quadrupole frequencies available in literature, we have determined the quadrupole moments of the ground and first excited states in  $^{99}\text{Ru}$  as well as the ground state in  $^{101}\text{Ru}$ . From the slope of the linear correlation between the calculated EFGs and the measured  $\nu_Q$ , we obtain the ground-state  $Q$  values for  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  as  $+0.0734(17)\text{b}$  and  $+0.431(14)\text{b}$  respectively, which show excellent agreement with the results reported in literature. The  $Q$  value for the  $3/2^+$  first excited state in  $^{99}\text{Ru}$  is found to be  $+0.203(3)\text{b}$ . This is considerably lower than the commonly accepted literature value of  $+0.231(12)\text{b}$ . The work presented here would be useful for precision determination of quadrupole moment of high spin states in other Ru isotopes and stimulate shell model calculations for an improved understanding of nuclear shape in these nuclei.

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