Nuclear Quadrupole Interaction at $^{187}\text{W}(\beta^-)^{187}\text{Re}$ in Tungsten Compounds

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The nuclear quadrupole interaction at $^{187}\text{W}(\beta^-)^{187}\text{Re}$ was determined by time differential perturbed angular correlation in WC, WS$_2$, WSe$_2$, WSi$_2$, and CaWO$_4$ to be (at 300 K): $v_Q = 335.9(2)$, $1094.9(1)$, $1031.6(1)$, $1131.5(1)$, and $1085.9(1)$ MHz, respectively. The asymmetry parameter $\eta$ was zero in all cases. For WSe$_2$ and CaWO$_4$ the temperature dependence of the nuclear quadrupole interaction was determined between 300 K and about 900 K. Ab initio calculations of electric field gradients, using the WIEN95-code, were carried out for WC, WS$_2$, WSe$_2$, and WSi$_2$ at W-sites and Re-impurities, and for CaWO$_4$ at W-sites. Good agreement with experimental data was found.

1. Introduction

Tungsten and tungsten compounds play an important role in industrial applications. Examples are W-filaments in bulbs, WC with 5–10% Co exhibiting extraordinary hardness (“WIDIA”), or W-based catalysts [1, 2]. Multilayers consisting of W and Si are used as X-ray monochromators [3]. W also plays a role in micro-organisms. Thermophilic archaea, e.g., use W-enzymes for methanogenesis [4, 5, 6]. Hence, it would be desirable to have a hyperfine spectroscopic tool to investigate the nuclear quadrupole interaction in such systems. Classical techniques like nuclear magnetic resonance or nuclear quadrupole resonance are hampered by the lack of suitable nuclei (the naturally occurring isotopes have either a nuclear spin $I = 0$ or $I = 1/2$ groundstate). Mössbauer spectroscopy on $^{182}\text{W}$ has a first excited state with $I = 2$ but suffers from poor energy resolution. An interesting alternative is offered by time differential perturbed angular correlation (TDPAC) of $\gamma$-rays from $^{187}\text{W}$ ($T_{1/2} = 24$ h) which feeds the 479.5 keV – 72 keV $\gamma-\gamma$-cascade in $^{187}\text{Re}$ via $\beta^-$-decay. The disadvantage is that the nuclear quadrupole interaction (NQI) is determined at $^{187}\text{Re}$, presumably on a W-lattice site, and not directly at a W-isotope. There are, however, important advantages counterbalancing this drawback:

(i) TDPAC is extremely sensitive, about $10^{10}$ atoms suffice; this is particularly important for biophysical applications.
(ii) The energy or frequency resolution of this TDPAC is excellent due to the very long halflife of the intermediate (206.2 keV) excited state ($T_{1/2} = 555.3$ ns).
(iii) The anisotropy of the $\gamma-\gamma$-cascade is large: $A_{22} = -13.1%$ [7].
(iv) The nuclear quadrupole moment of the 206.2 keV state is large: $Q = 3.04(5)$ b [7].

Despite these most favourable nuclear properties, applications with $^{187}\text{W}$-TDPAC were rather scarce [8, 9, 10] for the following reasons:

(i) Due to the large quadrupole moment, the NQI-frequencies are frequently rather high and require sub-nanosecond timing, i.e. BaF$_2$-scintillators.
(ii) The intermediate excited state has $I = 9/2$, which leads to a multitude of up to 10 lines for non-axial symmetry in a Fourier transformed TDPAC-spectrum.
(iii) The stop-energy of 72 keV is just heigh enough to produce prompt K-X-rays after K-edge absorption; this X-ray admixture reduces the effective anisotropy drastically; this effect is more severe with BaF$_2$-scintillators compared to NaI(Tl).

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Therefore $^{187}$W is not considered a very suitable isotope among TDPAC-spectroscopists. Despite these drawbacks we initiated a study with this nuclear probe in several W-compounds using a high efficiency 6-detector TDPAC-camera [11]. In this way, $10^8$...$10^9$ coincidences could be recorded per spectrum in total. Moreover, a new method of data analysis, namely cross correlation [12], was found to be rather useful to cope with the multiline problem due to $I = 9/2$. With these hard- and software improvements, $^{187}$W-TDPAC spectroscopy turns out to be rather promising, as demonstrated in this paper.

2. TDPAC and Nuclear Quadrupole Interaction

TDPAC usually requires a $\gamma$-$\gamma$-cascade. Due to angular momentum conservation the observation of $\gamma_1$ in a certain direction produces an aligned subensemble of nuclei whose subsequent emission of $\gamma_2$ is anisotropic. Hence, the coincidence countrate between $\gamma_1$ and $\gamma_2$ is anisotropic in general, whereas the individual emission characteristics of $\gamma_1$ and $\gamma_2$ are isotropic:

$$W(k_1,k_2) = \sum_k A_k(\gamma_1) A_k(\gamma_2) P_k(\cos \theta).$$  \hspace{1cm} (1)

Here, $k_1$ and $k_2$ are the emission directions of $\gamma_1$ and $\gamma_2$ with $\theta$ denoting the angle between them. The sum runs over even integers due to parity conservation of the electromagnetic interaction. Usually, $k = 0, 2$ is sufficient. $A_k(\gamma_1)$ and $A_k(\gamma_2)$ are coefficients depending on the nuclear spins involved in the transition and on mixing ratios for mixed multipolarities. In the case of the 479.5 keV - 72 keV cascade in $^{187}$Re we have: $A_2(\gamma_1) A_2(\gamma_2) \equiv A_{22} = -0.131$, $A_{44} = 0$. $P_k(\cos \theta)$ is a Legendre polynomial. If the nucleus in the intermediate excited state is subjected to extranuclear fields - in our case it interacts via its nuclear quadrupole moment with an electric field gradient (EFG) - the angular correlation of (1) is modified:

$$W(k_1,k_2,t) = e^{-t/t_N} \sum_k A_{kk} G_{kk}(t) P_k(\cos \theta).$$ \hspace{1cm} (2)

This time dependent angular correlation applies to random powder samples. The function $G_{kk}(t)$ is called perturbation function and contains all information about the NQI. The exponential factor accounts for the fact that the coincidence probability between $\gamma_1$ and $\gamma_2$ with a time-lag $t$ between them decreases with the lifetime $\tau_N$ of the intermediate excited state.

In the case of axial symmetry of the EFG-tensor, i.e. $\eta = (V_{xx} - V_{yy})/V_{zz} = 0$, we have for $I = 9/2$

$$G_{22}(t) = \frac{1}{5} \left( \frac{29}{165} \cos \omega t + \frac{14}{165} \cos 2\omega t \right)$$
$$+ \frac{3}{11} \cos 3\omega t + \frac{8}{55} \cos 4\omega t$$
$$+ \frac{14}{165} \cos 5\omega t + \frac{2}{55} \cos 7\omega t$$ \hspace{1cm} (3)

with $\omega = eQV_{zz}/24$ h and $eQ$ denoting the nuclear quadrupole moment of the intermediate excited state. $V_{zz}$ is the largest component of the EFG-Tensor. Frequently, the NQI-frequency is quoted as $\nu_Q = eQV_{zz}/\hbar = 12 \omega/\pi$.

Summing up, the coincidence countrate of (2) is periodically modulated by the perturbation function of (3). The larger $\tau_N$ ("exploration time"), the more oscillations are observable and, hence, the better the frequency resolution.

3. Spectrometer and Data Analysis

We used the 6-detector TDPAC-camera [11] equipped with conically capped BaF$_2$-scintillators. In this way, 6 coincidence spectra at $\theta = 180^\circ$ and 24 coincidence spectra at $\theta = 90^\circ$ can be recorded simultaneously. Because we allocated 1024 channels per subgroup (i.e., we used a 32 K multichannel analyzer) and because we anticipated high frequencies, we used approximately 1 ns per channel. In this way, only about 750 ns could be monitored which corresponds to about 1.5 halflifes of $^{187}$W only. Usually five to ten halflifes are observable before the signal to noise ratio becomes excessively small. This, however, would have required 4 K per subgroup or a 128 K multichannel analyzer which became available only recently. Hence, the frequency resolution could be improved by a factor of 4 easily compared to what is presented below. The experimental time resolution for the 479.5 keV - 72 keV cascade was about 850 ps.

The data analysis was performed as follows: First, the uncorrelated background of accidental coincidences was determined from the spectral region of $t < 0$ and subtracted from the raw data. Next, all spectra were shifted to a common origin of time ($t = 0$). The huge prompt contribution in each subgroup served for that purpose. Finally, the following ratio was formed:

$$R(t) = \frac{W(180^\circ)}{W(90^\circ)} + 2W(90^\circ)$$ \hspace{1cm} (4)
with
\[ W(180°) = \sum_{i,j=1; i \neq j} W_{ij}, \]
\[ W(90°) = \sum_{i,j=1; i \neq j} W_{ij} \]
without \( W_{ij} \).

Here, \( W_{ij} \) denotes the coincidences between detectors \( i \) (start) and \( j \) (stop). By forming this ratio, the exponential decay factors cancel and the detector efficiencies cancel to first order. Restricting to random powder samples and \( k = 2 \) (this is true in the present case) we have
\[ R(t) = A_{22} G_{22}(t). \]

\( R(t) \) is called the "time spectrum". Its cosine transform yields a comb of equidistant lines (for asymmetry parameter \( \eta = 2 \) (this is true in the present case) we have
\[ k = \frac{1}{2}, \]
\[ \eta = 2 \]
and
\[ \tau_{\text{FWHM}} \]
where \( \tau_{\text{FWHM}} \) denotes the full width at half maximum of the time resolution function (assumed Gaussian).

The following modifications of (6) are necessary, when actually fitting time spectra:

(i) \( A_{22} \) is reduced because of solid angle correction factors (the detector averages over the acceptance angle) and in the present case due to the X-ray admixture in the stop channel. Hence, \( A_{22} \) is treated as a free parameter.

(ii) The finite time resolution of the spectrometer leads to a progressive suppression of higher frequencies, which can be approximated by the following factor multiplying the cosine terms in (3):
\[ e^{-0.09 \tau_{\text{FWHM}} n^2 \omega^2}, \]
\[ n = 1, \ldots, 7, \]
where \( \tau_{\text{FWHM}} \) denotes the full width at half maximum of the time resolution function (assumed Gaussian).

(iii) A static inhomogeneous distribution of frequencies \( \omega \) (assumed Lorentzian) leads to an additional time dependent factor which causes a damping of the oscillations (or, equivalently, a line-broadening of the Fourier-transformed time spectrum):
\[ e^{-\delta \omega^2}, \]
\[ n = 1, \ldots, 7, \]
with \( \delta \) being the half width at half maximum of the frequency distribution function.

In practice, a time independent baseline shift is also fitted and treated as a free fitting parameter. In order to obtain a first good guess for the fitting parameter \( \omega \) we performed a cross-correlation analysis, as described in [12].

4. Sample Preparation

WC was purchased from Fluka. It crystallizes in the space group \( P6_3/m2 \) with lattice constants \( a = 2.9065 \) Å and \( c = 2.8366 \) Å. There is one formula unit per unit cell [13].

Single crystals of WS\(_2\) and WSe\(_2\) were prepared by vapour transport and generously provided by Prof. F. Lévy, EPF Laussane, and Prof. E. Bucher, University of Konstanz. Both layered dichalcogenides crystallize in the space group \( P6_3/mcc \) with lattice constants \( a = 3.1532 \) Å, \( c = 12.329 \) Å and \( a = 3.2882 \) Å, \( c = 12.96 \) Å, respectively. There are two formula units per unit cell [14, 15].

WS\(_2\) was purchased from Johnson Matthey. It crystallizes in the space group \( I4/mmc \) with lattice constants \( a = 3.2718 \) Å and \( c = 7.8403 \) Å. There are two formula units per unit cell [16].

CaWO\(_4\) was generously provided by Prof. G. Völkel and Dr. J. Simon, University of Leipzig, in the form of small single crystals. It crystallizes in the space group \( I4_1/amd \) with lattice constants \( a = 5.2429 \) Å and \( c = 11.3737 \) Å. There are 4 formula units per unit cell [17].

We expect axial symmetry for the EFG-Tensor in all cases because there is a threefold rotation axis in WC, WS\(_2\), and WSe\(_2\), a fourfold rotation axis in WS\(_2\), and a fourfold inversion axis in CaWO\(_4\).

All samples were neutron irradiated at the Forschungsreaktor München (FRM) at a thermal neutron flux of about \( 2 \times 10^{13} \) n/(cm\(^2\)s) for about 10 min to 2 hours. In principle, we should expect radiation damage as a consequence of prompt \( \gamma \)-deexcitation (\( E_{\text{max}} = 5.5 \) MeV) following the neutron capture. The recoil energy of \( E_{\text{recoil, max}} = 90 \) eV should be more than sufficient to produce near neighbour vacancies. However, we did not observe any indication for radiation damage in any of our samples. Thermal annealing of WS\(_2\) after irradiation at 800°C for 2 h did not produce any noticeable effect.

Measurements at elevated temperatures up to 764 K for WSe\(_2\) and 911 K for CaWO\(_4\) did not yield sharper lines or an increase in effective anisotropy \( A_{22} \). Hence, we believe that in all cases light displaced neighbouring at-

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1. W at (0, 0, 0) and C at (\( \frac{2}{3} \frac{1}{3} \frac{1}{2} \)).
2. W at (\( \frac{1}{3} \frac{1}{3} \frac{1}{4} \)), S and Se at (\( \frac{1}{4} \frac{2}{3} \frac{1}{6} \)), with \( u = 0.6225 \) for S and \( u = 0.6211 \) for Se, respectively.
3. W at (0, 0, 0) and Si at (0, 0, 0.3345).
4. Ca at (0, \( \frac{1}{3} \frac{5}{6} \)), W at (0, \( \frac{1}{3} \frac{1}{8} \)), and O at (0.1507, 0.0086, 0.2106).
oms are mobile enough at 433 K (the temperature during irradiation) to recombine with vacancies, i.e., the radiation damage is already annealed before we started the TDPAC measurements. Therefore all samples were used “as irradiated”. Because of the relatively short half-life of $^{187}$W (24 h) we irradiated 4 samples with weight ratios 1:2:4:8 simultaneously and changed samples every 24 h. The total data collection time per spectrum was 4–5 days.

In order to minimize selfabsorption in the sample, we used very small specimens (0.1–0.4 mg) only, unless stated otherwise. No isotope enrichment was necessary.

5. Results

5.1. TDPAC-Experiments

5.1.1. WC

The time spectrum for WC at room temperature together with its cosine transform is shown in Figure 1. The typical $I = 9/2$ random powder pattern for axial symmetry is immediately recognizable. There is some damping of the oscillation amplitude. Moreover, a dispersive-like distortion is visible around 550 Mrad/s which is a consequence of a mismatch of the anode signal to the constant fraction triggers, as verified with a 5 Gsamples/s digital oscilloscope in the averaging mode. There is also a slightly increasing baseline for the first 100 ns which leads to the low-frequency intensity in the cosine transformed spectrum. Finally, there is a sloping baseline in the range 100 ns–750 ns. The latter two effects could be eliminated totally by the use of a veto-logic which prevents triple and higher multiple coincidences. However, both baseline problems have no influence on the determination of the NQI-parameters. A least squares fitting analysis yielded $\omega = 87.94(5)$ Mrad/s, a Lorentzian damping of $\delta = 1.36(6)$% and an effective anisotropy of $\Delta_{\frac{\gamma}{2}} = -2.25(6)$%. A total of $1.6 \cdot 10^9$ coincidences was recorded for this spectrum.

![Fig. 1. Time spectrum for $^{187}$Re in WC (top) and its cosine transform (bottom).](image)
5.1.2. WS$_2$

The time spectrum for WS$_2$ at room temperature together with its cosine transform is shown in Figure 2. It is immediately clear that the NQI is much higher compared to the case of WC. There are still problems with the very slightly sloping baseline and electronic distortions in the first 50 ns of the time spectrum. In fact, these distortions were modelled and subtracted from the time spectrum prior to the cosine transformation. All harmonics but $I_{00}$ are clearly visible despite the high fundamental frequency. This is clearly due to the good time resolution of BaF$_2$-scintillators. A least squares fitting analysis yielded $\omega = 286.64(3)$ Mrad/s and an effective anisotropy of $A_{22}^{\text{eff}} = -1.21(3)\%$. No Lorentzian damping was required: in fact, the fit yielded a slightly negative value for $\delta$ when treated as a free parameter, which is unphysical. A total of $5 \cdot 10^8$ coincidences was recorded for this spectrum.

5.1.3. WSe$_2$

The time spectrum for WSe$_2$ at room temperature together with its cosine transform is shown in Figure 3. The spectrum closely resembles that for WS$_2$. There are no more baseline problems. They all could be eliminated by a triple coincidence veto. Electronic distortions were greatly reduced, but are corrected for prior to the cosine transformation. A least squares fitting analysis yielded $\omega = 270.08(3)$ Mrad/s, a Lorentzian damping of $\delta = 0.15(2)\%$ and an effective anisotropy of $A_{22}^{\text{eff}} = -1.9(1)\%$. A total of $3.8 \cdot 10^8$ coincidences was recorded for this spectrum.

We subsequently performed measurements at elevated temperatures up to 764 K in sealed quartz ampoules filled with inert gas. Typically $8 \cdot 10^7$ coincidences were sufficient to extract the NQI-parameters with sufficient accuracy. The time spectra for various temperatures (first 300 ns are shown only) and their cosine transforms are shown in Figure 4. Apparently the signal is almost lost at 764 K, much below the reported stability range for WSe$_2$ [18]. We cannot exclude the influence of oxidation due to residual oxygen in our closed quartz ampoules. Nevertheless, this observation is in keeping with the fact that our early attempts to anneal WSe$_2$ after neutron irradiation at 800°C for 2 hours led to a complete absence...
of a NQI-signal, whereas the same procedure applied to WS₂ had no deteriorating effect (it also did not improve the signal intensity or linewidth). Hence, WSe₂ is less stable and possibly more susceptible to oxidation than WS₂.

A further remark is necessary concerning line intensities in Figs. 3 and 4. For all experiments we used one single crystal of WSe₂, orientated roughly along the body diagonal of the cubic detector arrangement, i.e. along (111). For this geometry, the intensities differ slightly from those of the powder pattern. We have

\[ G_{22}(t) = 0 + \frac{1}{6}\cos\omega t + \frac{14}{99}\cos 2\omega t + \frac{23}{66}\cos 3\omega t + \frac{8}{33}\cos 4\omega t + \frac{7}{99}\cos 5\omega t + \frac{1}{33}\cos 7\omega t, \]  

which should be compared with (3) for random powder samples. The difference in the time independent term is irrelevant because it was treated as an adjustable parameter for technical reasons, anyway. Relevant differences exist for 2\( \omega \) and 4\( \omega \). The quality of the fits, however, did not improve when using (9) instead of (3). This is most likely due to the fact that the crystal orientation within the furnace was not accurately along (111) and might even have changed during the data collection. In Figs. 3 and 4 the fits with random powder intensities according to (3) are shown. There is practically no difference in the fitted frequencies using either (3) or (9). All fit results are summarized in Table 1. The temperature dependence of \( v_Q \) for WSe₂ is shown in Fig. 5 together with that of WS₂ taken from [10]. In addition, data for CaWO₄ are shown (see below). The solid lines represent least squares fits to the data points of the function

\[ v_Q(T) = v_Q(0)(1 - \alpha T^y). \]  

The fit for \( v_Q(0) \), \( \alpha \), and \( y \) are listed in Table 2.

5.1.4. WSi₂

The time spectrum for WSi₂ at room temperature together with its cosine transform is shown in Figure 6.
Fig. 4. Time spectra for $^{187}$Re in WSe$_2$ (left) and their cosine transforms (right) at various temperatures. In the time spectra the first 300 ns are shown only.
Table 1. Summary of fit results for $^{187}\text{Re}$ in WSe$_2$ at various temperatures.

| $T$ [K] | $\omega_1$ [Mrad/s] | Amplitude [%] | $\delta$ [%] | $\eta$ | $\nu_Q$ [MHz] | $|V_{zz}|$ [10$^{-21}$ V/m$^2$] |
| --- | --- | --- | --- | --- | --- | --- |
| 296 | 270.08(3) | -1.9(1) | 0.15(2) | 0 | 1031.6(1) | 14.0(2) |
| 435 | 266.27(7) | -2.6(1) | 0.24(2) | 0 | 1017.1(3) | 13.8(2) |
| 575 | 262.03(5) | -2.3(1) | 0.11(3) | 0 | 1000.9(2) | 13.6(2) |
| 598 | 261.19(4) | -2.2(1) | 0.09(2) | 0 | 997.7(2) | 13.6(2) |
| 764 | 255.45(9) | -0.5(1) | 0.00(2) | 0 | 975.7(5) | 13.3(2) |

Although the characteristic pattern for $I = 9/2$ is clearly visible, the spectrum suffers from the rather low anisotropy $A_{zz}^{\text{eff}} = -0.81(8)\%$ and relatively large Lorentzian damping of $\delta = 0.9(1)\%$, despite the high statistical accuracy ($1.4 \cdot 10^9$ coincidences). This is not due to parasitic activities due to neutron capture of Si which totally decayed prior to the start of our TDPAC-experiments, but presumably reflects the quality of the starting material. However, $\omega = 296.22(3)$ Mrad/s can be determined without problems.

5.1.5. CaWO$_4$

The time spectrum for CaWO$_4$ at room temperature together with its cosine transform is shown in Figure 7. There are no technical problems with the baseline and electronic distortions are very small. A least squares fitting analysis yielded $\omega = 284.30(2)$ Mrad/s, $A_{zz}^{\text{eff}} = -1.19(3)\%$, and no Lorentzian damping was required at all. A total of $8.1 \cdot 10^8$ coincidences was recorded for this spectrum. We subsequently performed measurements up to 511 K. The time spectra (only the first 300 ns are shown) and their cosine transforms are shown in Figure 8 at various temperatures. We recorded $0.7...1.4 \cdot 10^8$ coincidences per spectrum. The small amplitude of the signal at 767 K has a simple explanation: This was in fact the last measurement, and instead of a few very small single crystals we used all material of the previous experiments such that selfabsorption in the sample was severe. The origin of the sloping baseline in the spectrum...
at 911 K is unclear. It certainly is not due to pile up (see the other spectra in Figure 8) because we always used about the same source strength. It rather might be indicative for the beginning of thermal decomposition. The fit results are summarized in Table 3, $\nu_Q$ versus temperature is displayed in Fig. 5, and the fit parameters according to (10) are listed in Table 2.

### Table 3. Summary of fit results for $^{187}$Re in CaWO$_4$ at various temperatures.

| $T$ [K] | $\omega_1$ [Grad/s] | Amplitude [%] | $\delta$ [%] | $\eta$ [%] | $\nu_Q$ [MHz] | $|V_{zz}|$ [$10^{21}$ V/m$^2$] |
|--------|---------------------|--------------|--------------|----------|-------------|-----------------|
| 296    | 284.30(2)           | -1.19(3)     | 0.00         | 0.00     | 1085.9(1)   | 14.8(2)         |
| 453    | 281.98(6)           | -1.14(7)     | 0.00         | 0.00     | 1077.1(2)   | 14.7(2)         |
| 629    | 277.59(4)           | -1.22(6)     | 0.00         | 0.00     | 1060.3(2)   | 14.4(2)         |
| 767    | 273.64(7)           | -0.76(6)     | 0.00         | 0.00     | 1045.2(2)   | 14.2(2)         |
| 911    | 267.61(5)           | -1.61(9)     | 0.00         | 0.00     | 1022.2(2)   | 13.9(2)         |

5.2. Ab-initio Calculations of Electric Field Gradients

Calculations of electron densities and electric field gradients were carried out using the full potential linearized augmented plane wave (FLAPW) method as embodied in the program package WIEN95 [19]. The method is based on crystal periodicity. Because the TDPAC-measurements were carried out at Re-atoms due to the $^{187}$W($\beta^-$)$^{187}$Re transmutation, we had to consider Re impurities within the ideal crystal. We carried out the following three types of calculations:

(i) pure compound, unit cell,
(ii) pure compound, artificial supercell comprising many unit cells. This was done to facilitate comparison with
(iii) impurity system (Re at central W-site), supercell.

In particular we used the supercells listed in Table 4. Generally, we had one Re atom per seven W atoms. For WS$_2$, WSe$_2$, and WSi$_2$ we doubled the unit cell in the $a$- and $b$-directions only because in the $c$-direction there...
Fig. 7. Time spectrum for $^{187}\text{Re}$ in CaWO$_4$ (top) and its cosine transform (bottom).

Table 4. Size of used supercells in units of the unit cell dimensions and ratio of impurity (Re) atoms to W-atoms.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a_{\text{supercell}}$</th>
<th>$c_{\text{supercell}}$</th>
<th>Ratio Re:W</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>$2a$</td>
<td>$2c$</td>
<td>1:7</td>
</tr>
<tr>
<td>WS$_2$, WSe$_2$, WSi$_2$</td>
<td>$3a$</td>
<td>$3c$</td>
<td>1:27</td>
</tr>
<tr>
<td>CaWO$_4$</td>
<td>$2a$</td>
<td>$1c$</td>
<td>1:7</td>
</tr>
<tr>
<td></td>
<td>No supercell calculations performed.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

are two layers of W-atoms separated by two layers of S, Se, or Si, respectively, within one unit cell. We replaced one W-atom in one of the layers. In the case of WC we had to double the unit cell in the $c$-direction, too. Due to the small unit cell of WC, a supercell composed of $3 \times 3 \times 3$ unit cells could also be tested leading to an impurity to W ratio of 1:27. However, in this case no full convergence of the basis set could be reached due to main memory limitations. Furthermore, we investigated a hypothetical "ReC", assuming the same crystal structure and unit cell dimensions as for WC. The unit cell of CaWO$_4$ is too large, and so we did not perform supercell calculations yet.

We checked several convergence parameters. With the exception of CaWO$_4$, the treatment of the systems with standard unit cells needed only small plane wave basis sets due to small unit cells. We used an extended number of $k$-points (at least 100) in the irreducible wedge of the Brillouin zone. For most of the supercells, about 10 $k$-points were used and plane wave basis set convergence could also be reached. The CPU time per iteration was about two days for the supercells and a few minutes for the standard unit cells on a HP 9000/780 computer.

In Table 5 the results for $V_{zz}$ and $\eta$ at the central W and Re positions, respectively, are listed for the standard unit cell and supercell calculations. In principle, the results for single unit cells and the supercells without impurity should be the same, but due to different basis sets and $k$-meshes small differences occurred, indicating the accuracy limits of such calculations. Larger differences occurred between the single unit cell and the 1:27 unit cell for WC. This is due to the fact that for the large super-
Fig. 8. Time spectrum for $^{187}$Re in CaWO$_4$ (left) and their cosine transforms (right) at various temperatures. In the time spectra the first 300 ns are shown only.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Cell</th>
<th>Atom</th>
<th>Number</th>
<th>Position</th>
<th>$R_{\text{impurity-atom}}$ [a.u.]</th>
<th>$V_{zz}$ [$10^{-11}$ V/m$^2$]</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>single unit cell</td>
<td>W</td>
<td>1</td>
<td>(0, 0, 0)</td>
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<td>-13.60</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>-0.13</td>
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</tr>
<tr>
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<td>W</td>
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<td>C</td>
<td>6</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
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<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
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<td>-4.70</td>
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</tr>
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<td>-5.24</td>
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<td>4.547</td>
<td>-5.24</td>
<td>0.792</td>
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<td>7.496</td>
<td>-4.87</td>
<td>0.000</td>
</tr>
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<td></td>
<td>S</td>
<td>1</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
<td>7.496</td>
<td>-4.87</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S</td>
<td>1</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
<td>7.496</td>
<td>-4.87</td>
<td>0.000</td>
</tr>
<tr>
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<td>supercell 1:7</td>
<td>Re</td>
<td>1</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
<td>0.000</td>
<td>-17.90</td>
<td>0.000</td>
</tr>
<tr>
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<td>3</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
<td>10.524</td>
<td>-4.40</td>
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</tr>
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<td>3</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
<td>10.524</td>
<td>-4.40</td>
<td>0.018</td>
</tr>
<tr>
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<td>W</td>
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<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
<td>13.524</td>
<td>-17.55</td>
<td>0.000</td>
</tr>
<tr>
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<td>single unit cell</td>
<td>W</td>
<td>2</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
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<td>-15.20</td>
<td>0.000</td>
</tr>
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<td>4.547</td>
<td>-6.10</td>
<td>0.000</td>
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</table>

Table 5. Supercell calculations of EFGs for atomic sites in WC (unit cell and supercell), Re in WC, "ReC" (unit cell), CaWO$_4$, WS$_2$, Re in WS$_2$, WSe$_2$, Re in WSe$_2$, WSi$_2$, and Re in WSi$_2$. 

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The table above lists the supercell calculations of EFGs (Electric Field Gradient) for atomic sites in various compounds, including WC, ReW$_{13}$, CaWO$_4$, WS$_2$, Re in WS$_2$, WSe$_2$, Re in WSe$_2$, WSi$_2$, and Re in WSi$_2$. The entries include the compound, cell type, atom, number, position, impurity-atom $R_{\text{impurity-atom}}$ in atomic units, $V_{zz}$ in $10^{-11}$ V/m$^2$, and $\eta$. The calculations are performed for both single unit cell and supercell conditions, with and without impurities.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Cell</th>
<th>Atom</th>
<th>Number</th>
<th>Position</th>
<th>$R_{impurity-atom}$ [a.u.$^2$]</th>
<th>$V_{zz}$ [$10^{21}$ V/m$^2$]</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>supercell 1:7</td>
<td>W</td>
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<td>$(\frac{1}{6}, \frac{1}{3}, \frac{1}{4})$</td>
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<td>-14.65</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Se</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{1}{12})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>without impurity</td>
<td>Se</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.3789})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.1211})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Se</td>
<td>1</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{1}{12})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
</tr>
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<td></td>
<td></td>
<td>Se</td>
<td>1</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.3789})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Se</td>
<td>1</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.6211})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
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<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.8789})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
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<td>Se</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.6211})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.8789})$</td>
<td>7.227</td>
<td>-6.79</td>
<td>0.083</td>
</tr>
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<td>W</td>
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<td>-6.79</td>
<td>0.083</td>
</tr>
<tr>
<td>WSe$_2$</td>
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<td>with Re impurity</td>
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<td>3</td>
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<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
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<td></td>
<td>Se</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.3789})$</td>
<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.1211})$</td>
<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
</tr>
<tr>
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<td></td>
<td>Se</td>
<td>1</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{1}{12})$</td>
<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Se</td>
<td>1</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.3789})$</td>
<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
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<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
</tr>
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<td></td>
<td>Se</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.8789})$</td>
<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
</tr>
<tr>
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<td>W</td>
<td>3</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.8789})$</td>
<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
</tr>
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<td>W</td>
<td>1</td>
<td>$(\frac{1}{6}, \frac{2}{3}, \frac{0.3345})$</td>
<td>7.227</td>
<td>-9.55</td>
<td>0.936</td>
</tr>
<tr>
<td>WSi$_2$</td>
<td>single unit cell</td>
<td>W</td>
<td>2</td>
<td>$(0, 0, 0)$</td>
<td>0.000</td>
<td>-15.00</td>
<td>0.000</td>
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<td>Si</td>
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<td>W</td>
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<td>$(0, 0, 0)$</td>
<td>0.000</td>
<td>-14.83</td>
<td>0.000</td>
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<td>Si</td>
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<td>-1.01</td>
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<td>6.081</td>
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<td>0.002</td>
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</table>
In Table 5, also the values for \( V_{zz} \) and \( \eta \) for the other atoms in the pure and impurity systems are given. It is interesting to see that \( V_{zz} \), \( \eta \)-values at inequivalent lattice sites in the artificial supercells – which, however, are of course equivalent in the unit cell – turn out to be identical within the quoted accuracy, the cases of WSe₂ and WSi₂ being slightly less accurate. Note, that the nearest and next nearest neighbours of the Re impurity exhibit \( V_{zz} \), \( \eta \)-parameters vastly different from the pure systems.

We investigated the forces on the atoms. In the case of the systems without impurity the forces were nearly zero and no structure relaxation was necessary. In the case of the supercells we found forces of the order of 10 mRy/a.u. at the nearest neighbours of the Re atom. Due to the excessive computing time requirements we performed relaxations for the 1:7 supercell of WC only. In this case, where Re and W have similar size and chemical properties, the change of \( V_{zz} \) is in the order of the basis set.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cell</th>
<th>Atom</th>
<th>Number</th>
<th>Position</th>
<th>( R_{\text{impurity-atom}} ) [a.u.]</th>
<th>( V_{zz} ) ( \times 10^{21} ) V/m²</th>
<th>( \eta )</th>
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<td>Si 4</td>
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<td>W 1</td>
<td>4</td>
<td>( \frac{1}{2}, 0, ) 0.3345</td>
<td>7.846</td>
<td>-1.01</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W 1</td>
<td>4</td>
<td>( \frac{1}{2}, \frac{3}{2}, 0 ) 0.3345</td>
<td>8.565</td>
<td>-14.83</td>
<td>0.000</td>
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<tr>
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<td>W 1</td>
<td>4</td>
<td>( \frac{1}{2}, \frac{3}{2}, 0 ) 0.3345</td>
<td>8.565</td>
<td>-15.10</td>
<td>0.002</td>
</tr>
<tr>
<td>Si 2</td>
<td></td>
<td>W 1</td>
<td>4</td>
<td>( \frac{1}{2}, 0, 0 ) 0.3345</td>
<td>8.600</td>
<td>-15.10</td>
<td>0.000</td>
</tr>
<tr>
<td>Si 2</td>
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<td>W 1</td>
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<td>( \frac{1}{2}, 0, 0 ) 0.3345</td>
<td>9.925</td>
<td>-1.01</td>
<td>0.005</td>
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</tbody>
</table>

**CaWO₄** single unit cell

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cell</th>
<th>Atom</th>
<th>Number</th>
<th>Position</th>
<th>( R_{\text{impurity-atom}} ) [a.u.]</th>
<th>( V_{zz} ) ( \times 10^{21} ) V/m²</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC 4</td>
<td></td>
<td>W 4</td>
<td>4</td>
<td>( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} )</td>
<td>0.000</td>
<td>+15.0</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\( a \) Atomic unit. 1 a.u. = 5.29177 \( \times 10^{-11} \) m.

\( b \) Within the quoted accuracy, all values for \( V_{zz} \) and \( \eta \) on W and non-metal sites turned out to be identical.

\( c \) One k-point only!

**Table 6.** Calculated and experimental values for \( V_{zz} \) and \( \eta \) at various lattice sites. Note that it is in principle not possible to determine the sign of \( V_{zz} \) by \( \gamma \)-TDPAC.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LAPW (calc.)</th>
<th>Mössbauer (exp.)</th>
<th>TDPAC (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( V_{zz} ) [( \times 10^{21} ) V/m²]</td>
<td>( V_{Re} ) [( \times 10^{21} ) V/m²]</td>
<td>( V_{Re} ) [( \times 10^{21} ) V/m²]</td>
</tr>
<tr>
<td>WC</td>
<td>-13.6</td>
<td>-5.7</td>
<td>-12.1 (( \eta = 0.52 ))</td>
</tr>
<tr>
<td>WS₂</td>
<td>-18.6</td>
<td>-14.6</td>
<td>-18.6(5)</td>
</tr>
<tr>
<td>WSi₂</td>
<td>-15.2</td>
<td>-14.9</td>
<td>-15.0</td>
</tr>
<tr>
<td>WSH</td>
<td>-15.0</td>
<td>-18.5</td>
<td>-15.0</td>
</tr>
<tr>
<td>CaWO₄</td>
<td>+15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
sis set effects (less than 10%). Therefore a good basis set is more important than very time consuming calculations of small relaxation effects.

In Table 6 the most accurate calculated values are compared with the experimental values.

6. Discussion

6.1. Effective Anisotropy $A_{22}^{\text{eff}}$

The observed values of $A_{22}^{\text{eff}}$ ($\pm 1\ldots-2\%$) are rather low compared to the calculated value of $A_{22} = -13.1\%$ for the $479.5 \text{ keV} - 72 \text{ keV}$ cascade (assuming pure multipolarities). Unperturbed angular correlation experiments with solid state detectors and excellent energy resolution confirmed [20] that the $\gamma$-transitions are essentially of pure E2 and E1 character. There are two main reasons for the reduction of $A_{22}$:

(i) Solid angle correction factors $Q_2(\gamma_1)$ $Q_2(\gamma_2)$ average partly over $P_2(\cos \theta)$ due to the finite acceptance. We have no accurate values for the $Q_2$’s for our conically scintillators, but experience with other isotopes, e.g. $^{181}$Hf, tells us that for the rather short source-detector distances of 5–10 mm we should have $Q_{22} = 0.5$ in the worst cases [11].

(ii) The admixture of X-rays in the stop channel (72 keV) which is practically isotropic in coincidence with the 479.5 keV-line is considered the main reason for the further reduction of $A_{22}$ by at least another factor of 2. With NaI(Tl) scintillators $A_{22}^{\text{eff}} = -7\%$ (corrected for $Q_{22}$) was observed, whereas BaF$_2$-scintillators with a poorer energy resolution are doing much worse. We plan to cool our BaF$_2$-scintillators in order to achieve a better energy resolution (aim: $AE/E = 10\%$ at 662 keV). This would greatly help to increase $A_{22}^{\text{eff}}$.

Another trivial reason for the low $A_{22}^{\text{eff}}$ would be the fact that fraction of probe nuclei on regular lattice sites without neighbouring or more distant defects would give rise to a sharp NQI-signal, while all other probe nuclei associated with lattice defects merely give a rather broad frequency distribution with a very rapid decay of the anisotropy which might be hidden under the huge prompt contribution. This possibility can be ruled out because we should observe an increase of $A_{22}^{\text{eff}}$ during annealing, which was not the case. In addition, our prompt peak would masquerade a rapid decay of the anisotropy for 1–5 ns only, and there is no reason that all defect associated signals are so much higher in frequency than the regular signals. In order to clarify this point further, we plan experiments with $^{187}$W of extremely high specific activity, i.e. with low X-ray fluorescence probability.

6.2. Linewidth

The linewidth, assumed Lorentzian, was very small or even zero in all cases where the sample quality was checked by other techniques (e.g. STM for the layered dichalcogenides, or EPR for Na-doped CaWO$_4$). It was relatively high for WC and WSi$_2$, two compounds purchased commercially and checked for purity only. Apparently, the crystal quality of these polycrystalline substances is inferior to that of the single crystalline materials mentioned above. In principle, the linewidth could be the result of distant lattice defects (not correlated with the thermal neutron capture producing the $^{187}$W probe), produced e.g. by fast neutrons. Since we did not observe a significant line narrowing upon annealing, we rule out this possibility. In cases with $\delta = 0$ we expect to improve the frequency resolution by a factor of 4 by observing coincidences up to 3 $\mu s$.

6.3. NQI-Parameters at Room Temperature

The observation of axial symmetry ($\eta = 0$) is not surprising for the compounds studied due to the symmetry of their crystal structures.

It is little surprising that all NQI-frequencies are very roughly the same with the exception of WC. It looks as if the EFG at Re impurities in W-compounds is dominated by impurity specific contributions which would render the “fingerprint” method with this isotope useless. However, we believe that this coincidence is fortuitous. Clearly, the results for WS$_2$ and WSe$_2$ are expected to be similar because of the similarity of both structures. It is interesting to note that $\nu_3$ for WSe$_2$ is slightly lower compared to WS$_2$, contrary to the case of $^{181}$Ta in 2H-TaSe$_2$ and 2H-TaSe$_3$ at room temperature ($\omega = 820$ Mrad/s and 870 Mrad/s, respectively) [21]. This might be an impurity specific effect (see also below). The result for WS$_2$ is difficult to interpret because of the lack of comparative data. Inspection of Table 6 shows that the sign of $V_{zz}$ in CaWO$_4$ at W-sites is opposite to that of all other compounds where calculations were performed. Hence, the coincidence of the magnitude of $V_{zz}$ with those of the other compounds is indeed fortuitous.
The agreement between the experimental values for $|V_{zz}|$ at Re impurities on W-sites and the calculated $V_{zz}$ is excellent for WC, WS$_2$, WSe$_2$, and WSi$_2$, especially taking into account that the FPLAPW-method is not designed to investigate impurities and the ratio between impurity and W atoms is large compared to the experimental case. Obviously, the influence of the periodically continued impurities is rather small. This is supported by the small difference between $V_{zz}$ at a Re impurity in WC and at Re in the hypothetic "ReC". In fact, it is more important to improve the basis set than to increase the unit cell by more than a factor of two in all directions, as was done for WC, which led to a worse basis set.

The agreement between theory and experiment is even perfect for WS$_2$ when Mössbauer-data [22] for W-sites are considered. The fact that the EFG at Re impurities in WS$_2$ is smaller by 20% compared to that at a W-site might be considered an impurity specific effect. We do not think that a discussion in terms of Sternheimer factor differences [23] is meaningful. We find an increasing Re EFG with respect to the W EFG in WS$_2$, an almost constant one in WSe$_2$, and decreasing values in WS$_2$ and WC, despite the fact that the Sternheimer factor would predict the same tendency for all investigated compounds.

The calculated value for $V_{zz}$ at W-sites in WC is relatively high ($V_{zz} = -13.6 \times 10^{21}$ V/m$^2$), comparable to that obtained by Mössbauer spectroscopy (−12.1 $\times$ 10$^{21}$ V/m$^2$) [24]. The experimental result at $^{187}$Re is lower by a factor of roughly 3 compared to the W-site. Hence, the electronic charge distribution around the impurity is very different from that of a regular W-site. This is also shown by the EFG-calculations: The EFG is much smaller at Re impurities, with and without lattice relaxation. It is interesting to note in this context that WC is the only compound where the R-analogue does not exist [25]$^5$. Hence, the Re impurity is "trapped" at an "unfavouable" W-site after nuclear transmutation.

6.4. Temperature Dependence of $v_Q$

Inspection of Table 2 shows that $v_Q (T)$ closely follows a $T^{-3/2}$-behaviour for WS$_2$ and WSe$_2$, contrary to what is known from other layered transition metal dichalcogenides like 2H-TaS$_2$ [21], 2H-TaSe$_2$ [21], and 2H-NbSe$_2$ [26] with a linear temperature dependence over extended temperature ranges. The logarithmic temperature derivatives at 300 K, however, compare well. We have (in units of $10^{-4}$ K$^{-1}$): −1.2 (2H-WS$_2$), −1.0 (2H-WSe$_2$), −1.4 (2H-TaS$_2$), −1.3 (2H-TaSe$_2$), −2.1 (2H-NbSe$_2$). It is interesting to note that the temperature derivatives for the seleniums are a little bit smaller than those for the sulfides, possibly an effect of the higher mass of Se. The deviation from a linear temperature dependence, which was analyzed and explained by Torgeson and Borsa [26] to be a result of anharmonic lattice vibrations, is more difficult to explain. First, the original theory of Jena [27] was restricted to metals and is not applicable to large bandgap semiconductors. Second, we must not forget the impurity specific effects which might be superimposed onto those of the regular lattice. Curiously enough, a $T^{-3/2}$-temperature dependence was observed for many 3-dimensional (−isotropic) metals [28]. A wider temperature range, particularly below 300 K, should be considered before drawing any further conclusions.

The situation is different for CaWO$_4$: Here, the temperature exponent is larger (2.2) while the prefactor is at least two orders of magnitude lower compared to the layered dichalcogenides. The room temperature logarithmic derivative is small: \( \frac{d \ln v_Q}{dT} \bigg|_{300K} = -0.5 \times 10^{-4} \text{ K}^{-1} \). Again, no further conclusions should be drawn without low-temperature data.

7. Summary

Despite a number of technical problems – part of which were solved during this study, others have yet to be cured – it is clear that the nuclear TDPAC-probe $^{187}$W($\beta^-$)$^{187}$Re is extremely well suited for NQI-studies. The extraordinary frequency resolution of $\Delta \omega/\omega$, reaching values of 0.3% around 1 Grad/s (which can readily be improved to below 0.1%), offers a very sensitive means to detect dynamical broadening due to molecular tumbling in solution or due to intramolecular re-orientational motion in W-containing macromolecules. Fast scintillators with greatly improved energy resolution would boost the application of this isotope in material sciences as well as life sciences. Finally, ab initio calculations of EFG's and impurity specific effects will help to go beyond a "fingerprint" identification of compounds.
Acknowledgement

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