Neutron-resonance capture analysis on the VESUVIO spectrometer: Towards high-throughput material characterisation

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Abstract. We discuss the possibility to characterise nuclear quantum effects on the dynamics of heavy nuclei by means of neutron-resonance capture analysis on the VESUVIO spectrometer at ISIS. VESUVIO is equipped with yttrium-aluminium-perovskite gamma-sensitive detectors that can be used to record the Doppler-broadened line shape from a neutron-induced resonance in the neutron-energy range between 1 and 100 eV. The measurement of nuclear momentum distributions for heavy atoms using deep inelastic neutron scattering, the traditional technique for light-weight nuclei from hydrogen to fluorine, is currently severely limited by the resolution of the instrument. On the other hand, gamma-Dopplerimetry studies as the one presented here on gold allow for exquisite precision and short data-collection measurements, of the order of one hour, for the measurements, rendering the technique ideal for high-throughput investigations.

1. Introduction

The effect of quantum mechanics on the nuclear dynamics in condensed-matter systems is a topic of increasing interest [1, 2, 3]. Nuclei, especially at low temperatures and in strongly bonded systems, experience zero-point motions and other nuclear quantum effects dictated by the solution of a Schroedinger equation for their local potential. At present, a remarkable effort is invested in reproducing these effects in first-principles simulations [4, 5], so as to replace more standard, and sometimes inadequate, approaches such as the Einstein or Debye models for vibrations in crystals.

From the experimental point of view, deep inelastic neutron scattering (DINS) is a Compton-like technique where the momentum distribution of nuclei can be directly probed, and values of the nuclear mean kinetic energy can be extracted. The flagship among the instruments using DINS is the VESUVIO spectrometer [6, 7] at the ISIS pulsed neutron and muon source [8]. Recent studies using DINS have tackled the role of nuclear quantum effects in nano-confined water [9], caesium hydrogen sulfate [10], and zirconium-beryllium amorphous alloys [11]. Traditionally, DINS has been applied to the investigation of the dynamics of light- to moderate-weight elements, with the recent exception of niobium in radio-frequency...
superconducting cavities [12]. However, the higher the mass of an element, the more severe is the limitation from the instrument resolution function on the analysis of nuclear momentum distributions [3].

Neutron Resonance Capture Analysis (NRCA) [13, 14] is a technique traditionally employed to investigate the chemical composition of samples. It is based on the capture of a neutron with energies in the epithermal region, and the subsequent emission of a prompt-gamma cascade [15, 16]. The shape of the resonance spectrum is broadened by the motion of the nucleus, accordingly to the Doppler effect, and it is therefore affected by the momentum distribution and mean kinetic energy of the photon-emitting nucleus. In this sense, NRCA represents a powerful and complementary tool to DINS, as it exploits the intense cross sections for neutrons in heavy elements such as indium, caesium, tantalum, and gold, that cannot be tackled without difficulties by DINS studies.

In this article, we show how NRCA can be employed to obtain values of the nuclear mean kinetic energy, therefore gathering information on the lattice dynamics, in the case of the VESUVIO spectrometer. In particular, Section 2 discusses the theory behind NRCA, the way to extract reliable values of the mean kinetic energy from measured spectra, and the link to materials modelling and first-principles simulations. Section 3 presents the experimental set-up and describes the measurements performed at the VESUVIO spectrometer, and the results of the investigation are discussed in Section 4. Finally, conclusions are drawn in Section 5.

2. Methods

2.1. Neutron Resonance Capture Analysis

![Time-of-flight spectra](image)

**Figure 1.** Time-of-flight spectra recorded from one yttrium-aluminium-perovskite detector for one period of data acquisition with the analyser foil in (black continuous line and shadow) and foil out (red triangles). Their difference, corresponding to the foil-cycling procedure, is reported as the tiny green line and shadow.

The neutron scattering cross section in the proximity of a resonance centred at the energy value $E_0$ and multiplicity $g_J$ experienced by a neutron of incident energy $E$ and wavelength...
\( \lambda(E) \) can be expressed as the sum of the two contributions [14]

\[
\sigma_\gamma(E) = \frac{\lambda^2(E) g_J \Gamma_n \Gamma_\gamma}{4\pi (E - E_0)^2 + \Gamma^2/4},
\]

related to the processes where a neutron is absorbed and a gamma ray is emitted, and

\[
\sigma_n(E) = \frac{\lambda^2(E) g_J \Gamma_n^2}{4\pi (E - E_0)^2 + \Gamma^2/4} + 2\lambda(E) g_J \frac{R \Gamma_n (E - E_0)}{(E - E_0)^2 + \Gamma^2/4} + 4\pi b^2,
\]

defining the probability to have a neutron in the final state as well. Equation 2 is composed of three terms on the right-hand side, of which the first corresponds to the probability for a neutron to be resonantly absorbed and subsequently emitted, the third contribution corresponds to the total scattering term via the Fermi pseudo-potential with \( b \) the scattering length [17], and the second term arises from the interference between the two aforementioned channels [18]. The line shape of the resonance is well described by a Lorentzian function, according to the theory by Breit and Wigner [19], with a full width at half maximum (FWHM)

\[
\Gamma = \Gamma_n + \Gamma_\gamma.
\]

Finally, the total neutron-induced cross section is the sum of the two contributions

\[
\sigma_t(E) = \sigma_n(E) + \sigma_\gamma(E).
\]

The broadening of the resonance from the Lorentzian line shape is a consequence of the instability of the excited nucleus after the absorption of the incoming neutron, and the parameter \( \Gamma \) is defined from the half-life time of the metastable state [20].

In addition to the Lorentzian broadening, the resonance line shape is furthermore widened by two additional effects that manifest themselves as a Gaussian broadening. The first term, \( \delta \), arises from the uncertainty in the time-of-flight measurement because of the finite size of the moderator. At a spallation neutron source such as ISIS, the resolution of the measurement can be expressed as

\[
\delta^2 = \left( \frac{\partial E}{\partial L} \right)^2 \Delta L^2 + \left( \frac{\partial E}{\partial t} \right)^2 \Delta t^2,
\]

with \( L \) the distance between the moderator and the sample, \( \Delta L \) the associated uncertainty, \( t \) the time a neutron takes travelling the distance \( L \), and \( \Delta t \) the width of the neutron pulse. The second contribution to the Gaussian broadening of the resonance comes from the motion of the nucleus induced by its chemical bonding to surrounding atoms. Such Doppler broadening, \( \Delta \), can be expressed as proportional to the atom’s mean kinetic energy \( \langle E_K \rangle \) as [14]

\[
\Delta^2 = \frac{4}{3} \frac{mM}{(m + M)^2} E_0 \langle E_K \rangle \simeq \frac{4}{3} E_r \langle E_K \rangle,
\]

where the final equality [21] holds when the recoil energy \( E_r \) is approximated as

\[
E_r \simeq \frac{mM}{(m + M)^2} E_0,
\]

with \( m \) and \( M \) the mass of the neutron and the struck atom, respectively. Reference [21] also discusses the origin of the Doppler broadening from the convolution of the nuclear cross section
\[ \sigma(E) \] with the dynamic structure factor \( S(Q, \Delta E) \), with \( Q \) and \( \Delta E \) the momentum and energy transferred by the neutron to the system of interest. One has

\[
S(Q, \Delta E) = \frac{1}{\sqrt{2\pi \Delta}} \exp \left( -\frac{(E - E_f)^2}{2\Delta^2} \right).
\] (8)

Finally, one can define the Doppler-broadened experimental cross sections as

\[
\sigma^D(E) = \frac{1}{\sqrt{2\pi \Delta}} \int_{-\infty}^{\infty} \sigma(E - \eta) \exp \left( -\frac{\eta^2}{2\Sigma^2} \right) d\eta,
\] (9)

where the convolution can be applied to \( \sigma_n(E) \), \( \sigma_\gamma(E) \), or \( \sigma_t(E) \) separately. For additional details, the reader is referred to Ref. [14].

2.2. First-principles calculations

The first-principles vibrational analysis was performed using CASTEP [22], a total energy package based on the plane-wave pseudo-potential density functional theory method. The exchange-correlation functional developed by Perdew, Burke and Ernzerhof in the general gradient approximation was adopted to describe the exchange-correlation energy. The effective interaction between the valence electrons and atom cores were modelled by on-the-fly optimized norm-conserving pseudo-potentials, which allow to choose a relatively small plane-wave basis set without compromising the computational accuracy. The kinetic energy cut-off at 500 eV, and the dense Monkhorst-Pack k-point mesh spanning less than 0.04 Å\(^{-1}\) in the Brillouin zone were chosen. To calculate lattice dynamics, a super cell defined by a cut-off radius of 5 Å was built. Before the calculation of vibrational properties, the crystal structure was geometrically optimized to find the energy minimum. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme was employed in the geometry optimisation, in which the convergence criteria for the structure optimisation were set to 5.0\( \times \)10\(^{-6}\) eV per atom, 0.01 eV Å\(^{-1}\), 0.02 GPa and 5.0\( \times \)10\(^{-4}\) Å for energy, maximum force, maximum stress, and maximum displacement, respectively. On the basis of the crystal configuration in the minimal energy, the frequencies of the phonon modes and their dispersion were calculated by the finite-displacement method.

According to the discussion in Refs. [3, 23, 24], the mean kinetic energy of an atom can be deduced from the calculated vibrational density of states \( G(\omega) \), within the approximation of harmonic vibrations, as

\[
\langle E_K \rangle = 3 \int_0^\infty \frac{\hbar \omega}{4} G(\omega) \coth \left( \frac{\hbar \omega}{2k_B T} \right) d\omega,
\] (10)

where \( \omega \) is the frequency of each vibrational mode, and the hyperbolic-cotangent term takes into account the Boltzmann term for the population of excited states for the mode of energy \( \hbar \omega \) at every temperature \( T \) of the system.

3. Experimental Details

Measurements were performed at the VESUVIO spectrometer [6, 7] on a commercially available Au foil [25] of thickness 10 µm. The sample was inserted in the VESUVIO closed-circuit refrigerator (CCR) for temperature control, and the temperature of the sample was deduced using the sensor at the end of the sample stick, \( T_2 \) about 10 cm away from the sample, and the temperature of the CCR, \( T_1 \). Measurements were about 30-minute long when a proton current of 160 µA was flowing in the ISIS synchrotron, and each run had a statistics corresponding to 90 µAh of proton charge. After setting each temperature in the range 20 K to 220 K, three runs were acquired, the first one being discarded during the data analysis because of the significant
Figure 2. On the top, the transmission of a series of thin metal foils. In particular, the thickness is chosen so as to have a minimum transmission at the centre of the resonance \( \simeq e^{-1} \).

On the bottom, the attenuation correction in the case of a \(^{197}\text{Au}\) foil of thickness 5.5 µm (blue triangles), 55 µm (green squares), and 110 µm (blue triangles).

During a run, six periods of data acquisition are traditionally recorded on VESUVIO, corresponding to different positions of the analyser foils used to select the final energy of neutron scattered by the sample, so as to obtain DINS spectra [26, 27]. This procedure, at the base of DINS experiments [3], was not useful for the present experiment. However, it was decided to mimic normal operations for future concurrent measurements. Therefore, the spectra from the six acquisition periods were summed together in order to increase the statistical quality of the data. Figure 1 shows the spectra corresponding to the first and second periods as recorded.
by detector 151 in front scattering. The two spectra, namely the solid black line and the red markers, almost perfectly overlap over the entire time-of-flight range from 50 µs to 600 µs. The tiny difference, shown as a green line in the same figure, corresponds to the DINS spectrum. It is composed by the gold neutron Compton profile, on the right, and a residual intensity from the gamma rays emitted by the sample and slightly attenuated when passing through the filter-in period. Such filter-in-filter-out difference is hereafter considered as an experimental background to be subtracted from the data. An additional background from the empty CCR was separately measured and similarly subtracted from the data during the fit.

Experimental data were fitted using the function

\[ f(E) = A E^\alpha \sigma^D_\gamma(E) \left( \frac{1 - \exp \left( n\sigma^D_\gamma(E)d \right)}{n\sigma^D_\gamma(E)d} \right) + B \exp(E), \]

where the Doppler-broadened gamma cross section needs to be corrected by the self attenuation of the sample, defined by its thickness \(d\), number density \(n\), and the total cross section. The attenuation correction is therefore defined by the thickness of the sample and its scattering power. The neutron transmission from a series of metal foils is shown in Figure 2 using the tabulated values of the total neutron cross section available in the ENDF-B/VII libraries [28]. Here, the thickness of the foils is chosen so as to be in the thin-foil limit, that is the value of the transmission corresponding to the centre of the resonance peak equals \(e^{-1}\). The attenuation correction is then shown in the same Figure 2 for several values of the foil thickness in the case of gold. One can appreciate how the attenuation correction, already in the thin-foil limit, suppresses the intensity at the peak centre at the expenses of the peak wings, therefore apparently broadening the shape of the resonance. Equation 11 shows the explicit dependence upon the incident-beam spectrum through the parameter \(\alpha\), with the expected condition \(\alpha > -1\) at spallation neutron sources.

4. Results and Discussion

Data were analysed in three different stages, differing by the number of free parameters in the fit. In the first stage, the value of \(\alpha\) was considered as a free parameter. As its average value was found in agreement with recent measurements [7, 29], it was subsequently fixed to the value \(-0.92\). In the second stage, the average of the fitted values of \(\Gamma\) was found to be \(\Gamma = 136 \pm 4\) meV, in good agreement with the values reported in a recent review [30] on the neutron-induced cross section from gold \(^{197}\)Au, \(\Gamma = 139.2\) meV. Values of \(\Gamma_n = 15.2\) meV, \(\Gamma_\gamma = 125\) meV from the same reference were fixed in the fitting model. Final results, with both \(\alpha\) and \(\Gamma\) fixed, are shown in Table 1 together with the run number, the temperatures measured by the sensors in the stick \(T_2\) and the CCR \(T_1\), the width of the Gaussian broadening \(\Sigma\) prior to the subtraction of the resolution component, and the centre of the resonance peak, \(E_0\). One can notice that the temperature measured by the stick is generally about 1 – 2 K above the temperature measured by the CCR, suggesting a similar uncertainty on the sample temperature. The values of \(E_0\) in the Table are slightly in excess to the value of 4906 meV generally reported in the nuclear libraries [30], for it contains the average contribution of the recoil energies \(E_r\) due to the scattering immediately preceding the creation of the compound nucleus in the resonant state [20], as previously described in Equations 6 and 7. Figure 3 (left) shows the quality of the fit using Equation 11 on the spectrum from run 1. One can notice a slight oscillation of the difference of the data and fitting function around the peak centre. Considering the otherwise satisfactory result over a broad energy range, we conclude that such discrepancy at the peak position can be directly ascribed at the statistics corresponding to the short acquisition time of the measurement.

The experimental results for the values of \(\Sigma\), after subtraction of the resolution component \(\delta\), provide estimates for the Doppler broadening \(\Delta\) and the gold mean kinetic energy \(\langle E_K \rangle\) as a
Table 1: Estimated values for the temperature of the sample, as measured using the sensor on the CCR ($T_1$) and on the sample stick ($T_2$), and the fitted values of the Gaussian broadening $\Sigma$ and peak centre ($E_0$) for each experimental run. Some runs have been discarded as the sample temperature during the data acquisition changed more than 2 K.

| Run | $T_1$ [K] | $T_2$ [K] | $\Sigma$ [meV] | $E_0$ [meV] |
|-----|-----------|-----------|----------------|-------------|
| 1   | 19.99     | 20.95     | 21.55          | 4935        |
| 2   | 20.00     | 20.97     | 21.80          | 4935        |
| 4   | 39.98     | 41.61     | 22.04          | 4935        |
| 5   | 39.98     | 41.53     | 22.27          | 4935        |
| 7   | 60.00     | 62.11     | 23.83          | 4935        |
| 8   | 60.01     | 62.57     | 23.87          | 4935        |
| 10  | 80.00     | 82.08     | 24.86          | 4935        |
| 11  | 80.00     | 83.32     | 25.00          | 4935        |
| 13  | 100.00    | 101.56    | 26.37          | 4936        |
| 14  | 100.01    | 103.30    | 26.17          | 4935        |
| 16  | 120.00    | 121.25    | 27.69          | 4936        |
| 17  | 120.01    | 123.26    | 28.36          | 4935        |
| 19  | 140.01    | 141.33    | 27.94          | 4936        |
| 20  | 140.01    | 143.10    | 29.13          | 4936        |
| 22  | 160.00    | 161.30    | 29.36          | 4936        |
| 23  | 160.01    | 162.97    | 30.61          | 4936        |
| 25  | 180.01    | 181.58    | 30.40          | 4936        |
| 26  | 180.02    | 183.09    | 31.96          | 4936        |
| 28  | 200.00    | 201.74    | 33.23          | 4936        |
| 29  | 200.00    | 203.12    | 33.21          | 4936        |
| 31  | 220.01    | 222.12    | 34.18          | 4936        |

function of the sample temperature. The theoretical predictions, together with the experimental values for $\langle E_K \rangle$ are reported in Figure 4. The resolution component, $\delta$, according to Equation 5 provides a value $\delta \simeq 17.8$ meV, with no expected dependence upon the sample temperature. However, a slightly reduced value of $\delta = 15$ meV was used to get the best agreement between the simulation and the experimental data in Figure 4. Of the two datasets, one can notice how Dataset 2 systematically shows the best agreement to the theoretical prediction. This behaviour suggests that the time needed for the sample to reach the set temperature was slightly longer than expected, and only the third measurement for each nominal temperature can be considered having reached the set point. Such behaviour could be easily tested in future experiments by applying a sensor directly on the sample. Figure 4 (right) also shows the difference between two experimental spectra at the temperatures of 20 K and 200 K. One can notice how the difference of the spectra is largely exceeding the dimension of the associated error bars, suggesting the high sensitivity of the technique. Moreover, the difference in the resonance peaks markedly resembles the difference in neutron Compton profiles discussed in Reference [31], therefore suggesting that the fitting procedure discussed in that paper could be readily applied to the case of parametric studies of gamma resonances as well.

5. Outlook and Conclusions
We have presented experimental results from an NRCA study performed at the VESUVIO spectrometer on a gold foil in the range of temperature 20 K to 220 K. We have demonstrated how the instrument can acquire data of exquisite quality with a duration of the measurements
Figure 3. On the left, the fit (black line) of the experimental data (red squares) corresponding to run 1 ($T \simeq 20$ K), together with the difference of experimental data and fit, reported as a green line. On the right, the maximum difference on the experimental data between run 1 ($T \simeq 20$ K) and run 31 ($T \simeq 220$ K).

Figure 4. Experimental values of the mean kinetic energy of $^{197}$Au as a function of temperature as obtained from the experimental run in Dataset 1 (blue squares) and Dataset 2 (red triangles), as compared to the theoretical prediction based on a CASTEP simulation.
of the order of one hour, an order of magnitude improvement with respect to traditional acquisition times on electron-volt spectrometers. Moreover, VESUVIO proves to be a highly versatile instrument where several neutron-based techniques can be applied concurrently. This assessment paves the way to possible high-throughput parametric investigations, e.g., studying the change of the mean kinetic energy of a heavy nucleus as a function of temperature or time by analysing the change in the shape of a well-resolved resonance. Finally, we note that an additional enhancement of the signal-to-background ratio can be achieved by including a thermal-neutron filter along the incident beam, so as to suppress the background from gamma rays generated within the block house and in the beam stop, as suggested by Onorati et al in a separate contribution to this volume [32].

Acknowledgements
The authors gratefully acknowledge the UK Science & Technology Facilities Council for financial support and access to beam time at the ISIS Facility, and are grateful to Dr T Minniti for useful discussions. Computing resources were provided by STFC Scientific Computing Department’s SCARF cluster.

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